CORIELL, Sam Ray, 1935—
RAMAN AND INFRARED SPECTRA OF DEUTERATED PENTABORANE FREQUENCY ASSIGNMENT
AND NORMAL COORDINATE ANALYSIS FOR NORMAL AND DEUTERATED PENTABORANE.

The Ohio State University, Ph.D., 1961
Chemistry, physical

University Microfilms, Inc., Ann Arbor, Michigan
RAMAN AND INFRARED SPECTRA OF DEUTERATED PENTABORANE
FREQUENCY ASSIGNMENT AND NORMAL COORDINATE ANALYSIS
FOR NORMAL AND DEUTERATED PENTABORANE

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By

Sam Ray Coriell, B. Sc.

The Ohio State University
1961

Approved by

[Signature]
Adviser
Department of Chemistry
ACKNOWLEDGMENT

The author would like to express his deepest gratitude to Professor William J. Taylor, who both suggested the investigation and has guided it to its final form. It is impossible to adequately acknowledge Professor Taylor's generosity in time and advice.

The author would also like to thank Dr. A. B. Garrett and Dr. S. G. Shore of this department for their advice on the preparation and handling of pentaborane and Dr. T. W. Hildebrandt and F. M. Gong of the Numerical Computation Laboratory for their invaluable assistance in programming the 704 computer.
## CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>A. Early Structural Concepts for the Boron Hydrides</td>
<td>1</td>
</tr>
<tr>
<td>B. Bridge Structure for Diborane</td>
<td>2</td>
</tr>
<tr>
<td>C. Establishment of Pyramidal Model for Pentaborane</td>
<td>4</td>
</tr>
<tr>
<td>D. Previous Spectroscopic Data and Assignments for Pentaborane</td>
<td>9</td>
</tr>
<tr>
<td>E. Outline of Present Investigation</td>
<td>11</td>
</tr>
<tr>
<td>II. STRUCTURE AND BONDING OF PENTABORANE</td>
<td>14</td>
</tr>
<tr>
<td>A. Structural Parameters</td>
<td>14</td>
</tr>
<tr>
<td>B. Bonding in Pentaborane</td>
<td>16</td>
</tr>
<tr>
<td>III. EXPERIMENTAL</td>
<td>20</td>
</tr>
<tr>
<td>A. Preparation of Deuterated Pentaborane</td>
<td>20</td>
</tr>
<tr>
<td>B. Purity of Normal and Deuterated Pentaborane</td>
<td>24</td>
</tr>
<tr>
<td>1. Purity of Deuterated Pentaborane</td>
<td>24</td>
</tr>
<tr>
<td>2. Purity of Normal Pentaborane</td>
<td>26</td>
</tr>
<tr>
<td>3. Residual Hydrogen in B(_5)D(_9)</td>
<td>29</td>
</tr>
<tr>
<td>C. Infrared Spectroscopy</td>
<td>32</td>
</tr>
<tr>
<td>1. Accuracy and Calibration of Wavelength Scale</td>
<td>32</td>
</tr>
<tr>
<td>2. Transmission and Absorption Coefficients</td>
<td>36</td>
</tr>
<tr>
<td>3. Operating Conditions</td>
<td>37</td>
</tr>
<tr>
<td>4. Infrared Spectra, Frequencies, and Absorption Coefficients</td>
<td>38</td>
</tr>
<tr>
<td>D. Raman Spectroscopy</td>
<td>51</td>
</tr>
<tr>
<td>1. Raman Spectrograph and Light Source</td>
<td>51</td>
</tr>
<tr>
<td>2. Raman Tube and Sample</td>
<td>53</td>
</tr>
<tr>
<td>3. Raman Displacements or Frequencies</td>
<td>55</td>
</tr>
<tr>
<td>4. Polarization Measurements</td>
<td>58</td>
</tr>
<tr>
<td>5. Measurement of Intensities</td>
<td>75</td>
</tr>
<tr>
<td>6. Failure of the Reciprocity Law</td>
<td>83</td>
</tr>
<tr>
<td>7. Experimental Data</td>
<td>88</td>
</tr>
<tr>
<td>IV. SYMMETRY AND SELECTION RULES</td>
<td>104</td>
</tr>
<tr>
<td>V. MOMENTS OF INERTIA AND BAND TYPES</td>
<td>111</td>
</tr>
</tbody>
</table>
## CONTENTS (contd.)

**VI. NORMAL COORDINATE ANALYSIS** ........................................ 115

A. Introduction .................................................................................. 115
B. Definition of Coordinates .............................................................. 115
C. S-Vectors .......................................................................................... 120
D. Symmetry Coordinates ................................................................. 123
E. S-Vectors for Symmetry Coordinates ............................................. 135
F. Force Constant Matrices ................................................................. 139
G. Redundancy Conditions ................................................................... 140
H. Elimination of Redundancies and Final Form of F and G Matrices ... 159
I. Program of Solution of the Secular Equation .................................. 161
J. Selection of Force Constants to Be Retained ................................... 178
K. Method of Steepest Descents for Determination of Force Constants ... 182
L. Calculated Frequencies and Normal Coordinates ............................ 192

**VII. ISOTOPIC EFFECTS IN VIBRATIONAL SPECTRA** ...................... 202

A. Introduction .................................................................................... 202
B. Order Rule ....................................................................................... 209
C. Non-Crossing Rule and a Proposed Reversal Rule ............................ 208
D. Product Rule ..................................................................................... 221
E. Sum Rules ........................................................................................ 227
F. Small Isotope Effect ......................................................................... 230

**VIII. ASSIGNMENT OF VIBRATIONAL FREQUENCIES** ..................... 236

A. Introduction .................................................................................... 236
B. Terminal Hydrogen and Deuterium Stretching Frequencies .............. 245
C. Assignment of A<sub>1</sub> Frequencies ............................................. 251
   1. Polarized Raman Lines ................................................................ 251
   2. Bridge Stretching Frequencies .................................................... 252
   3. Boron-Boron Stretching Frequencies and the Small Isotope Effect ... 256
   4. Hydrogen Bending and Bridge Rocking Frequencies ..................... 264
   5. Application of Order, Product, and Reversal Rules ....................... 270
D. Assignment of E Frequencies .......................................................... 274
   1. Introduction .................................................................................. 274
   2. Bridge Stretching Frequencies .................................................... 275
## CONTENTS (contd.)

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3. Vertical B-H Bending Frequencies</td>
<td>277</td>
</tr>
<tr>
<td>4. Horizontal B-H Bending Frequencies</td>
<td>279</td>
</tr>
<tr>
<td>5. Bridge Rocking and Apex $B_0-H_0$ Bending Frequencies</td>
<td>281</td>
</tr>
<tr>
<td>6. Boron-Boron Stretching Frequencies</td>
<td>286</td>
</tr>
<tr>
<td>E. Assignment of $A_2$, $B_1$, and $B_2$ Frequencies</td>
<td>292</td>
</tr>
<tr>
<td>1. $A_2$ Frequencies</td>
<td>292</td>
</tr>
<tr>
<td>2. Selection Rules and Calculated Values for $B_1$ and $B_2$ Frequencies</td>
<td>293</td>
</tr>
<tr>
<td>3. High Frequency $B_1$ and $B_2$ Modes</td>
<td>294</td>
</tr>
<tr>
<td>4. Low Frequency $B_1$ and $B_2$ Modes</td>
<td>299</td>
</tr>
<tr>
<td>F. Overtones and Combinations</td>
<td>307</td>
</tr>
<tr>
<td>IX. THERMODYNAMIC FUNCTIONS OF PENTABORANE</td>
<td>312</td>
</tr>
<tr>
<td>AUTOBIOGRAPHY</td>
<td>320</td>
</tr>
</tbody>
</table>
TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Structural Parameters of Pentaborane</td>
<td>15</td>
</tr>
<tr>
<td>2. Infrared Spectra of ( \text{B}_5\text{D}_9 )</td>
<td>45</td>
</tr>
<tr>
<td>3. Infrared Spectra of ( \text{B}_5\text{H}_9 )</td>
<td>47</td>
</tr>
<tr>
<td>4. Raman Spectrum of Deuterated Pentaborane</td>
<td>96</td>
</tr>
<tr>
<td>5. Raman Spectrum of Normal Pentaborane</td>
<td>97</td>
</tr>
<tr>
<td>6. Character Table for ( C_{1v} ) Point Group</td>
<td>105</td>
</tr>
<tr>
<td>7. Classification of Vibrational Modes of Pentaborane</td>
<td>106</td>
</tr>
<tr>
<td>8. Symmetry Type of Combinations and Overtones</td>
<td>110</td>
</tr>
<tr>
<td>9. Moments of Inertia of Pentaborane</td>
<td>112</td>
</tr>
<tr>
<td>10. Coordinates of Pentaborane</td>
<td>124</td>
</tr>
<tr>
<td>11. Unit Vectors along the Bonds</td>
<td>127</td>
</tr>
<tr>
<td>12. s-Vectors for the Internal Coordinates</td>
<td>128</td>
</tr>
<tr>
<td>13. Symmetry Coordinates</td>
<td>133</td>
</tr>
<tr>
<td>14. S-Vectors</td>
<td>136</td>
</tr>
<tr>
<td>15. Definition of Valence Force Constants</td>
<td>145</td>
</tr>
<tr>
<td>16. Transformation Matrices</td>
<td>148</td>
</tr>
<tr>
<td>17. Symmetry Force Constant Matrices</td>
<td>150</td>
</tr>
<tr>
<td>18. Force Constant Matrix</td>
<td>153</td>
</tr>
<tr>
<td>19. Redundancy Conditions</td>
<td>162</td>
</tr>
<tr>
<td>20. ( U^{-1} ) Matrices</td>
<td>171</td>
</tr>
<tr>
<td>21. ( G )-Matrices</td>
<td>174</td>
</tr>
<tr>
<td>Table</td>
<td>Page</td>
</tr>
<tr>
<td>-------</td>
<td>------</td>
</tr>
<tr>
<td>22. Valence-Type Force Constants Retained for Pentaborane</td>
<td>195</td>
</tr>
<tr>
<td>23. Values of Force Constants</td>
<td>195</td>
</tr>
<tr>
<td>24. Calculated $A_1$ and $E$ Frequencies</td>
<td>196</td>
</tr>
<tr>
<td>25. Calculated $B_1$, $B_2$, and $A_2$ Frequencies</td>
<td>197</td>
</tr>
<tr>
<td>26. Normal Coordinates</td>
<td>198</td>
</tr>
<tr>
<td>27. Abundance of Boron Isotope Species of Pentaborane</td>
<td>234</td>
</tr>
<tr>
<td>28. Calculated $B^{10}$-$B^{11}$ Isotopic Splitting</td>
<td>235</td>
</tr>
<tr>
<td>29. Activity of Vibrational Modes of Pentaborane</td>
<td>236</td>
</tr>
<tr>
<td>30. Classification of Vibrational Modes of Pentaborane</td>
<td>242</td>
</tr>
<tr>
<td>31. Assignments of Diborane</td>
<td>243</td>
</tr>
<tr>
<td>32. Isotopic Assignment and Frequency Shifts for Boron-Boron Stretching Frequencies</td>
<td>263</td>
</tr>
<tr>
<td>33. Correlation of $A_1$ Frequencies by the Order and Product Rules</td>
<td>272</td>
</tr>
<tr>
<td>34. Correlation of $E$ Frequencies by the Order and Product Rules</td>
<td>290</td>
</tr>
<tr>
<td>35. Calculated Values of $A_2$, $B_1$, and $B_2$ Frequencies for $B_5H_9$ and $B_5D_9$</td>
<td>293</td>
</tr>
<tr>
<td>36. Assigned Values of $B_1$ and $B_2$ Frequencies for $B_5H_9$ and $B_5D_9$</td>
<td>305</td>
</tr>
<tr>
<td>37. Alternative Assignment of Low-Frequency $B_1$ and $B_2$ Modes of $B_5H_9$ and $B_5D_9$</td>
<td>306</td>
</tr>
<tr>
<td>38. Possible Assignments as Overtones or Combinations of Bands of $B_5H_9$ and $B_5D_9$ Not Assigned as Fundamentals</td>
<td>311</td>
</tr>
<tr>
<td>39. Thermodynamic Functions of Normal Pentaborane</td>
<td>316</td>
</tr>
</tbody>
</table>
**ILLUSTRATIONS**

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Structure of Pentaborane</td>
<td>8</td>
</tr>
<tr>
<td>2</td>
<td>Experimental Arrangement for Preparation of $B_5D_9$</td>
<td>21</td>
</tr>
<tr>
<td>3</td>
<td>Infrared Spectra of $B_5D_9$ in the NaCl Region</td>
<td>40</td>
</tr>
<tr>
<td>4</td>
<td>Infrared Spectrum of $B_5D_9$ in the KBr region</td>
<td>41</td>
</tr>
<tr>
<td>5</td>
<td>Infrared Spectra of $B_5H_9$ in the NaCl Region</td>
<td>42</td>
</tr>
<tr>
<td>6</td>
<td>Infrared Spectrum of $B_5H_9$ in the KBr region</td>
<td>43</td>
</tr>
<tr>
<td>7</td>
<td>Raman Spectra of $B_5D_9$ and $B_5H_9$</td>
<td>92</td>
</tr>
<tr>
<td>8</td>
<td>Development Factor $J$ versus Mean Optical Density</td>
<td>98</td>
</tr>
<tr>
<td>9</td>
<td>Variation of Vibrational Frequencies of Pentaborane with Isotopic Hydrogen Mass</td>
<td>209</td>
</tr>
</tbody>
</table>
I. INTRODUCTION

A. Early Structural Concepts for the Boron Hydrides

The structure of the boron hydrides was for many years a major puzzle of structural chemistry, because of the obvious electron deficiency of these compounds as judged from the usual concept of electron pair bonds. Aside from BH, which is observed only spectroscopically, the most important hydrides of boron are \( \text{B}_2\text{H}_6 \) (diborane), \( \text{B}_4\text{H}_{10} \) (tetraborane), \( \text{B}_5\text{H}_9 \) (stable pentaborane), \( \text{B}_5\text{H}_{11} \) (unstable pentaborane), \( \text{B}_6\text{H}_{10} \) (hexaborane), and \( \text{B}_{10}\text{H}_{14} \) (decaborane). Prior to the availability of definite structural data and its proper interpretation, theories of the structure of the boranes were of necessity based on plausible valence structures. In the early period the structures were most often assumed to be hydrocarbon-like, so that \( \text{B}_2\text{H}_6 \) was assigned the structure of ethane, \( \text{C}_2\text{H}_6 \), and \( \text{B}_4\text{H}_{10} \) the structure of butane, \( \text{C}_4\text{H}_{10} \). Since the boron atom has only three valence electrons, one less than carbon, these postulated structures would of course be electron-deficient, and it was necessary to assume the existence of resonating forms containing both one-electron and electron-pair bonds. These ideas were so well established that the early electron-diffraction investigations of Bauer et al.\(^1\) were interpreted as confirming the hydrocarbon-like structures. In addition to the structures of \( \text{B}_2\text{H}_6 \) and \( \text{B}_4\text{H}_{10} \) referred to above, \( \text{B}_5\text{H}_9 \) was

---

1. S. H. Bauer, Chem. Rev., 21, 43 (1942), and references given there.
assigned a methylenecyclobutane structure by Bauer and Pauling\textsuperscript{2} in 1936. Among the structures rejected by these authors was the tetragonal pyramid now known to be correct. There was considerable justification for this as their radial distribution curve, based on visual estimates of electron diffraction intensities, showed two strong peaks at 1.73 and 2.52 Å, both of which were assigned to B-B interactions. As will be seen subsequently, the strength of the peak at 2.52 Å was overestimated, and it is now assigned to a number of approximately coincident B-B and B-H distances.

B. Bridge Structure for Diborane

The most important single step toward a correct understanding of the borane structures was the verification of the hydrogen bridge structure of diborane. This structure,

\[
\text{H}_\text{H}_\text{B}_\text{B}_\text{H}_\text{H}
\]

was originally proposed many years ago.\textsuperscript{3,4} As stated, Bauer\textsuperscript{5} rejected it in favor of the ethane-like structure in his electron diffraction investigation in 1937. However, shortly after this the Raman spectrum of diborane was obtained by Anderson and Burg\textsuperscript{6} and the infrared spectrum by

\textsuperscript{3}W. Dilthey, Z. angew. Chem., \textbf{24}, 596 (1921).
\textsuperscript{4}A. F. Core, Chem. and Ind., \textbf{5}, 642 (1927).
\textsuperscript{5}S. H. Bauer, J. A. C. S., \textbf{52}, 1096 (1937).
Stitt. These spectra strongly supported the bridge model of symmetry, $V_h$, as opposed to either the staggered or eclipsed ethane model of symmetry $D_{3d}$ or $D_{3h}$. The most detailed justification for this conclusion was given by Bell and Longuet-Higgins, who also carried out a normal coordinate analysis based on the bridge model. A summary of the arguments for the bridge model has been given by Bell and Emeleus. The spectra are more complex than that of ethane, indicating a lower symmetry for diborane. The Raman spectrum shows two intense polarized B-H stretching frequencies at 2102 and 2523 cm$^{-1}$, which definitely establishes the existence of two types of hydrogen atoms in the molecule and eliminates the ethane structure. There is also a low-frequency infrared band at 412 cm$^{-1}$ which is essentially inconsistent with the ethane structure but is easily interpreted as bending of the molecule at the hydrogen bridge. It was also impossible to reconcile the statistical and calorimetric entropies for diborane with the ethane structure unless a barrier to internal rotation much larger than that of ethane was assumed. Subsequently the infrared spectrum of diborane was studied under high resolution by Price and Anderson and Barker. The

rotational fine-structure of several infrared bands are definitely characteristic of an asymmetric top, as represented by the bridge model, and completely incompatible with a symmetric top, as represented by the ethane model. Improved Raman data has been obtained by Webb, Neu, and Pitzer.\textsuperscript{14} About the same time as the bridge model was conclusively established by the spectroscopic data, Nekrasov and Shtutser\textsuperscript{15,16} showed that the original electron diffraction intensities of Bauer\textsuperscript{17} could be reproduced even better by the bridge model than the ethane model assumed by Bauer. Bauer\textsuperscript{18} also subsequently tested the bridge model and found it to be satisfactory, with essentially the same parameters as calculated by Nekrasov and Shtutser. Both of these revised interpretations of the electron diffraction data establish that the two bridge hydrogens lie in a plane perpendicular to the plane of the remaining atoms. Thus the molecule resembles ethylene, with the two bridge bonds playing the role of the double bond.

C. Establishment of Pyramidal Model for Pentaborane

We now return to the consideration of pentaborane, B$_5$H$_9$, which had been assigned the methylenecyclobutane structure by Bauer and Pauling\textsuperscript{19} in 1936. In 1945 at a time when the evidence for the bridge

\begin{itemize}
\item \textsuperscript{15} B. V. Nekrasov, J. Gen. Chem. USSR, 10, 1021, 1156 (1940).
\item \textsuperscript{16} B. V. Nekrasov and V. V. Shtutser, J. Gen. Chem. USSR, 10, 832 (1948).
\item \textsuperscript{17} S. H. Bauer, J. A. C. S., 59, 1096 (1937).
\item \textsuperscript{18} S. H. Bauer, Chem. Rev., 31, 43 (1942).
\item \textsuperscript{19} Bauer and Pauling, \textit{op. cit.}.
\end{itemize}
structure of diborane was nearly conclusive, Pitzer\textsuperscript{20} proposed a five-membered ring of cyclopentadiene-like structure for $\text{B}_5\text{H}_9$, with a pair of hydrogen bridges replacing each of the double bonds of cyclopentadiene. At about the same time Pauling was privately advocating the tetragonal pyramidal structure.\textsuperscript{21,22} The Raman and infrared spectra of liquid $\text{B}_5\text{H}_9$ were obtained by Taylor et al.\textsuperscript{23} in this laboratory in 1950. The Raman spectrum contained a broad band at 1840 cm$^{-1}$ and the infrared a strong band at 1800 cm$^{-1}$ which by comparison with the bridge-stretching frequencies of diborane established the presence of one or more hydrogen bridges in pentaborane. On this basis they discarded the methylenecyclobutane structure. A conclusive decision between the pyramidal and cyclopentadiene structures was not considered possible on the basis of the spectral data alone, although the pyramidal model was favored on the basis of the low-frequency boron bending modes to be expected for the two structures. Three such bending modes are predicted for a cyclopentadiene model, and only one for the pyramidal model. The Raman spectrum shows a very weak band at 470 cm$^{-1}$, which was assigned to the skeletal bending mode of the pyramidal model, but no lower frequency Raman lines were observed. The lowest frequency band in the infrared spectrum occurs at 568 cm$^{-1}$ A comparison of the calorimetric entropy of pentaborane gas as

\textsuperscript{20} K. S. Pitzer, \textit{J. A. C. S.}, \textbf{67}, 1126 (1945).
measured by Johnston et al.,\textsuperscript{24} with statistical-spectroscopic entropies, based upon tentative frequency assignments and estimated moments of inertia for the two models, strongly favored the more symmetrical pyramidal model. It was also pointed out that the pyramidal model gave better agreement with the original electron diffraction data of Bauer and Pauling.

The structure of pentaborane was reinvestigated by electron diffraction by Hedberg, Jones, and Schomaker.\textsuperscript{25,26} They rejected the methylcyclobutane structure of Bauer and Pauling and also the cyclopentadiene structure of Pitzer.\textsuperscript{27} Following the initial consideration of several other structures they were influenced by the spectroscopic and calorimetric data to reconsider the pyramidal model rejected by Bauer and Pauling but now advocated by Pauling. They found excellent agreement with the data was obtained with a tetragonal model of symmetry $C_{4v}$, with the boron atoms forming a square pyramid. Four hydrogen atoms were assumed to occupy bridge positions between the borons at the base of the pyramid, while the remaining five hydrogen atoms were bonded normally, one to each boron.

Essentially concurrently with the preceding investigation the x-ray diffraction by single crystals of pentaborane was studied by


\textsuperscript{25} K. Hedberg, M. E. Jones, and V. Schomaker, J. A. C. S., 73, 3538 (1951).


\textsuperscript{27} Pitzer, \textit{op. cit.}
Dulmage and Lipscomb.\textsuperscript{28,29} This investigation established conclusively the symmetry $C_{4v}$ for the molecule, and the pyramidal configuration of the boron atoms. The location of the hydrogen atoms, particularly the bridge hydrogens, was established partly on the basis of packing considerations in the crystal. Their final structural parameters are in good agreement with those of Hedberg, Jones, and Schomaker.\textsuperscript{30} The pyramidal structure of stable pentaborane which is now firmly established by these two investigations is illustrated in Figure 1. The detailed structural parameters will be presented subsequently.

The rotational microwave spectrum of $\text{B}_5\text{H}_9$ has been studied by Hrostowski, Myers, and Pimentel,\textsuperscript{31} and in more detail by Hrostowski and Myers,\textsuperscript{32} who also extended the measurements to $\text{B}_5\text{D}_9$ and several partially deuterated pentaboranes. Their results establish that the molecule is a symmetric rotor, further confirming the pyramidal model, and yield accurate values for the moments of inertia of the isotopic species about axes perpendicular to the top axis. These in turn make possible the calculation of precise boron-boron distances.

\begin{itemize}
\item \textsuperscript{28} W. J. Dulmage and W. N. Lipscomb, \textit{J. A. C. S.}, 73, 3539 (1951).
\item \textsuperscript{29} W. J. Dulmage and W. N. Lipscomb, \textit{Acta. Cryst.}, 5, 260 (1952).
\item \textsuperscript{30} Hedberg, Jones, and Schomaker, op. cit.
\end{itemize}
B BASE BORON
B₀ APEX BORON
H BASE HYDROGEN
H₀ APEX HYDROGEN
H' BRIDGE HYDROGEN

STRUCTURE OF PENTABORANE, B₉H₉

FIG. 1
D. **Previous Spectroscopic Data and Assignments for Pentaborane**

As previously discussed, the infrared and Raman spectra of $B_5H_9$ were reported by Taylor et al.\(^{33}\) Their Raman spectra, photographed with a Lane-Wells f/3 Spectrograph, were of excellent quality and are still the only available Raman data for $B_5H_9$. On the other hand their infrared spectra for the KBr and NaCl regions were obtained with the now obsolete Perkin-Elmer Model 12B spectrophotometer, which operated with a D. C. signal rather than the A. C. signal of modern chopped-beam instruments. As a result their infrared spectra were of inferior quality by present day standards, although all the principal bands were observed. Improved infrared spectra covering the range 400-4000 cm\(^{-1}\) have been obtained by Hrostowski and Pimentel\(^{34}\) for $B_5H_9$ and the deuterated molecule $B_5D_9$. They used a Perkin-Elmer Model 21 double chopped-beam spectrophotometer for the NaCl region, and a Model 12-C single chopped-beam spectrometer for the KBr and LiF regions. Their results confirm the 20 odd infrared bands reported by Taylor et al. for $B_5H_9$, but they resolved many additional weaker bands, some of which coincide with Raman bands reported by Taylor et al.

On the basis of their improved infrared data for $B_5H_9$ and $B_5D_9$, and the Raman data of Taylor et al. for $B_5H_9$, Hrostowski and Pimentel make a partial assignment of the vibration frequencies for normal and deuterated pentaborane. A critical evaluation and comparison of their assignment will be given subsequently in connection with the complete

---


assignment attempted in the present investigation, and only a few remarks will be made here. Hrostowski and Pimentel did not carry out a normal coordinate analysis, and attempted only a fragmentary identification of frequencies with particular modes of vibration. They made use of the small frequency shifts in certain infrared bands resulting from the replacement of the $^{11}B$ isotope by $^{10}B$, but ignored the similar and even more definite isotope shifts in certain Raman bands reported by Taylor et al. These small isotope shifts are important in identifying boron stretching modes. For the most part Hrostowski and Pimentel simply assigned the observed frequencies which they regarded as fundamentals to one of the four optically active symmetry classes of the $C_{4v}$ point group, $A_1$, $E$, $B_1$, or $B_2$. In the absence of any Raman data on the deuterated molecule $B_5D_9$, they did not have available all the fundamental frequencies in classes $A_1$ and $E$, some of which are strong in the Raman spectrum but too weak to identify as fundamentals on the basis of the infrared spectrum alone. Furthermore, classes $B_1$ and $B_2$ are active only in the Raman, so no fundamentals of these classes were available to Hrostowski and Pimentel. As a result they were not able to use the product rule as a check on their assignment of $B_5H_9$ and $B_5D_9$ frequencies within each symmetry class, but used it simply to calculate the missing fundamentals. Class $A_2$ is inactive in both the infrared and Raman spectra so that Hrostowski and Pimental were able only to guess the frequencies of the two modes in this class. The normal coordinate analysis carried out in the present investigation indicates one of the $A_2$ modes in $B_5H_9$ was assigned an impossibly low frequency.
In view of these deficiencies in their assignment, and the number of frequencies estimated, the virtually exact agreement between the statistical entropy of \( B_5^9 \), 65.73 cal. deg.\(^{-1}\) mole\(^{-1}\) at 296° K., calculated by Hrostowski and Pimentel, and the calorimetric entropy,\(^{35}\) 65.75 cal. deg.\(^{-1}\) mole\(^{-1}\), is largely fortuitous as they state. In fact, their low frequency \( A_2 \) mode which is simply a guess contributes 0.65 cal. deg.\(^{-1}\) mole\(^{-1}\) to the entropy.

E. Outline of Present Investigation

The preceding discussion makes clear the importance of obtaining the Raman spectrum of \( B_5^9 \), so that the frequency assignment for \( B_5^9 \) and \( B_5^9 \) may be based on complete infrared and Raman data for both molecules. The product rule is of greatest utility only when the maximum number of fundamentals are experimentally observed for both isotopic molecules. The importance of Raman polarization data in identifying totally-symmetric modes is well known. In the present investigation \( B_5^9 \) has been prepared in sizable quantity, and its Raman spectrum and polarization data observed using exposures as long as 400 hours. The infrared spectra of gaseous \( B_5^9 \) and \( B_5^9 \) in the KBr and NaCl regions have also been remeasured with a Perkin-Elmer Model 21 spectrophotometer, using the narrowest possible slits and extremely slow rates of scanning. These spectra seem somewhat superior in resolution of detail to the infrared spectra of Hrostowski and Pimentel. More important is the observation of a new fundamental for \( B_5^9 \), which appears in good strength at 511

\(^{35}\) Johnston, Kerr, Clarke, and Hallet, op. cit.
12 cm.\(^{-1}\) in the infrared and is also observed at 507 cm.\(^{-1}\) in the Raman spectrum.

On the basis of the Raman spectrum of \(\text{B}_5\text{D}_9\) and the improved infrared spectra for \(\text{B}_5\text{H}_9\) and \(\text{B}_5\text{D}_9\) obtained in this investigation, and the Raman spectrum of \(\text{B}_5\text{H}_9\) observed by Taylor \textit{et al.} in this laboratory, as complete as possible an assignment of the observed fundamental frequencies of \(\text{B}_5\text{H}_9\) and \(\text{B}_5\text{D}_9\) has been made. This assignment was based initially on such general aids as (1) selection rules for the molecular point group; (2) polarization or depolarization of Raman bands; (3) band contours (although because of the ratio of the moments of inertia these have proved of little value); (4) the major isotope shifts observed on replacement of hydrogen by deuterium, in combination with the order rule which limits individual frequency ratios and the product rule correlating all ratios in a given symmetry class; (5) small boron \(10^\text{B} - 11^\text{B}\) isotope shifts; (6) comparison with the frequency assignments for diborane, \(\text{B}_2\text{H}_6\); and (7) comparison of the calculated statistical entropy and the calorimetric entropy, as an overall check on the assignment of the lower frequencies. In this way complete assignments for all \(A_1\) and \(E\) modes of both \(\text{B}_5\text{H}_9\) and \(\text{B}_5\text{D}_9\) were obtained, although with some uncertainty still attached to the assignment of a few frequencies. On the other hand the assignments for the \(A_1\) and \(B_2\) classes, which are active only in the Raman, remain quite fragmentary with only about half of the fundamentals definitely observed, and of course the inactive \(A_2\) modes cannot be assigned at all on this basis.
Following the completion of the initial assignment as described, a complete normal coordinate analysis was carried out for all symmetry classes of $B_5H_9$ and $B_5D_9$. This calculation had several objectives: (1) to strengthen the assignment of observed fundamentals; (2) to supply reasonably quantitative values for fundamentals not observed due to inactivity or low intensity, thus making possible the calculation of thermodynamic functions for $B_5H_9$ and $B_5D_9$ over a wide temperature range; (3) to yield values of bond stretching and bending force constants for this unusual electron-deficient molecule; (4) to obtain the approximate form of the normal modes of vibration, and to study the correlation of these modes in $B_5H_9$, $B_5D_9$, and the as yet unavailable tritiated molecule $B_5T_9$; and, finally, (5) to develop a new and more nearly automatic method for the solution of the secular equation and calculation of force constants using the IBM 704 computer, based on the minimization by successive steepest descents of the sum of errors of the calculated frequencies. All of these objectives have been attained to a considerable degree.
II. STRUCTURE AND BONDING OF PENTABORANE

A. Structural Parameters

As discussed in the introduction, the structure of pentaborane has been determined by x-ray and electron diffraction and microwave techniques. A three-dimensional view of the pentaborane structure has been given in Figure 1. The drawing is modeled after a figure in reference 3. The apex boron atom has been distinguished from the base boron atoms by a subscript 0. It will frequently be convenient to denote the bridge hydrogen atoms by a prime as in the figure. However, when it is necessary to specify individual atoms, as in the normal coordinate analysis, the following notation will be used: \( H_0 \) and \( B_0 \), the apex hydrogen and boron atoms; \( B_1 \), \( B_2 \), \( B_3 \), and \( B_4 \), the base boron atoms in rotation; \( H_1 \), \( H_2 \), \( H_3 \), and \( H_4 \), the non-bridge hydrogen atoms with \( H_1 \) bonded to \( B_1 \); and \( H_5 \), \( H_6 \), \( H_7 \), and \( H_8 \), the bridge hydrogen atoms with \( H_5 \) bonded to \( B_1 \) and \( B_2 \), \( H_6 \) bonded to \( B_2 \) and \( B_3 \), etc. The structural parameters for pentaborane as given by x-ray and electron diffraction and microwave methods are given in Table 1. The data was conveniently summarized in this form by Hrostowski and Myers.\(^4\) The microwave data was not sufficient to determine all the structural parameters. The procedure

\(^3\) H. J. Hrostowski and R. J. Myers, 22, 262 (1954).
\(^4\) Ibid.
TABLE 1

STRUCTURAL PARAMETERS OF PENTABORANE

<table>
<thead>
<tr>
<th></th>
<th>X-ray*</th>
<th>Electron Diffraction**</th>
<th>Microwave***</th>
</tr>
</thead>
<tbody>
<tr>
<td>( B_0 - B )</td>
<td>1.66</td>
<td>1.700</td>
<td>1.687</td>
</tr>
<tr>
<td>±0.02</td>
<td>±0.017</td>
<td>±0.005</td>
<td></td>
</tr>
<tr>
<td>( B - B )</td>
<td>1.77</td>
<td>1.805</td>
<td>1.800</td>
</tr>
<tr>
<td>±0.02</td>
<td>±0.014</td>
<td>±0.003</td>
<td></td>
</tr>
<tr>
<td>( B_0 - H_0 )</td>
<td>1.21</td>
<td>1.234</td>
<td>(1.18)</td>
</tr>
<tr>
<td>±0.05</td>
<td>±0.017</td>
<td>(1.22)</td>
<td>(1.26)</td>
</tr>
<tr>
<td>( B - H )</td>
<td>1.20</td>
<td>1.066</td>
<td></td>
</tr>
<tr>
<td>±0.07</td>
<td>±0.003</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( B - H' )</td>
<td>1.35</td>
<td>1.359</td>
<td>1.39</td>
</tr>
<tr>
<td>±0.04</td>
<td>±0.077</td>
<td>1.35</td>
<td></td>
</tr>
<tr>
<td>( B_0 - B - H ) angle</td>
<td>115°</td>
<td>120°</td>
<td>134°20'</td>
</tr>
<tr>
<td>±5°</td>
<td>±20°</td>
<td>±30'</td>
<td></td>
</tr>
<tr>
<td>( B_0B B - B )</td>
<td>190°</td>
<td>187°</td>
<td>192°</td>
</tr>
<tr>
<td>±5°</td>
<td>±10°</td>
<td>±2°</td>
<td></td>
</tr>
</tbody>
</table>

Distances are in Angstrom units.


followed was to assume values for the \( B-H \) (and \( B_0-H_0 \)) bond length and calculate the remaining parameters. The three subcolumns in the microwave column of the table give the values of the \( B-H' \) bond length, the \( B_0-B-H \) angle, and the \( B_0BB-BBH' \) angle for three different choices of the
B-H bond length. The agreement between the microwave, electron
diffraction, and x-ray results is fairly good. The electron diffraction
and microwave parameters are for gaseous pentaborane, while those from
x-ray diffraction refer of course to crystalline pentaborane. The fact
that the bond distances as determined by x-ray diffraction are slightly
smaller than those determined by the other two methods may be due to a
torsional motion of the molecule in the solid.\textsuperscript{5} For all calculations in
this dissertation, the microwave values with the B-H bond length equal to
1.22 Å have been used.

B. Bonding in Pentaborane

A brief qualitative discussion of the bonding in pentaborane will
now be given. For more detailed analyses, the reader is referred to the
literature.\textsuperscript{6,7,8} As is typical of the boron hydrides, pentaborane is
electron deficient, i.e., the number of available valence orbitals
exceeds the number of valence electrons. Counting only the $1s$ orbital
of hydrogen and the $2s$ and three $2p$ orbitals of boron, pentaborane has
29 available orbitals. On the same basis, it has 24 valence electrons.
The non-bridge hydrogens are assumed to form normal single bonds to the
boron atoms, using one electron from hydrogen and one from boron. The

\begin{footnotesize}
\begin{enumerate}
\item W. H. Eberhardt, B. Crawford, Jr., and W. N. Lipscomb,
\item W. N. Lipscomb, Adv. in Inorganic and Radiochemistry, Vol.
\end{enumerate}
\end{footnotesize}
bridge hydrogen atoms form a three-center bond with the two neighboring boron atoms. Each boron atom may be considered as contributing $\frac{1}{2}$ electron to this bond, while the hydrogen atom contributes 1 electron. There remains for the pyramidal boron-boron bonding one orbital and one electron on each base boron atom and three orbitals and two electrons on the apex atom. Although the boron bonding might be regarded as made up of two single $B_0$-B bonds and a three-center $B-B_0B$ bond, with two resonance forms, a simple molecular orbital picture is perhaps better.

By taking the proper linear combinations of the four base boron orbitals, one orbital of symmetry $A_1$, one of symmetry $B_1$, and one degenerate $E$ orbital can be formed. From the three apex boron orbitals, one $A_1$ and one degenerate $E$ orbital can be formed. Combining the base and apex orbitals, it is found that two bonding orbitals of symmetry $A_1$ and $E$ (doubly degenerate) are formed. The six electrons are then considered to occupy these orbitals. This leads essentially to bonding of the apex boron atom to each of the base boron atoms, and little direct bonding between base boron atoms. The bonding between base boron atoms is essentially through the bridge hydrogens.

The preceding scheme would appear to require hybridization of the $2s$ and three $2p$ orbitals about each boron atom to give the most effective directed orbitals. Taking the $z$-axis along the four-fold symmetry axis, the $2s$ and $2p_z$ orbitals of the apex boron atom may be hybridized to yield two oppositely directed $\sigma$ orbitals of symmetry $A_1$. One of these forms the $B_0-H$ bond and the other participates in the $A_1$ molecular orbital of the boron pyramid. The $2p_x$ and $2p_y$ orbitals of $B_0$ are then
available for the molecular orbital of symmetry E. At the base boron atoms it is evident that roughly tetrahedral hybridization of the 2s and three 2p orbitals is required, in order to form the B-H bond, the two bridge or B-H' bonds, and (through molecular orbitals) the B_0-B bond. However, the formal bond angles calculated from the structural parameters in Table 1 indicate a considerable degree of strain or departure from tetrahedral symmetry in these hybridized orbitals. The calculated value of H'-B-H' angle (see Fig. 1) is only 85.5°. Since no combination of orbitals for sp^3 hybridization can yield two directed orbitals at an angle less than 90°, it is clear that the orbitals cannot be directed along the formal B-H' bonds. The minimum angle of 90° is obtained for two pure p orbitals, and to maintain orthogonality the remaining two hybrid orbitals would be oppositely directed with an angle of 180°. This result is quite unreasonable, as the observed value of the B_0-B-H angle is 136°. This difficulty is largely removed by the simple theory of strained bonds proposed by Kilpatrick and Spitzer,^9 and applied by them to cyclopropane and cyclobutane. They proposed that in the case of strained bonds the strongest orbitals will be those having the greatest value in the formal bond direction, regardless of whether the maximum value of the orbital occurs in this direction (by the value of the orbital here is meant the angular part). Applying this criterion to the H'-B-H' angle, with a formal value of 85.5° (θ_{12} of their Table 1), the predicted value of the B_0-B-H angle (θ_{34} of their table) is 116.5°. This is an increase of 7° over the tetrahedral angle, but still 19.5° less than the

---

observed angle of $136^\circ$. This suggests that the hybrid orbital which participates in the boron molecular orbitals is not directed along the edge of the boron pyramid (or toward $B_0$), but several degrees above the edge. This shift in direction would appear to make possible increased overlap with the $2p_x$ and $2p_y$ orbitals of $B_0$. These conclusions differ from those of Eberhardt, Crawford, and Lipscomb,\textsuperscript{10} who do not take account of the abnormally small value of the $H'-B-H'$ angle, and erroneously state that the configuration of the formal bonds about a base boron is approximately trigonal, with the axis passing through $B$ and $B_0$. As a result they conclude that the $B-B_0$ bond orbital is directed along the formal bond direction or edge of the pyramid. The structural parameters show that the configuration of the bonds about a base boron has approximately $C_{2v}$ symmetry as assumed in the preceding discussion.

\textsuperscript{10} Eberhardt, Crawford, and Lipscomb, \textit{op. cit.}
III. EXPERIMENTAL

A. Preparation of Deuterated Pentaborane

The deuterated pentaborane was prepared by catalytic exchange of normal pentaborane, $\text{B}_5\text{H}_9$, with deuterium, by the method of Hrostowski and Pimentel. However, for the investigation of the Raman spectrum it was necessary to prepare approximately 3 grams of the deuterated compound, which is a much greater quantity than was required by Hrostowski and Pimentel for the infrared spectrum. The method was therefore modified to increase its efficiency. Hrostowski and Pimentel depended on diffusion of pentaborane through the catalyst, which is relatively slow in the presence of deuterium at the partial pressure required. In the present investigation a pump or blower was incorporated in the system to continuously circulate the deuterium-pentaborane mixture over the catalyst. A schematic diagram of the experimental arrangement is given in Figure 2.

The deuterium was purchased from the Stuart Oxygen Company, San Francisco, California. The chromia-alumina dehydrogenation catalyst (Harshaw No. CR-0102 T 1/8") was supplied by the Harshaw Chemical Company. Normal pentaborane, $\text{B}_5\text{H}_9$, was obtained through the courtesy of Professor A. B. Garrett of this department, and was prepared by the Olin-Mathieson

EXPERIMENTAL ARRANGEMENT FOR PREPARATION OF $B_5D_9$. 

Diagram showing the experimental setup with labels for each component:
- Pressure Gauge
- Vacuum Cold Trap
- Circulating Pump
- Catalyst
- Tube Furnace
- Condensing Bulbs
- Manometer
- Stopcock or Valve

Caption: FIG. 2
Company. Normal pentaborane has a melting point of $-46.8^\circ C$ and boiling point of $60.0^\circ C$. The vapor pressure of the liquid at $20^\circ C$ is 168 mm Hg. Deuterated pentaborane has a melting point of $-47.0^\circ C$, boiling point of $59.0^\circ C$, and vapor pressure of 176 mm Hg at $20.0^\circ C$.2

A description of the procedure employed in preparing the deuterated pentaborane will now be given. High vacuum techniques were used. The vacuum was checked many times during the preparation with a McLeod gauge; a pressure below $10^{-4}$ mm Hg was considered satisfactory. A vacuum-tight Bourdon gage was sufficiently accurate for measurement of gas pressures during the exchange. A mercury manometer in the vacuum system was not in contact with the pentaborane circulating in the system. Silicone stopcock grease was used on the vacuum stopcocks, which were regreased about every two weeks to prevent freezing. The pyrex glass and metal parts of the vacuum system were joined by two pyrex-copper seals. Copper tubing was employed in the metal part of the system. All joints were soft soldered. Needle valves with vacuum tight bellows were used where fine control of flow was needed. The circulating pump was essentially a fan or blower enclosed in a cylindrical container. A magnet was placed through the shaft of the fan, and a magnetic stirrer used to drive the blower. The bearings, where the shaft made contact with the container, were lubricated with graphite.

About 3 grams (4.5 cc.) of pentaborane was introduced into the system. The volume of the system was large enough for this quantity of pentaborane to exist in the gaseous state without condensation to the liquid at room temperature. When the pentaborane was not being exchanged

with deuterium, it was condensed in a bulb and kept as the solid at liquid nitrogen temperatures. Before each exchange the catalyst was heated to about 450° C. and pumped on for at least twenty-four hours. After the catalyst had cooled to room temperature, the pentaborane was allowed to warm and vaporize, yielding a pressure of about 170 mm. Hg of pentaborane in the system. Deuterium was then added to the system until the total pressure was slightly less than atmospheric. The mixture was then circulated over the catalyst by the circulating pump. The exchange reached equilibrium after about two days and appeared to be statistical in nature, i.e., the percentage of deuterium in pentaborane was the same as the percentage of deuterium in the hydrogen-deuterium mixture. After equilibrium was reached, the gas mixture was passed slowly through a cold trap while being evacuated by the vacuum pump. The pentaborane condensed in the trap while the deuterium-hydrogen mixture was pumped into the hood. After all the hydrogen-deuterium mixture had been pumped out, the pentaborane was transferred from the cold trap to one of the condensing bulbs. The catalyst was then reactivated and the entire procedure repeated with fresh deuterium. A small amount of pentaborane was lost in each exchange. This was probably due to some of it passing through the cold trap and some being adsorbed on the catalyst, then being lost when the catalyst was reactivated.

After each exchange a small sample of vapor was withdrawn and the degree of exchange measured by infrared absorption, using the procedure discussed in section B3 below. After eight exchanges approximately three grams of pentaborane containing 1.26 atomic percent
hydrogen and 98.74 atomic percent deuterium was obtained. The mean
factor by which the atomic percent of hydrogen was reduced in each
exchange was therefore the eighth root of 0.0126, or 0.58. Assuming
approximate partial pressures in each exchange of 170 mm Hg for penta-
borane and 500 mm Hg for the added deuterium gas, and random distribu-
tion of hydrogen and deuterium between the pentaborane and hydrogen gas
following the exchange, a calculated value of \(9 \times 170/(9 \times 170 + 2 \times 550) = 0.58\) for the mean exchange factor is obtained, which is in
excellent agreement with the observed value.

B. Purity of Normal and Deuterated Pentaboranes

1. Purity of Deuterated Pentaborane

Little direct evidence is available for the purity of the
deuterated pentaborane prepared in this investigation other than the high
purity of the normal pentaborane and deuterium used as starting materials
(the purity of the normal pentaborane is discussed below). It can be
concluded that the catalyst used for deuteration did not produce conver-
sion to other boranes for otherwise the infrared spectra in the early
stages of the deuteration would have shown the known bands of other boron
hydrides, and such bands were not observed. The direct evidence for the
purity of the \(B_5D_9\) sample rests principally on the excellent agreement
between the infrared spectra of the present sample and that prepared by
Hrostowski and Pimentel.\(^3\) The agreement is essentially perfect in the
NaCl region. In the KBr region one band was obtained with consideraly

\(^3\) Hrostowski and Pimentel, \textit{op. cit.}
greater strength in the present investigation, but as will be discussed subsequently this is believed due to differences in the instruments used in the KBr region. No conceivable impurity could contribute a single band in the KBr region and no bands in the NaCl region. The agreement of the spectra of the present sample and that of Hrostowski and Pimentel must be given considerable weight because the normal pentaborane used was obtained from different sources (Hrostowski and Pimentel used $B_5H_9$ supplied by the General Electric Company), and would be unlikely to contain other boron hydrides in the same amounts as impurities.

The only other boron deuteride for which infrared and Raman spectra are available appears to be $B_2D_6$. The absence of $B_2D_6$ from the $B_5D_9$ sample is shown by the failure to observe in the spectra of the latter the strong infrared and Raman bands of $B_2D_6$ which occur at 1850 and 1870 cm$^{-1}$, respectively.

It would have been desirable to carry out a purification of the sample by fractional distillation or crystallization. However, this was not attempted because of the inevitable loss of the limited sample, all of which was needed for the Raman spectra. Furthermore the manipulation of this substance is both difficult and hazardous. Finally, as discussed above there was no reason to suspect the presence of any significant impurity.

The vapor pressure of the $B_5D_9$ sample was observed at $0^\circ C.$ with a small mercury manometer and agreed within the limited accuracy of about 2 mm. Hg with the reported value of 68.6 mm. Hg.  

2. Purity of Normal Pentaborane

The purity of normal pentaborane is of interest in the present investigation because it is the starting material for the preparation of deuterated pentaborane, and also because the spectra of $B_5H_9$ as well as $B_5D_9$ is required for the vibrational assignment. $B_2H_6$, $B_4H_{10}$, $B_5H_{11}$, and $B_6H_{10}$ are the only boranes sufficiently volatile to require consideration as impurities in $B_5H_9$. Their boiling points (or vapor pressures) are $B_2H_6$, -92.5° C.; $B_4H_{10}$, 18° C.; $B_5H_{11}$, 63° C.; and $B_6H_{10}$, 7.2 mm. Hg at $0^\circ C.$; according to Schlesinger and Burg. These values are open to some question, as the same authors give the boiling point of $B_5H_9$ as 48° C., while the more recent vapor pressure measurements of Shapiro and Ditter yield 60.0° C. In any case it would appear relatively easy to remove other boranes, with the possible exception of $B_5H_{11}$, from $B_5H_9$ by fractional distillation at reduced pressure. It is known that the sample of $B_5H_9$ used for the study of the Raman spectrum by Taylor et al. and for the measurement of the calorimetric entropy by Johnston et al. was subjected to careful fractional distillation to remove other

boranes during its preparation by the General Electric Company. The
calorimetric measurements showed, through a study of the fraction melted
versus temperature below the true melting point, that this sample had a
purity in excess of 99.9 mole percent. It seems likely that the sample
of Hrostowski and Pimental which was obtained from the same source was
subjected to a similar purification procedure, but no discussion of the
preparation or purity of their sample is given by these authors. As
previously stated the sample of B\textsubscript{5}H\textsubscript{9} used in the present investigation
was obtained from the Olin-Mathieson Company, but no statement of purity
was supplied with the sample.

Fortunately the position of the stronger bands in the infrared
spectra of B\textsubscript{2}H\textsubscript{6}, B\textsubscript{4}H\textsubscript{10}, B\textsubscript{5}H\textsubscript{11}, and B\textsubscript{6}H\textsubscript{10}
are known and this makes it possible to set rather accurate upper limits on the concentrations of
these boranes in B\textsubscript{5}H\textsubscript{9}. A quantitative method for the estimation of the
first three boranes listed above in B\textsubscript{5}H\textsubscript{9} has been given by McCarty, Smith,
and McDonald\textsuperscript{10}, based on the absorbance or optical density of the sample
at 1625, 1805, 2150, and 2470 cm\textsuperscript{-1} (6.15, 5.54, 4.65, and 4.05 microns),
calculated relative to a linear base line drawn between the absorption
minima at 1690 and 2855 cm\textsuperscript{-1} (5.92 and 3.50 microns). These four
absorptions are due primarily to B\textsubscript{5}H\textsubscript{11}, B\textsubscript{4}H\textsubscript{10}, B\textsubscript{5}H\textsubscript{9}, and B\textsubscript{2}H\textsubscript{6}, respectively, but B\textsubscript{5}H\textsubscript{9} also shows considerable absorption at 1625 cm\textsuperscript{-1}, and
B\textsubscript{2}H\textsubscript{6} at 1805 cm\textsuperscript{-1}. The authors have therefore developed four simulta­
taneous linear equations relating the partial pressures of the four
species to the optical densities. These equations have been applied to

\textsuperscript{10} L. V. McCarty, G. C. Smith, and R. S. McDonald, Anal.
the sample of \( B^5\) used for the preparation of \( B^5D^9 \) in the present investigation and yield the following concentrations in mole percent: \( B^2H_6, 0.23; B^4H_{10}, 0.20; B^5H_{11}, 0.05; \) and \( B^5H^9, 99.52. \) Except for \( B^2H_6 \) these values are below the minimum detectable concentrations which are given by McCarty et al. as \( B^2H_6, 0.2; B^4H_{10}, 0.6; \) and \( B^5H_{11}, 0.7. \) The same method was applied to infrared spectra of \( B^5H^9 \) in the NaCl region measured in this laboratory in 1954 and referred to subsequently in the presentation of the infrared data.\(^{11}\) The concentrations calculated for this sample are \( B^2H_6, -0.12; B^4H_{10}, 0.39; B^5H_{11}, -0.01; \) and \( B^5H^9, 99.74 \) mole percent. The method of McCarty et al. does not include \( B^6H_{10}. \) However the infrared spectrum for the latter was obtained subsequently by Gibbins and Shapiro\(^{12}\) and shows a moderately strong absorption band at 750 cm\(^{-1}\) which appears to be entirely absent in the infrared spectra of both of the preceding samples of \( B^5H^9, \) leading to a calculated upper limit of 1.0 mole percent \( B^6H_{10}. \) This is simply the estimated minimum detectable concentration, and does not imply that \( B^6H_{10} \) is necessarily present as an impurity.

We have not attempted to apply these methods to the calculation of the impurities in the sample of \( B^5H^9 \) of Hrostowski and Pimental, because the required optical densities are not obtainable with sufficient accuracy from their published data. A similar statement applies to the earlier infrared data of Taylor et al. However, since these infrared spectra show no significant bands not also present in the spectra of the

\(^{11}\) W. J. Taylor, unpublished data.

two samples considered above, it may be concluded that they were of essentially the same high purity. As discussed previously the purity of the sample of Taylor et al. was also established calorimetrically.

3. Residual Hydrogen in $B_5D_9$

The residual hydrogen in the $B_5D_9$ sample, or conversely the completeness of deuteration of the $B_5H_9$, is of interest since such residual hydrogen will be distributed among several isotopic species ($B_5D_8H$, $B_5D_7H_2$, etc.) which will have spectra differing from those of either $B_5D_9$ of $B_5H_9$. The fraction of hydrogen remaining in the partially deuterated pentaborane was calculated by comparing the peak absorption coefficient (defined in Section C) for the strong band due to B-H stretching in the sample with that in pure pentaborane. The ratio of these coefficients was assumed to be equal to the fraction of hydrogen in the pentaborane which remained unreplaceed by deuterium. This assumes that the hydrogen atoms in the partially deuterated species occur at random positions in the molecule and contribute additively to the absorption.

The absorption coefficient for the B-H stretching mode observed at approximately 2600 cm.$^{-1}$ in pure $B_5H_9$ is calculated as 902 (cm.$^{-1}$-mm. Hg)$^{-1}$ from the data of this investigation (Table 3). However, this value is of considerably lower accuracy than the values obtained for the other principal absorptions. This is a result of the fact that for this, the strongest absorption in pentaborane, only 7 percent of the incident energy was transmitted at the lowest pressure at which the infrared spectrum of $B_5H_9$ was measured (12 mm. Hg.).
It seems preferable, therefore, in the calculation of purity to use an absorption coefficient for B-H stretching based on the infrared data of Hrostowski and Pimentel, who measured the infrared spectrum of \( \text{B}_5 \text{H}_9 \) at 3 mm. Hg where the transmission is approximately 30 percent. These authors also used a LiF prism in the range 2100-4000 cm\(^{-1}\) and partially resolved the B-H stretching absorption into a peak at 2598 and a shoulder at 2610 cm\(^{-1}\), with absorption coefficients of 1270 and 1130 (cm\(^{-1}\)-mm. Hg\(^{-1}\)), respectively. Only a suggestion of this structure appears in spectra measured with the NaCl prism, which has a low dispersion at this and higher frequencies (this accounts for some of the apparent discrepancies for the higher frequencies as given in Table 3).

The infrared active B-H stretching modes of \( \text{B}_5 \text{H}_9 \) may be classified as two \( A_1 \) modes and an \( E \) mode of the molecular point group \( C_{4v} \). The \( E \) mode must involve primarily base B-H stretching (symmetry considerations prohibit \( B_0 \)-H\(_0 \) stretching in this mode although some \( B_0 \)-H\(_0 \) bending may occur). One of the \( A_1 \) modes may be expected to involve predominantly apex \( B_0 \)-H\(_0 \) stretching, and the other base B-H stretching. However, the molecular configuration as discussed previously suggests that the latter mode will have a relatively low intensity as the motion of the protons is approximately perpendicular to the molecular symmetry axis while the activity of an \( A_1 \) mode arises from the parallel component of the dipole moment. The absorption maxima at 2598 and shoulder at 2610 cm\(^{-1}\) observed by Hrostowski and Pimental may therefore be reasonably interpreted as due to an \( A_1 \) and an \( E \) B-H stretching mode of \( \text{B}_5 \text{H}_9 \). It seems likely that the more intense absorption at 2598 cm\(^{-1}\) is the \( E \) mode as
the vibrational dipole for the $E$ mode involves additive contributions from four B-H bonds. The higher frequency component at 2610 cm$^{-1}$ would then represent the $A_1$ mode. This is supported by the Raman spectrum of $B_5^9D_9$, in which the B-D stretching mode is split into two components of which the higher frequency component is strongly polarized and therefore $A_1$ (the B-H stretching in the Raman spectrum of $B_5^9H_9$ is obscured by a strong mercury line).

The absorption coefficient of the B-H stretching mode at approximately 2600 cm$^{-1}$ observed in the present investigation for the final sample of $B_5^9D_9$ (after eight exchanges) was 16 (cm.$\cdot$mm. Hg)$^{-1}$, as given in Table 2. At the low concentrations of residual hydrogen remaining in the sample this absorption will be primarily due to the B-H bond in the isotopic species $B_5^8D_8H$ (base hydrogen) and $B_5^8D_8H_0$ (apex hydrogen), in the ratio 4 to 1. The effective absorption coefficient of the mixture due to B-H stretching will be a weighted average of the absorption coefficients of these isotopic species. In view of the discussion in the preceding paragraph it is reasonable to take as the effective absorption coefficient a weighted average, $(4 \times 1270 + 1130)/5 = 1242$, of the coefficients for the $E$ and $A_1$ modes which represent predominantly base and apex B-H stretching, respectively. The fraction of residual hydrogen in the $B_5^9D_9$ is therefore estimated as 16/1242, or 1.29 atomic percent, and the fraction of deuterium as 98.71 atomic percent.

Pentaborane containing 98.7 atomic percent deuterium, which is randomly distributed, will consist of 88.97 mole percent $B_5^9D_9$, 10.46 mole percent $B_5^8D_8H$, 0.55 mole percent $B_5^8D_8H_2$, 0.017 mole percent $B_5^6D_6H_3$, and
negligible percentages of more highly hydrogenated species. Assuming
the hydrogen atom in the principal isotopic species, $\overset{\alpha}{B}_5D_8H$, to be
distributed randomly among the available positions, this would correspond
to 1.16 mole percent $\overset{\alpha}{B}_5D_8H_0$, with the hydrogen in the apex position,
4.65 mole percent $\overset{\alpha}{B}_5D_8H_1$, with the hydrogen in one of the bridge posi-
tions, and 4.65 mole percent $\overset{\alpha}{B}_5D_8H_2$, with the hydrogen in one of the non-
bridge base positions. The infrared spectra obtained after the seventh
and eighth (last) exchanges were compared. Except for a decrease in
intensity at the 2600 cm.$^{-1}$ region (B-H stretching vibration), the
spectrum obtained after the eighth exchange was very similar to that
obtained after the seventh exchange. There is no reason to believe that
the isotopic species $\overset{\alpha}{B}_5D_8H$ affected significantly the frequency of any
of the stronger infrared or Raman bands assigned subsequently as funda-
mentals of $\overset{\alpha}{B}_5D_9$. If the frequency of a particular band in one of the
species of $\overset{\alpha}{B}_5D_8H$ differed significantly from the corresponding frequency
in $\overset{\alpha}{B}_5D_9$ it would simply be resolved as a separate weak absorption maximum
with at most about 5 percent of the strength of the principal maximum.

C. Infrared Spectroscopy

1. Accuracy and Calibration of Wavelength Scale

The infrared spectra of pentaborane vapor were measured with a
Perkin-Elmer Model 21 double-beam spectrophotometer.\textsuperscript{13} NaCl and KBr
prisms were used to cover the ranges 2.5 to 15 microns (4000 to

\textsuperscript{13} A detailed description of the construction and performance
of this instrument is given by the designers, J. U. White and M. D.
670 cm.\(^{-1}\) and 15 to 25 microns (670 to 400 cm.\(^{-1}\)), respectively. The wavelength cam and counter of the spectrometer read wavelength in microns with a precision of 0.001 micron. The wavelengths at the maxima of unusually sharp bands can be observed directly on the counter with this precision, and this procedure has been used to determine the boron isotope splitting for one band. However, this procedure would be extremely time-consuming if applied throughout the spectrum generally. In any case, the absolute accuracy of the wavelength scale is stated by the manufacturer to be 0.017 to 0.025 microns in the NaCl region and 0.035 in the KBr region, while the reproducibility is half these figures for wavelengths greater than 5 microns. It was therefore considered adequate to follow the usual procedure of reading wavelengths directly from the spectral tracing, and applying calibration corrections determined in the same manner. The wavelength scale on the paper reads directly to 0.05 micron and can be estimated reliably to the nearest 0.01 micron. The maximum error in reading the wavelengths may be expected to be ±0.005 micron. As this is considerably smaller than the reproducibility of approximately 0.01 micron in the NaCl region and 0.02 micron in the KBr region specified by the manufacturer, the errors in reading do not appear to be a serious factor. An error of 0.01 micron in wavelength represents errors in wave numbers of 0.25 cm.\(^{-1}\) at 500 cm.\(^{-1}\), 1 cm.\(^{-1}\) at 1000 cm.\(^{-1}\), 2.25 cm.\(^{-1}\) at 1500 cm.\(^{-1}\), 4 cm.\(^{-1}\) at 2000 cm.\(^{-1}\), and 6.25 cm.\(^{-1}\) at 2500 cm.\(^{-1}\). Although these errors may appear relatively large at the higher frequencies they are not particularly significant in observations of the spectra of complex
molecules at resolutions such that rotational structure is not resolved. Under these conditions it is impossible to locate band centers accurately, and the usual procedure is to take the peak frequency as the band center (frequency in the absence of molecular rotation). Another factor which militates against attaching too much significance to accuracies of wavelengths in the present type of investigation directed toward a normal coordinate analysis is the virtual impossibility in a complex molecule of determining anharmonicity corrections to more than a few fundamental frequencies.

The wavelength scale was calibrated to the nearest 0.01 micron with standard absorption bands of water vapor, carbon dioxide, and polystyrene film. The wavelengths for carbon dioxide and polystyrene film in the NaCl region were taken from the infrared grating measurements of Flyler and Peters. Oetjen, Kao, and Randall have given the wavelengths of water lines in the 5 to 8 micron range, measured on a grating instrument. The calibration in the KBr region was based on a calibration spectrum of atmospheric water and carbon dioxide made with this prism by the manufacturer. Aside from the 14.986 micron fundamental of carbon dioxide, this showed a number of weak absorptions with wavelengths assigned as follows: 13.88, 16.23, 17.24, 17.37, 19.015, 19.33, 19.91, 21.17, 21.87, 22.61, 23.85, and 25.17 microns. Of these 13.88 may be identified as a CO\textsubscript{2} line. The remainder appear to be weak lines in the

---


pure rotation spectrum of water vapor, or unresolved groups of such lines. The rotation spectrum of water vapor has been measured under high dispersion over the range 18 to 75 microns by Randall et al.\textsuperscript{16} The absorptions given above which lie in this range agree within an average of 0.014 microns with the position of lines in the rotation spectrum of H\textsubscript{2}O as reported by these authors. The wavelengths given by the manufacturer have been accepted because the contour and wavelength at the maximum for such incompletely resolved lines is dependent to some extent on the characteristics of the individual instrument.

Although the present instrument has a cam which provides a linear wavelength scale, and the wavelengths in microns are the primary data, the usual practice in fundamental investigations of vibrational spectra of reporting the position or "frequency" of absorption bands in wave numbers (cm.\textsuperscript{-1}) will be followed. The latter are directly proportional to vibrational energy increments through the formula $\Delta E = h c \tilde{\nu}$, where $\Delta E$ is energy in ergs, $h$ is Planck's constant ($6.626 \times 10^{-27}$ erg sec.), $c$ is the velocity of light in vacuo ($2.998 \times 10^{10}$ cm. sec.\textsuperscript{-1}), and $\tilde{\nu}$ is wave numbers (cm.\textsuperscript{-1}). The failure to give the primary wavelengths as well as wave numbers is justified by the defined relation between the two, $\tilde{\nu} (cm.\textsuperscript{-1}) = 10^4/\lambda$ (microns), so that no error is introduced by the conversion.

2. Transmission and Absorption Coefficients

An important advantage of a double-beam spectrophotometer such as the Perkin-Elmer Model 21 is the high accuracy achieved in measurement of percent transmission (or optical density). This is achieved by comparing the intensity in the reference and sample beams by means of an accurately linear optical wedge using a null balancing principle which does not depend on linearity of the amplified signal from the thermocouple but only on its correct phasing. The absolute accuracy depends on the accuracy of the optical wedge and the sensitivity of balancing, and is stated by the manufacturer to be ± 0.5 percent in transmission between 20 and 100 percent transmission, and ± 1.0 percent between 0 and 20 percent transmission.

The infrared spectra of pentaborane vapor were measured with the sample in a gas cell of 10 cm. optical path length (l) at a known pressure (P). The cell windows were NaCl or KBr as appropriate. The sample transmissions are corrected for absorption and reflection losses at the cell windows by determining also the transmission of the evacuated cell as a function of wavelength. Let $T_o$ and $T$ be the percent transmissions of the cell and of the cell plus sample at a given wavelength and gas pressure. The calculated transmission of the sample alone is then $T' = T/T_o$, and the optical density is $\log_{10}(T_o/T)$. Here $(1/T')$ equals the familiar expression $(I_o/I)$, where $I_o$ and $I$ are the intensities of the beams incident upon and transmitted by the sample. However, it is the transmissions $T_o$ and $T$, and not $I_o$ and $I$, that are directly measured. The optical densities have been used in setting upper limits on the concentrations of other boranes in pentaborane.
Of more fundamental interest is the absorption coefficient in molar or other convenient units. This is the quotient of the optical density by the path length and the concentration, or in gases the pressure. We have chosen to calculate the absorption coefficients in the arbitrary units used by Hrostowski and Pimentel, so that the results of the two investigations would be directly comparable. The absorption coefficient has therefore been defined by the expression

\[
\frac{10^5}{Pl} \log_{10}\left(\frac{T_o}{T}\right),
\]

where \(l\) is the path length (10 cm.), and \(P\) the gas pressure in mm. Hg.

3. Operating Conditions

All the infrared spectra of \(B_5^{14}H\) and \(B_5^{18}D\) (except a few preliminary spectra not reported here) were scanned under conditions recommended by the designer\(^{17}\) for obtaining the maximum resolution consistent with a scanning speed of about 1 hour per micron (or 13 hours for scanning the NaCl region). The Model 21 spectrophotometer is provided with an electronic servo system which varies the widths of the entrance and exit slits to maintain the power reaching the detector (through the reference beam) at an approximately constant value throughout a run. At the same time approximately constant resolution is obtained. The instrument is provided with several slit "schedules" for work of varying resolution and scanning speed. The schedule used in the present investigation provides the following nominal slit widths (microns) at the wavelengths (microns) indicated: 7 at 2.5; 18.5 at 5;

---

17. White and Liston, op. cit.
55 at 10; 145 at 14; and 272 at 15. This slit schedule is stated to give a resolution (wavelength difference for two lines just resolved) which is about 1.5 to 2.0 times the theoretical Rayleigh limit. For two traversals of a 75 mm. rock salt prism, as in the Littrow arrangement of the present spectrometer, the Rayleigh limit is calculated to be 0.01 micron at a wavelength of 10 microns (1 cm.\(^{-1}\) at 1000 cm.\(^{-1}\)). The narrow slits used to obtain high resolution reduce the power reaching the detector, and thus the signal available for balancing the optical wedge system, and it is therefore necessary to scan at slow speeds. The rates of scanning in the present investigations varied from 0.8 to 1.2 microns per hour. The suppression control was set at or near the maximum value (8 to 10), to further decrease the rate of scanning when the absorption by the sample was changing rapidly with wavelength. The spectra were recorded at maximum gain or amplification (10), and the setting of the "response" or band pass filter (4:4) was such as to give the greatest possible suppression of noise arising in the detector.

4. Infrared Spectra, Frequencies, and Absorption Coefficients

The most significant infrared spectral data obtained for \(B_{5^9}\) and \(B_{5^9}\) will be presented in this section. The infrared (and Raman) spectra of both molecules are needed in order to make as complete an assignment of vibrational frequencies as possible. Although the infrared spectra of both \(B_{5^9}D_{5^9}\) and \(B_{5^9}H_{5^9}\) have been reported by Hrostowski and Pimentel, it was felt that the availability of full scale spectral curves would make the present assignment more reliable by providing resolution of detail not visible in the small published spectra.
Furthermore, the spectra of Hrostowski and Pimentel were measured on the Perkin-Elmer Model 21 only in the NaCl region; in the KBr region they used the Model 12C single-beam instrument which does not give as reliable transmission measurements as the double-beam Model 21. For this reason it was considered particularly important to obtain new spectra in the KBr region using the Model 21. A prism recently repolished by the manufacturer was used for this purpose, so that instrumental losses of radiation should be at a minimum (KBr fogs very easily). It will be seen subsequently that the repetition of the KBr spectra, especially, was well justified as a new fundamental was observed for \( \text{B}_5 \text{D}_9 \). The infrared spectra have also provided a more accurate value than previously available for what is interpreted as \( \text{B}^{10}\text{B}^{11} \) isotopic splitting of the 800 cm\(^{-1} \) band in \( \text{B}_5 \text{H}_9 \). Finally, the full scale spectra have been useful in confirming the absence of other boranes in the pentaborane used, as discussed in the section on purity.

The infrared spectra of \( \text{B}_5 \text{D}_9 \) in the NaCl region at 150 and 16 mm Hg pressure are given in Figure 3. In Figure 4 the infrared spectra of \( \text{B}_5 \text{D}_9 \) in the KBr region at pressures of 148 and 60 mm Hg are shown. Infrared spectra for \( \text{B}_5 \text{H}_9 \) in the NaCl region at pressures of 12 and 150 mm Hg are given in Figure 5. Figure 6 shows the infrared spectrum of \( \text{B}_5 \text{H}_9 \) at a pressure of 38 mm Hg in the KBr region. A standard 10.0 cm absorption cell with either NaCl or KBr windows was used for all the measurements. The infrared spectra of \( \text{B}_5 \text{H}_9 \) at high resolution in the NaCl region (Figure 5) were measured by Taylor in 1954 to replace the
INFRARED SPECTRA OF B₄H₆ IN THE Kβ REGION

FIG. 6
earlier inadequate infrared spectra of Taylor et al.,\textsuperscript{18}\ and since these spectra were already available the measurements were not repeated at high resolution in this investigation. An infrared spectrum in the same region of the $\text{B}_9\text{H}_9$ sample used in this investigation was obtained at somewhat lower resolution and faster scanning speeds. Except for the lesser resolution of detail, this spectrum was in complete agreement with that of Taylor. As discussed previously this spectrum was used to estimate upper limits on the concentrations of possible boron hydride impurities in the pentaborane. The other spectra given in the figures and obtained in this investigation were recorded with the same high resolution as those of Taylor for $\text{B}_9\text{H}_9$ in the NaCl region, as discussed in the preceding section.

In Tables 2 and 3 the wavelengths in microns, the frequencies in wave numbers, and the absorption coefficients for $\text{B}_9\text{D}_9$ and $\text{B}_9\text{H}_9$, respectively, are given. The first three columns give the wavelengths, frequencies, and absorption coefficients obtained in the present investigation, while the fourth and fifth columns give the values of Hrostowski and Pimentel for the frequencies and absorption coefficients. In general there is excellent agreement between the two frequency measurements. In order to obtain a quantitative estimate of the agreement, the wave numbers given by Hrostowski and Pimentel were converted to wavelengths to the nearest 0.01 micron, and compared with the wavelengths of this investigation. It is the wavelengths and not the frequencies that are interpolated on the spectral tracings, and which

\textsuperscript{18} Taylor, Beckett, Tung, Holden, and Johnston, \textit{op. cit.}
<table>
<thead>
<tr>
<th>Wavelength (microns)</th>
<th>Present Investigation</th>
<th></th>
<th>Hrostowski and Pimentel</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wave numbers (cm.⁻¹)</td>
<td>Absorption coefficient</td>
<td>Wave numbers (cm.⁻¹)</td>
</tr>
<tr>
<td>3.85</td>
<td>2600</td>
<td>16</td>
<td>2600</td>
</tr>
<tr>
<td>3.96</td>
<td>2525</td>
<td>4</td>
<td>2520</td>
</tr>
<tr>
<td>4.16</td>
<td>2475 sh</td>
<td>6</td>
<td>2475</td>
</tr>
<tr>
<td>4.22</td>
<td>2370</td>
<td>8</td>
<td>2370</td>
</tr>
<tr>
<td>4.49</td>
<td>2225</td>
<td>6</td>
<td>2235</td>
</tr>
<tr>
<td>4.60</td>
<td>2175</td>
<td>7</td>
<td>2180</td>
</tr>
<tr>
<td>4.76</td>
<td>2100</td>
<td>6</td>
<td>2100</td>
</tr>
<tr>
<td></td>
<td>2005</td>
<td></td>
<td>2005</td>
</tr>
<tr>
<td>5.05</td>
<td>1980</td>
<td>602</td>
<td>1972</td>
</tr>
<tr>
<td>5.08</td>
<td>1967</td>
<td>671</td>
<td>1962</td>
</tr>
<tr>
<td>5.60</td>
<td>1786</td>
<td>7</td>
<td>1780</td>
</tr>
<tr>
<td>6.05</td>
<td>1653</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>6.42</td>
<td>1558</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>6.50</td>
<td>1538</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>6.60</td>
<td>1515</td>
<td>17</td>
<td>1520</td>
</tr>
<tr>
<td>6.64</td>
<td>1506</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>6.71</td>
<td>1490 sh</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>6.80</td>
<td>1471</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>7.08</td>
<td>1412</td>
<td>37</td>
<td>1420</td>
</tr>
<tr>
<td>7.18</td>
<td>1393</td>
<td>44</td>
<td>1397</td>
</tr>
<tr>
<td></td>
<td>1397</td>
<td></td>
<td>1392-1300</td>
</tr>
<tr>
<td>7.50</td>
<td>1333</td>
<td>80</td>
<td>1338</td>
</tr>
<tr>
<td>7.76</td>
<td>1289</td>
<td>56</td>
<td>1292-1300</td>
</tr>
<tr>
<td>8.17</td>
<td>1224</td>
<td>18</td>
<td>1230</td>
</tr>
<tr>
<td>8.37</td>
<td>1195 sh</td>
<td>30</td>
<td>1198</td>
</tr>
<tr>
<td>8.46</td>
<td>1182</td>
<td>34</td>
<td>1186</td>
</tr>
<tr>
<td>8.50</td>
<td>1176</td>
<td>32</td>
<td>1180</td>
</tr>
<tr>
<td></td>
<td>1110 sh</td>
<td></td>
<td>1110sh</td>
</tr>
<tr>
<td>9.35</td>
<td>1070</td>
<td>334</td>
<td>1068</td>
</tr>
<tr>
<td>9.46</td>
<td>1057</td>
<td>546</td>
<td>1056</td>
</tr>
<tr>
<td>9.55</td>
<td>1047 sh</td>
<td>310</td>
<td>1046 sh</td>
</tr>
<tr>
<td>10.19</td>
<td>981</td>
<td>18</td>
<td>972-980</td>
</tr>
<tr>
<td>10.37</td>
<td>964</td>
<td>18</td>
<td>964</td>
</tr>
<tr>
<td>Wavelength (microns)</td>
<td>Present Investigation</td>
<td>Hrostowski and Pimentel</td>
<td></td>
</tr>
<tr>
<td>----------------------</td>
<td>-----------------------</td>
<td>-------------------------</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Wave numbers (cm⁻¹)</td>
<td>Absorption coefficient</td>
<td>Wave numbers (cm⁻¹)</td>
</tr>
<tr>
<td>10.41</td>
<td>961</td>
<td>19</td>
<td>960</td>
</tr>
<tr>
<td>10.52</td>
<td>951</td>
<td>12</td>
<td>946sh</td>
</tr>
<tr>
<td>10.55</td>
<td>948</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>11.45</td>
<td>873</td>
<td>16</td>
<td>874</td>
</tr>
<tr>
<td>11.68</td>
<td>856</td>
<td>26</td>
<td>856</td>
</tr>
<tr>
<td>11.76</td>
<td>850</td>
<td>24</td>
<td>849</td>
</tr>
<tr>
<td>11.85</td>
<td>844</td>
<td>23</td>
<td>842</td>
</tr>
<tr>
<td>12.99</td>
<td>770sh</td>
<td>219</td>
<td>771</td>
</tr>
<tr>
<td>13.12</td>
<td>762sh</td>
<td>285</td>
<td>761</td>
</tr>
<tr>
<td>13.32</td>
<td>751</td>
<td>392</td>
<td>752</td>
</tr>
<tr>
<td>13.40</td>
<td>746</td>
<td>422</td>
<td>746</td>
</tr>
<tr>
<td>13.50</td>
<td>741</td>
<td>409</td>
<td>740</td>
</tr>
<tr>
<td>13.62</td>
<td>734sh</td>
<td>225</td>
<td>732sh</td>
</tr>
<tr>
<td>14.97</td>
<td>668</td>
<td>16</td>
<td>668</td>
</tr>
<tr>
<td>15.46</td>
<td>647</td>
<td>38</td>
<td>648</td>
</tr>
<tr>
<td>15.67</td>
<td>638</td>
<td>39</td>
<td>639</td>
</tr>
<tr>
<td>19.16</td>
<td>522</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>19.53</td>
<td>512</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>20.04</td>
<td>499</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>21.79</td>
<td>459</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>22.03</td>
<td>454</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>22.32</td>
<td>448</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>22.47</td>
<td>445</td>
<td>20</td>
<td>442</td>
</tr>
<tr>
<td>22.78</td>
<td>439</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>23.09</td>
<td>433</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>23.31</td>
<td>429</td>
<td>15</td>
<td>430</td>
</tr>
<tr>
<td>24.10</td>
<td>415</td>
<td>6</td>
<td></td>
</tr>
</tbody>
</table>

sh - shoulder.
## TABLE 3

**INFRARED SPECTRA OF B₅H₉**

<table>
<thead>
<tr>
<th>Wavelength (microns)</th>
<th>Present Investigation</th>
<th>Hrostowski and Pimental</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wave numbers (cm⁻¹)</td>
<td>Absorption coefficient</td>
</tr>
<tr>
<td>2.86</td>
<td>3500</td>
<td>7</td>
</tr>
<tr>
<td>2.90</td>
<td>3450sh</td>
<td>6</td>
</tr>
<tr>
<td>3.02</td>
<td>3310</td>
<td>7</td>
</tr>
<tr>
<td>3.11</td>
<td>3215</td>
<td>10</td>
</tr>
<tr>
<td>3.24</td>
<td>3085</td>
<td>10</td>
</tr>
<tr>
<td>3.83</td>
<td>2610</td>
<td>902</td>
</tr>
<tr>
<td>4.07</td>
<td>2460</td>
<td>7</td>
</tr>
<tr>
<td>4.21</td>
<td>2375sh</td>
<td>5</td>
</tr>
<tr>
<td>4.46</td>
<td>2240</td>
<td>8</td>
</tr>
<tr>
<td>4.64</td>
<td>2155</td>
<td>9</td>
</tr>
<tr>
<td>4.74</td>
<td>2110</td>
<td>10</td>
</tr>
<tr>
<td>4.87</td>
<td>2055sh</td>
<td>9</td>
</tr>
<tr>
<td>5.01</td>
<td>1996sh</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.22</td>
<td>1916</td>
<td>25</td>
</tr>
<tr>
<td>5.41</td>
<td>1848sh</td>
<td>71</td>
</tr>
<tr>
<td>5.49</td>
<td>1821sh</td>
<td>107</td>
</tr>
<tr>
<td>5.52</td>
<td>1812</td>
<td>118</td>
</tr>
<tr>
<td>5.58</td>
<td>1792sh</td>
<td>93</td>
</tr>
<tr>
<td>5.77</td>
<td>1733sh</td>
<td>28</td>
</tr>
<tr>
<td>6.11</td>
<td>1637</td>
<td>35</td>
</tr>
<tr>
<td>6.15</td>
<td>1626</td>
<td>36</td>
</tr>
<tr>
<td>6.36</td>
<td>1572sh</td>
<td>17</td>
</tr>
<tr>
<td>6.70</td>
<td>1493</td>
<td>106</td>
</tr>
<tr>
<td>6.85</td>
<td>1460</td>
<td>161</td>
</tr>
<tr>
<td>6.92</td>
<td>1445</td>
<td>245</td>
</tr>
<tr>
<td>7.03</td>
<td>1422</td>
<td>268</td>
</tr>
<tr>
<td>7.10</td>
<td>1408</td>
<td>312</td>
</tr>
<tr>
<td>7.16</td>
<td>1397sh</td>
<td>190</td>
</tr>
<tr>
<td>7.42</td>
<td>1348sh</td>
<td>57</td>
</tr>
<tr>
<td>7.89</td>
<td>1267</td>
<td>12</td>
</tr>
<tr>
<td>7.95</td>
<td>1258</td>
<td>10</td>
</tr>
<tr>
<td>Wavelength (microns)</td>
<td>Present Investigation Wave numbers (cm(^{-1}))</td>
<td>Absorption coefficient</td>
</tr>
<tr>
<td>----------------------</td>
<td>-----------------------------------------------</td>
<td>-----------------------</td>
</tr>
<tr>
<td>8.17</td>
<td>1224</td>
<td>8</td>
</tr>
<tr>
<td>8.38</td>
<td>1193</td>
<td>10</td>
</tr>
<tr>
<td>8.41</td>
<td>1189</td>
<td>8</td>
</tr>
<tr>
<td>8.44</td>
<td>1185</td>
<td>8</td>
</tr>
<tr>
<td>8.75</td>
<td>1143</td>
<td>13</td>
</tr>
<tr>
<td>8.87</td>
<td>1127</td>
<td>25</td>
</tr>
<tr>
<td>9.25</td>
<td>1081</td>
<td>14</td>
</tr>
<tr>
<td>9.58</td>
<td>1044</td>
<td>35</td>
</tr>
<tr>
<td>9.69</td>
<td>1032sh</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>9.68</td>
<td>1032sh</td>
</tr>
<tr>
<td>10.12</td>
<td>988</td>
<td>3</td>
</tr>
<tr>
<td>10.16</td>
<td>984</td>
<td>3</td>
</tr>
<tr>
<td>10.76</td>
<td>929sh</td>
<td>108</td>
</tr>
<tr>
<td>10.92</td>
<td>916sh</td>
<td>156</td>
</tr>
<tr>
<td>11.12</td>
<td>899sh</td>
<td>297</td>
</tr>
<tr>
<td>11.16</td>
<td>896</td>
<td>322</td>
</tr>
<tr>
<td>11.24</td>
<td>890</td>
<td>298</td>
</tr>
<tr>
<td>11.33</td>
<td>883</td>
<td>276</td>
</tr>
<tr>
<td>12.06</td>
<td>829sh</td>
<td>11</td>
</tr>
<tr>
<td>12.12</td>
<td>825</td>
<td>14</td>
</tr>
<tr>
<td>12.20</td>
<td>820</td>
<td>15</td>
</tr>
<tr>
<td>12.24</td>
<td>817</td>
<td>16</td>
</tr>
<tr>
<td>12.32</td>
<td>812</td>
<td>17</td>
</tr>
<tr>
<td>12.38</td>
<td>808</td>
<td>27</td>
</tr>
<tr>
<td>12.50</td>
<td>800</td>
<td>26</td>
</tr>
<tr>
<td>12.52</td>
<td>799sh</td>
<td>18</td>
</tr>
<tr>
<td>12.61</td>
<td>793</td>
<td>11</td>
</tr>
<tr>
<td>13.44</td>
<td>744</td>
<td>1</td>
</tr>
<tr>
<td>14.27</td>
<td>701</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>14.28</td>
<td>701</td>
</tr>
<tr>
<td>15.95</td>
<td>627</td>
<td>103</td>
</tr>
<tr>
<td>16.29</td>
<td>614</td>
<td>126</td>
</tr>
<tr>
<td>16.53</td>
<td>605</td>
<td>103</td>
</tr>
<tr>
<td>17.09</td>
<td>585sh</td>
<td>38</td>
</tr>
<tr>
<td>17.61</td>
<td>568</td>
<td>38</td>
</tr>
</tbody>
</table>

sh - shoulder.
should have a relatively constant error. Errors in wave numbers are
greatly exaggerated at high frequencies. The average difference between
the wavelengths reported in the two investigations for 37 wavelengths
of $^{5}D_9$ is ±0.022 microns, and for 48 wavelengths of $^{5}H_9$ is ±0.015
microns. Two bands of $^{5}D_9$ show anomalously large errors of .06 and .14
microns, evidently because in both greater structure is resolved in the
present investigation. If these two are eliminated the average differ-
ence for $^{5}D_9$ is reduced to 0.017 microns. The differences appear to be
essentially random in sign, indicating no systematic difference in wave-
length scales. A part of the difference in wavelength readings must be
assigned to the great difficulty of attaching a precise wavelength to
poorly resolved features of the spectrum, such as shoulders of bands.
Another factor is the effect of noise in obscuring or altering apparent
peak position. Still other causes contributing to the differences is
the rather irregular spacing of the available and commonly used calibra-
tion points in the infrared, and random errors in interpolation on the
wavelength scale. Lack of reproducibility or perfect smoothness in the
wavelength cam or gears may also play a part. The manufacturer estimates
a wavelength reproducibility of approximately 0.01 micron in the NaCl
region and 0.02 micron in the KBr region. In view of this and the
other contributing factors the mean errors do not seem excessive.

In the region above 2100 cm.$^{-1}$ Hrostowski and Pimentel used a
LiF prism, which has much greater dispersion in this region than NaCl.
Therefore their combination or overtone frequencies above 2100 cm.$^{-1}$
are more reliable than those of this investigation. The only fundamental
frequencies in this range are the B-H stretching modes of $^{5}H_9$, which
they resolve into a band at 2598 cm$^{-1}$ and a shoulder at 2610 cm$^{-1}$ as discussed previously.

The resolution of the infrared spectra obtained in the present investigation in the NaCl region seems about the same as that of Hrostowski and Pimentel, which is to be expected in view of the use of the same model of spectrometer in both investigations. In several cases lines separated by 3 or 4 cm$^{-1}$ are clearly resolved. Hrostowski and Pimentel give enlarged spectral tracings for several bands, including the 800 and 1400 cm$^{-1}$ bands of $B_5H_9$. For these two bands the resolution is noticeably better in the spectra of $B_5H_9$ taken by Taylor.

The absorption coefficients of the two investigations in the NaCl region, measured in both cases with the double-beam Model 21 spectrometer are not in very good agreement. The average deviation from the mean is ±15 percent for 35 bands of $B_5D_9$ and the same figure for 42 bands of $B_5H_9$. The deviations are as great as 60 percent for some bands. This is surprising in view of the accuracy of ±0.5 to 1.0 percent in transmission claimed by the manufacturer. The reproducibility of the transmission scale of the present instrument does approximate 1.0 percent in transmission. The differences in absorption coefficients between the two investigations may be due in part to failure of the Beer-Lambert law and the fact that the pressures used were not identical. Such failures are known to occur in the measurement of what are basically line spectra (when the rotational structure is considered) at resolutions incapable of resolving the fine structure. Apparent absorption coefficients then depend on slit width and other instrumental characteristics. One technique which has been used to overcome these difficulties is the
introduction of inert gas at high pressure to broaden the fine structure.

The spectra in the KBr region were also obtained with the double-beam instrument in this investigation, while Hrostowski and Pimentel used a single-beam Model 12C Perkin-Elmer spectrometer. In the KBr region intensity measurements with a single-beam instrument are complicated by the rapid decrease of the black-body radiation from the Nernst glower with increasing wavelength. It is therefore likely that their absorption coefficients and band contours are not as reliable in this region. The differences are only qualitative, however, except that a $512 \text{ cm}^{-1}$ band of $\text{B}_2\text{D}_9$ which is undoubtedly a fundamental is recorded in the present investigation with sufficient strength to be unmistakable (peak absorption 40 percent at 150 mm. Hg). On Hrostowski and Pimentel's spectra a slight indication of this band appears, but so weakly that it could not reasonably be interpreted as a fundamental and they entirely ignore it. The previous discussion of purity virtually eliminates the possibility that this band is due to an impurity. No impurity would be likely to produce this single band without also producing observable bands in other regions of the spectrum.

**D. Raman Spectroscopy**

1. **Raman Spectrograph and Light Source**

The Raman spectra were recorded photographically with the Lane-Wells High Speed Raman Spectrograph. In this spectrograph the light passes through a collimating lens followed by three dense flint glass prisms in succession, giving a cumulative dispersion of 0.053 to 0.038 mm/A in the Raman region, equivalent to 100 cm.$^{-1}$ per mm. at 1000 cm.$^{-1}$
The resolution is 0.6 Å or 3 cm.\(^{-1}\) at 4358 Å, which is adequate for Raman work because the lines have a breadth of at least 3 cm.\(^{-1}\). The Schmidt-type camera has a speed of f/3 and focal length of 30 cm. All optical components and prisms have anti-reflection MgF\(_2\) coatings, and baffles are provided to reduce to a minimum stray light reaching the film.

The light source consists of two low-pressure, high intensity, water-cooled mercury arcs. The active length of the arcs is about 25 cm. in length, and they are placed vertically at the foci of two elliptic cylinder reflectors on opposite sides of the Raman tube, with the Raman tube at the other focus of each reflector. These low-pressure lamps provide a source of the mercury 4358.35 Å line that is relatively free of continuous background or of pressure broadening of the principal line. The ratio of the intensity of the exciting line to background is of the order of 10\(^4\) or better. The scattered radiation emerges from a window at the lower end of the vertical Raman tube, is totally reflected by a 45° prism, and then passes horizontally through the condensing lens into the slit of the spectrometer. A Wratten 2A filter in the form of a film circling the Raman tube removed radiation of wavelength shorter than the exciting line. Gelatin film impregnated with Dupont Rhodamine 5 GDN Extra dye (30 mg. of solid dye per square foot)\(^{19}\) served as a filter for the wavelengths greater than 4358 Å. A solution of praseodymium chloride is often recommended for the long wavelength region adjacent to the exciting line, but it causes significant loss of intensity and was

\(^{19}\) This film was prepared by the Brigham Gelatine Company, Randolph, Vermont.
found not to be necessary as the arcs used give little continuous radiation in this region.

2. Raman Tube and Sample

The Raman tube was constructed from precision Pyrex tubing of .64 cm. internal diameter. A ground and polished disc of Pyrex glass, 10 mm. in diameter, and of good optical quality was sealed on one end of the tube. During the sealing operation the tube was rotated and a pinpoint flame was used. The central part of the disc was protected from the flame by covering it with a small graphite disc. In this way a clear undistorted window of diameter equal to the internal diameter of the tube was provided for the passage of the scattered radiation. The tube and window were oven annealed, and the tube was then sealed to the vacuum system and tested for leaks. The deuterated pentaborane, which had been prepared as previously described, was condensed into the Raman tube with liquid nitrogen. The tube was filled to a depth of 12.5 cm. which is equivalent to a volume of 4 ml. Based on an estimated density of 0.67 gm./ml. for liquid $B_{5}D_{9}$ at 20° C., this corresponds to 2.7 gm. or 0.037 moles of $B_{5}D_{9}$. Sufficient nitrogen gas was then introduced to bring the total pressure, including the pressure of the pentaborane vapor, to near atmospheric pressure at room temperature. The Raman tube was then sealed off and detached from the vacuum system. The portion of the tube above the level of the liquid pentaborane, and extending somewhat below the meniscus, was then rendered opaque to light with optically black paint and black tape. The upper part of the tube thus
served as the conventional light trap for unwanted radiation scattered upward. A short length (about 1 cm.) of the tube adjacent to the window was similarly blackened to minimize reflection or refraction of the exciting radiation into the beam entering the spectrometer. The length of the illuminated column of liquid was about 10 cm., corresponding to a volume of 3.2 ml. of liquid B,DD, active in Raman scattering. The lower end of the Raman tube was also fitted with a blackened metal fitting with a central opening of the same internal diameter as the Raman tube to prevent light conducted downward through the glass walls of the latter from reaching the spectrometer. These procedures are all standard in Raman spectroscopy but were particularly necessary in connection with the exceptionally long exposures (400 hours) required in the present investigation.

After filling and preparing the Raman tube in this manner, it was mounted in the arc housing. The distances of the arc housing and condensing lens from the spectrometer were adjusted to admit the maximum flux of scattered light to the collimating lens of the spectrometer. Ideally the two ends of the active portion of the Raman tube which are furthest from and closest to the spectrometer should be focused on the slit and collimator of the spectrometer, respectively. These conditions could not be met very closely with the small Raman tube used in this investigation and the focal length of the condensing lens available, but what appeared to be the best compromise was chosen. The proper

---

alignment of the Raman tube is accomplished by replacing it with a dummy tube having a ground glass disc at one end divided by two ruled lines crossing at the center. This tube can be mounted in the lamp housing on the same axis as the Raman tube. A small light source is placed at the center of the collimating lens, and the position of the arc housing adjusted until the image of the slit projected by the light is centered on the glass disc. This procedure is repeated several times, reversing the dummy tube, until both ends of the latter are accurately aligned. The intensity of scattering of Raman and Rayleigh radiation, combined with stray light is sufficient so that in a darkened room the alignment can be checked by sighting visually from the slit of the spectrometer and condensing lens back toward the Raman tube with the arcs on. When correctly aligned the end view of the Raman tube then appears as a faintly luminous violet circle, representing the liquid sample, surrounded by a somewhat more luminous concentric annulus representing the illuminated glass wall of the tube.

3. Raman Displacements or Frequencies

The Raman spectra are recorded on a strip of 8 mm. film which is held on the focal curve of the spectrometer by a mechanically precise film holder. Either before or after the Raman exposures an argon arc spectrum is recorded on the same film, using a small arc and reflecting prism which is swung into position before the spectrometer slit. Ordinarily the Raman spectrum or spectra are recorded in the center of the film, and the lines of the argon spectrum both above and below the center to eliminate errors of parallax in comparing positions. This is
possible, using suitable masks to uncover only the desired sectors of the slit, because the Lane-Well spectrograph is accurately stigmatic.

The determination of the displacements of the Raman lines from the 4358.35 Å exciting line is based on two sharp argon emission lines at 4131.73 Å and 4965.12 Å, using a method developed by Taylor and Tung. The film is aligned parallel to the axis of the comparator, and the positions of these two lines and each Raman line measured relative to an arbitrary origin along the axis. The detailed procedures used will be discussed subsequently. Let d be the linear distance reading at the position of a given Raman line, and \( d_1 \) and \( d_2 \) the readings for the 4131.73 Å and 4965.12 Å argon lines, respectively, and define the dimensionless ratio \( x = \frac{d - d_1}{d_2 - d_1} \). It will be noted that \( x \) is independent of small dimensional changes in the film during development or drying provided these are uniform. An interpolation formula similar to the Hartmann formula but based on wave numbers rather than wave lengths is used. Let \( \lambda \) be the wave length in centimeters reduced to vacuo for the Raman line at position \( d \), and \( \lambda_e = 4358.35 \times 10^{-8} \) cm. the corresponding wavelength for the exciting line of the mercury arc. The Raman displacement or "frequency" (as it is conventionally if inaccurately referred to), in wave number or \( \text{cm}^{-1} \) units is then

\[
\Delta \tilde{\nu} = (1/\lambda) - (1/\lambda_e)
\]

Taylor and Tung found it possible to represent over the range -1800 to +4750 \( \text{cm}^{-1} \), which includes the Stokes region for all known fundamental vibration frequencies and a considerable part of the anti-Stokes region, very closely by the formula

\[
\Delta \tilde{\nu}'(\text{cm}^{-1}) = (A/(B - x)) - C - Dx
\]

The values of the constants were determined by inserting the known values of \( \lambda \) and observed values of \( x \) for about 50 lines of the iron arc spectrum and 30 argon lines in this spectral range. The values of the constants giving the best fit to the calibration lines were \( A = 50093.61 \), \( B = 3.809018 \), \( C = 14409.42 \), and \( D = 620.58 \). In order to simplify the determination an extensive table was prepared using a computer which gives \( \Delta \tilde{\nu}' \) as calculated from the preceding formula and these constants with a precision of 0.01 cm\(^{-1}\) for all values of \( x \) from -0.2000 to 1.2000 at intervals of 0.0001. The small deviations from this smooth interpolation formula and table were then calculated for each of the calibration lines. Let \( \delta \tilde{\nu} \) be the deviation of the observed \( \Delta \tilde{\nu} \) for a calibration line from the \( \Delta \tilde{\nu}' \) calculated from the preceding formula and given in the main table referred to. The \( \delta \tilde{\nu} \)'s were plotted versus \( x \) and a smooth correction curve obtained. The great majority of the calibration points lay within \( \pm 1 \) cm\(^{-1}\) of this curve. From the smooth correction curve a small auxiliary table was prepared giving \( \delta \tilde{\nu} \) to 0.01 cm\(^{-1}\) for values of \( x \) from -0.20 to 1.20 at intervals of 0.01. The maximum value of \( \delta \tilde{\nu} \) is 2.51 cm\(^{-1}\), and it does not exceed \( \pm 0.40 \) cm\(^{-1}\) over the range \( \Delta \tilde{\nu} = -1300 \) to 3650 cm\(^{-1}\). By the combined use of the main table for \( \Delta \tilde{\nu}' \) and auxiliary table for \( \delta \tilde{\nu} \), the corrected displacement, \( \Delta \tilde{\nu} = \Delta \tilde{\nu}' + \delta \tilde{\nu} \), for a Raman line can be quickly obtained from the measured value of \( x \) for the line. Although the formal precision of the tables is 0.01 cm\(^{-1}\), the accuracy of the method as estimated from the 80 calibration lines is a few tenths of a wave number. This is more than sufficient for Raman investigations of the vibrational spectra of
liquids, as all such Raman lines have widths of at least a few wave numbers, due to orientation and perturbation effects in the liquid.

The stronger lines of the Raman spectrum of deuterated pentaborane were measured on a Mann comparator equipped with a 30 power microscope and reading directly to 0.001 mm. This corresponds to approximately 0.1 cm.$^{-1}$ at 1000 cm.$^{-1}$ Several settings of the cross hairs of the microscope were made on the center of each Raman line and an average taken. Because of the breadth of the lines the final value is reported only to 1 cm.$^{-1}$ Because of the graininess of the high-speed film used, the weaker Raman lines were not visible under the high magnification of the microscope of the comparator. They were, however, easily visible in the telescope of a cathetometer, and were measured in this way with a precision of 0.01 mm., equivalent to about 1 cm.$^{-1}$ at 1000 cm.$^{-1}$ The frequencies for several of the stronger lines as measured simultaneously on the cathetometer showed an average deviation of 1.5 cm.$^{-1}$ and a maximum deviation of 3 cm.$^{-1}$ from the more accurate values obtained with the comparator.

4. **Polarization Measurements**

The polarization characteristics of the Raman radiation from a molecule is of great importance as it indicates whether the vibration responsible for a given Raman band belongs to the totally symmetric (identity) representation or to a non-totally symmetric representation of the point group of the molecule. Three principal methods appear to have been used for polarization measurements of Raman radiation. In
order to clarify these, especially the method used in the present investigation, it will be helpful to give an outline of the theory. An excellent discussion has been given by Wilson, Decius, and Cross, and the present treatment will follow theirs rather closely. However, the theory can be further clarified by a more complete breakdown of the elementary scattering processes than is given by these authors.

The $x$ axis is taken as the axis of the Raman tube, and is thus the direction of observation of the scattered radiation. The exciting or incident radiation is assumed to lie in a plane perpendicular to the axis of the Raman tube (this condition was approximately satisfied in the present investigation by collimation of the beam during the polarization measurements). It will be sufficient to consider a beam of incident radiation traveling along the $y$ axis, say. Three cases are of interest with regard to the polarization of the incident radiation: (a) polarization of the electric vector perpendicular to the axis of the Raman tube, designated ($\perp$); (b) polarization parallel to the axis of the Raman tube, designated ($\parallel$); and (c) unpolarized radiation. For incoherent radiation the intensities for case (c) are simply the sums of the intensities for cases (a) and (b), so that it is sufficient to treat cases (a) and (b). It is clear that in cases (a) and (b) the electric vector of the incident radiation is directed along the $z$ and $x$ axis, respectively.

In classical electromagnetic theory an oscillating electric dipole of amplitude \( \mu \) radiates electromagnetic radiation which at large distances has only transverse components of the electric and magnetic fields. These are equal in magnitude and perpendicular to each other and to the radius vector. The electric vector lies in a plane containing the axis of the dipole, and the radiation at any point is therefore polarized in this plane. In terms of the usual polar angles, \( r \), \( \theta \), and \( \phi \), with the dipole and polar axis coinciding, this is the plane \( \phi = \text{const}. \) The magnitudes of the electric and magnetic vectors are both proportional to \( \sin \theta \), and therefore the Poynting energy flux vector has a magnitude proportional to \( \sin^2 \theta \). Introducing the constants of proportionality in the units used,\(^{23}\) the mean energy flux per unit time per unit solid angle in a direction at angle \( \theta \) to the dipole axis is \( I = 2\pi^3 \sqrt{4} \mu^2 \sin^2 \theta / c^3 \). The cases of interest here are \( \theta = \pi/2 \), for which \( I = 2\pi^3 \sqrt{4} \mu^2 / c^3 \), and \( \theta = 0 \), for which \( I = 0 \) (that is, there is no radiation emitted along the dipole axis).

The scattering molecules are assumed to be all alike, and to have principal polarizability components \( \alpha_{xx}^0 \), \( \alpha_{yy}^0 \), and \( \alpha_{zz}^0 \), and principal axes \( x^0 \), \( y^0 \), and \( z^0 \) fixed in the molecules. For the present the vibration of the molecules will be ignored, so that we are considering initially the classical theory of the polarization of Rayleigh scattering. Let the instantaneous direction cosines of these axes relative to the space-fixed \( x \), \( y \), and \( z \) axes be \( c_{ii}^i \) (\( i = x, y, z; i^i = x^0, y^0, z^0 \))

\(^{23}\) Ibid.
for a given molecule. The polarizability tensor of the molecule relative to the space-fixed axes is in general not diagonal and has components given by the transformation equation

\[ \alpha_{ij} = \sum_{k=1}^{4} \alpha_{o}^{k} c_{ii}^{'}, c_{jj}^{'}. \]

In the subsequent analysis there is required the mean value of the squares of the polarizability components relative to space-fixed axes, \( \overline{\alpha_{ij}^2} \), averaged over all orientations of the molecule with equal weight for all orientations. Since the principal polarizability components are independent of molecular orientation this becomes

\[ \overline{\alpha_{11}^2} = \frac{1}{5} \sum_{i,j} (\alpha_{11}^o)^2 + 2 \frac{1}{15} \sum_{i<j} \alpha_{11}^o \alpha_{j1}^o, \]

But \( c_{ii}^{'}, c_{jj}^{'} \) equals 1/5 for \( i = j \) and 1/15 for \( i \neq j \), and

\[ c_{ij}^{'}, c_{ji}^{',} \] (\( i \neq j \)) equals 1/15 for \( i = j \) and -1/30 for \( i \neq j \).

Therefore \( \overline{\alpha_{11}^2} = 1/5 \sum_{i,j} (\alpha_{11}^o)^2 + 2/15 \sum_{i<j} \alpha_{11}^o \alpha_{j1}^o \),

and \( \overline{\alpha_{1j}^2} = 1/15 \sum_{i,j} (\alpha_{1j}^o)^2 - 1/15 \sum_{i<j} \alpha_{11}^o \alpha_{1j}^o \), (\( i \neq j \))

It is convenient to express these results in terms of the spherical part of the polarizability, or mean of the principal polarizability components, \( \alpha \), and the anisotropic part, \( \beta \), defined by

\[ \alpha = 1/3 \sum_{i=1}^{4} \alpha_{11}^o, \quad \text{and} \quad \beta^2 = 1/2 \sum_{i<j} (\alpha_{11}^o - \alpha_{1j}^o)^2 \]

In terms of \( \alpha \) and \( \beta \),

\[ \sum_{i=1}^{4} (\alpha_{11}^o)^2 = (9 \alpha^2 + 2 \beta^2)/3, \]

\[ \sum_{i<j} \alpha_{11}^o \alpha_{1j}^o = (9 \alpha^2 - \beta^2)/3. \]
and therefore \( \alpha_{ii}^2 = \frac{(45 \alpha^2 + 4 \beta^2)}{45} \),

and \( \alpha_{ij}^2 = \beta^2/15 \) \( i \neq j \).

Returning to the case (a) of incident radiation polarized perpendicular to the axis of the Raman tube (x-axis), and therefore having its electric vector of amplitude \( E_0^\prime \) directed along the z axis, a molecule with given orientation will have induced in it dipoles of amplitude \( \mu_x = \alpha_{xz} E_0^\prime \), \( \mu_y = \alpha_{yz} E_0^\prime \), and \( \mu_z = \alpha_{zz} E_0^\prime \).

From the preceding discussion of an oscillating dipole, the component \( \mu_x \) does not radiate along the x-axis or the direction of observation, while the components \( \mu_y \) and \( \mu_z \) radiate in this direction with intensities \( 2 \pi^3 \gamma^4 \alpha^2 \frac{E^2_0}{c^3} \) and \( 2 \pi^3 \gamma^4 \alpha^2 \frac{E^2_0}{c^3} \). These intensities may be rewritten as \( A_0 \alpha^2_{yz} \) and \( A_0 \alpha^2_{zz} \), where \( A_0 = 16 \pi^4 \gamma^4 \frac{I_0}{c^4} \) and \( I_0 = (c/8 \pi E_0^2) \). The intensity of the polarized incident radiation. Furthermore, the radiation scattered by \( \mu_y \) and \( \mu_z \) along the x-axis is polarized with its electric vector along the y and z axes, respectively. On averaging over molecular orientation and summing over all N molecules, the intensities of radiation scattered along the x-axis and polarized along the y and z axes, for incident radiation directed along the y axis and polarized along the z axis, or perpendicular to the axis of the Raman tube, are \( I_y(\perp) = NA_0 \alpha^2_{yz} \) and \( I_z(\perp) = NA_0 \alpha^2_{zz} \), respectively. Similarly, for case (b), with incident radiation polarized along the x-axis or parallel to the axis of the Raman tube, the intensities of radiation scattered along the x-axis and polarized along the y and z axes are \( I_y(\|) = NA_0 \alpha^2_{yx} \) and \( I_z(\|) = NA_0 \alpha^2_{zx} \), respectively. On inserting the values previously obtained for the mean square (space-fixed)
polarizability components, these four intensities reduce to $I_z(\perp) = (NA_0/45)(45\alpha^2 + 4\beta^2)$ and $I_y(\perp) = I_y(\parallel) = I_z(\parallel) = (NA_0/15)\beta^2$.

In the polarization method introduced by Edsall and Wilson,\textsuperscript{24} which was used in the present investigation of $B_5D_9$ and also that of Taylor et al.\textsuperscript{25} for $B_5H_9$, the depolarization ratio, $\rho$, which is measured is the ratio of the total scattered intensities (of both polarizations) for incident radiation polarized parallel and perpendicular, respectively to the axis of the Raman tube, or

$$
\rho = \frac{[I_y(\parallel) + I_z(\parallel)]}{[I_y(\perp) + I_z(\perp)]} = 6\beta^2/(45\alpha^2 + 7\beta^2).
$$

Another method is based on the measurement for case (a) of the ratio of $I_y$ to $I_z$, yielding the depolarization ratio

$$
\rho_a = \frac{I_y(\perp)}{I_z(\perp)} = 3\beta^2/(45\alpha^2 + 4\beta^2).
$$

Still another method uses unpolarized incident radiation, and the scattered intensities are obtained by superposition of cases (a) and (b). The depolarization ratio measured is the total intensity of scattered light polarized along the y axis divided by the total intensity polarized along the z axis, or

$$
\rho_n = \frac{[I_y(\perp) + I_y(\parallel)]}{[I_z(\perp) + I_z(\parallel)]} = 6\beta^2/(45\alpha^2 + 7\beta^2).
$$

Methods such as the last two in which the scattered light is analyzed into two polarized components require that the illumination of the sample be approximately unidirectional. To obtain sufficient light intensity a lens system is then generally required, and the latter in

\textsuperscript{24} J. T. Edsall and E. B. Wilson, Jr., J. Chem. Phys., 6, 124 (1938).

\textsuperscript{25} Taylor, Beckett, Tung, Holden, and Johnston, op. cit.
turn dictates the use of a small source. The advantage of the Edsall-Wilson method in which the incident light is polarized, and analysis of the scattered light is not required, is that the illumination of the sample is restricted only by the condition that it lie approximately in planes perpendicular to the Raman tube. The method is therefore suited to illumination of the Raman tube by two or more arcs, with reflectors to concentrate the radiation. In all the preceding methods failure to restrict the incident light to planes perpendicular to the Raman tube or direction of observation introduces so-called convergence errors into the measured depolarization ratios. These have been discussed by Bhagavantam. 26

The introduction of quantum theory modifies the preceding analysis of scattered intensities and polarization in a relatively simple way if certain reasonable approximations are made. The quantum theory of Raman and Rayleigh scattering was extensively discussed by Placzek. 27 A very clear discussion of the theory beginning from first principles, including a discussion of Placzek's approximation, is given by Born and Huang. 28 They do not consider explicitly the effect of molecular rotation as they are concerned primarily with crystals; a discussion of rotational states and averaging in the quantum theoretical treatment is given by Wilson.


Decius, and Cross.\textsuperscript{29} Placzek's treatment is semi-classical in the sense that the scattered radiation is regarded as arising from an electric dipole induced by the incident radiation field. The transition electric moment between the initial and final states is formulated using the perturbed wave functions of the system in the presence of the field, retaining only terms linear in the field. The result is that the Raman scattering associated with a given transition is the same as the classical scattering due to the electric moment calculated from the field and an effective polarizability called the transition polarizability. The latter is a symmetric second-order tensor which differs in general for each transition. The \( ij \) component of the transition polarizability for initial and final states symbolized by quantum numbers \( n \) and \( n' \) is

\[
\alpha_{ij}^{nn'}(\nu) = \frac{1}{\hbar} \sum_{n''} \left\{ \left[ (M_i)_{nn''} (M_j)_{n''n'}/(\nu_{n''n'} + \nu) \right] + \left[ (M_j)_{nn''} (M_i)_{n''n'}/(\nu_{n''n'} - \nu) \right] \right\}
\]

where the sum extends over all third states with quantum numbers \( n'' \). The frequency associated with the transition \( n'' \rightarrow n' \) is denoted by \( \nu_{n''n'} \), and the matrix element of the \( i \) th component of the electric moment between these states by \( (M_i)_{n''n'} \). \( \nu \) is the frequency of the incident radiation. The Rayleigh scattering for a given state \( n \) is determined similarly by the polarizability tensor \( \alpha_{ij}^{nn}(\nu) \). For \( \nu = 0 \) the latter reduces to the polarizability of the \( n \) th state in a static

\textsuperscript{29} Wilson, Decius, and Cross, \textit{op. cit.}
electric field. All these results were first obtained by Kramers and Heisenberg in connection with their dispersion theory.  

The polarizability \( \alpha_{ij}^{nn'} \) replaces the classical polarizability \( \alpha_{ij} \) of the preceding analysis. It was seen there that the classical scattering with polarization along the \( i \) th axis arising from light polarized along the \( j \) th axis is proportional to \( \alpha_{ij}^2 \). The corresponding part of the Raman scattering arising from the quantum transition \( n \rightarrow n' \) is therefore proportional to \( (\alpha_{ij}^{nn'})^2 \), with the same proportionality constant as in the classical case. Placzek has simplified the expression for the transition polarizability for the adiabatic or Born-Oppenheimer approximation in which the electronic and nuclear coordinates are separable. The total wave function is then a product of a wave function for the nuclear motion and an electronic wave function, with the nuclear coordinates entering as parameters in the latter. As is well known the eigenvalues associated with the electronic wave functions play the role of the potential energy in the Schrödinger equation satisfied by the nuclear wave functions. In Placzek's approximation for vibrational and rotational Raman scattering it is assumed that: (1) the electronic state is unchanged in the transition; (2) the electronic state is non-degenerate; (3) the nearest electronic state is separated from this by an energy large compared to the energy of nuclear motion; and (4) the frequency of the exciting light is large compared to the Raman frequency displacements arising from transitions between nuclear states. Normally the electric state of interest will be the ground electronic state, which will be represented in quantum number 0. The vibrational

and rotational coordinates will be represented by \( Q \) and \( R \), respectively. It will be assumed that the nuclear wave function for the ground electronic state is separable into a product of vibrational and rotational wave functions, specified by quantum numbers \( v \) and \( r \), respectively. The transition polarizability \( \alpha_{ij}^{nn'}(\nu) \) may therefore be indicated more explicitly as \( \alpha_{ij}^{ovr,ov'r'}(\nu) \), or for simplicity \( \alpha_{ij}^{vr,v'r'}(\nu) \) since the electronic state does not change. Placzek showed that

\[
\alpha_{ij}^{vr,v'r'}(\nu) = [\alpha_{ij}^{oo}(\nu,Q,R)]_{vr,v'r'},
\]

where \( \alpha_{ij}^{oo}(\nu,Q,R) \) is the polarizability of the ground electronic state with the nuclear coordinates constrained to have the fixed values \( Q \) and \( R \). \( \alpha_{ij}^{oo}(\nu,Q,R) \) is computed from the preceding expression for \( \alpha_{ij}^{nn'}(\nu) \) by setting \( n = n' = 0 \), restricting the sum over \( n'' \) to all other electronic states, and computing the matrix elements of the electronic moment with the approximate Born-Oppenheimer electronic functions. As the latter depend on \( Q \) and \( R \) as parameters it is evident that \( \alpha_{ij}^{oo}(\nu,Q,R) \) will also. Finally, as indicated by the immediately preceding equation \( \alpha_{ij}^{vr,v'r'}(\nu) \) is the matrix element of \( \alpha_{ij}^{oo}(\nu,Q,R) \) computed relative to the vibrational and rotational wave functions obtained in the same Born-Oppenheimer approximation.

In order to further reduce the expression for \( \alpha_{ij}^{vr,v'r'}(\nu) \) the polarizability \( \alpha_{ij}^{oo}(\nu,Q,R) \) is expanded in powers of the normal coordinates \( Q_s \) as defined in the theory of small harmonic vibrations,

\[
\alpha_{ij}^{oo}(\nu,Q,R) = \alpha_{ij}^{oo}(\nu,Q_0,R) + \sum_s \alpha_{ij,s}^{oo}(\nu,Q_0,R) Q_s + \sum_{s,t} \alpha_{ij,st}^{oo}(\nu,Q_0,R) Q_s Q_t + \ldots .
\]
Here $Q$ symbolizes the entire set of normal coordinates, and $Q_0$ their values in the equilibrium molecular configuration. Then

$$\alpha_{ij}^{v''r'}(\nu) = \left[ \alpha_{ij}^{oo}(\nu, Q_0, R) \right]_{rr'} \delta_{vv'} + \sum_s \left[ \alpha_{ij}^{oo}(\nu, Q_0, R) \right]_{rr'} \left( Q_s \right)_{vv'}$$

$$+ \sum_{s'} \left[ \alpha_{ij}^{oo}(\nu, Q_0, R) \right]_{rr'} \left( Q_{s'} \right)_{vv'} + \cdots$$

Here $\delta_{vv'}$ vanishes unless $v_s = v_{s'}$ for all $s$ in which case $\delta_{vv'} = 1$.

The matrix element $\left[ \alpha_{ij}^{oo}(\nu, Q_0, R) \right]_{rr'}$ and $\left[ \alpha_{ij}^{oo}(\nu, Q_0, R) \right]_{rr'}$ are related to the Rayleigh and rotational Raman scattering, respectively (the latter vanishes if $\alpha_{ij}^{oo}(\nu, Q_0, R)$ has equal principal components or spherical symmetry). The matrix elements of the normal coordinates in the harmonic approximation are well known. $\left( Q_s \right)_{vv'}$ vanishes unless $v'_{s} = v_{s} \pm 1$ and $v'_{t} = v_{t}$ for $t \neq s$, in which case it equals $\left( Q_s \right)_{vv'} = a_s \bar{v}_s^{\frac{1}{2}}$ where $a_s = (\hbar / 2 \pi^2 v_s) \frac{1}{4}$ and $\bar{v}_s$ is the greater of the quantum numbers $v_s$ and $v'_{s}$. Similarly, $\left( Q_s^2 \right)_{vv'}$ vanishes unless $v'_{s} = v_s$ or $v'_{s} = v_s \pm 2$ and $v'_{t} = v_{t}$ for $t \neq s$; in the case $v'_{s} = v_s \pm 2$ which is of interest here $\left( Q_s^2 \right)_{vv'} = a_s^2 [v_s (\bar{v}_s - 1)]^{\frac{1}{4}}$. For $s \neq t$,

$$\left( Q_s Q_t \right)_{vv'} = \left( Q_s \right)_{vv'} \left( Q_t \right)_{vv'} = a_s a_t (v_s v_t)^{\frac{1}{4}}$$

so that $\left( Q_s Q_t \right)_{vv'}$ vanishes unless $v'_{s} = v_s \pm 1$, $v'_{t} = v_t \pm 1$, and $v'_{u} = v_u$ for $u \neq s, t$. It is therefore clear that in the preceding equation the terms involving $\left( Q_s \right)_{vv'}$, $\left( Q_s^2 \right)_{vv'}$, etc. are responsible for the appearance of the vibration
Q, as a fundamental, first overtone, etc. in the Raman spectrum, while the term involving \((Q_\text{g} Q_\text{t})_{VV}\) is responsible for sum and difference bands of \(Q_\text{g}\) and \(Q_\text{t}\). All of these transitions may occur in either the Stokes or anti-Stokes spectrum, depending upon whether the final state has a lesser or greater energy than the initial state.

The further discussion will be restricted to the fundamental Raman bands in the Stokes spectrum, for which \(v_\text{g} = 0, v' = v = 1\), and \((Q_\text{g})_{VV} = a_\text{g}\). The polarizability responsible for the activity (or inactivity) of the vibration \(Q_\text{g}\) as a fundamental is therefore

\[
a_\text{g} \left[ \alpha_{ij}^{(\infty)}(\gamma, Q, R) \right]_{rr'},
\]

It is clear from its definition as a product of matrix elements of the components of electric moment, \(M_i\) and \(M_j\), that the polarizability of the ground electronic state, \(\alpha_{ij}^{(\infty)}(\gamma, Q, R)\), and its derivative with respect to \(Q_\text{g}\), \(\alpha_{ij,\gamma}^{(\infty)}(\gamma, Q_\text{g}, R)\), transform as symmetric second-order tensors under rotations of the molecule and can therefore be diagonalized by an orthogonal transformation. That is, there will exist a particular orientation of the molecule, specified by the values \(R_\text{o}\) of the rotational coordinates (e.g., the Eulerian angles), for which \(\alpha_{ij,\gamma}^{(\infty)}(\gamma, Q_\text{g}, R)\) has only diagonal components, or \(\alpha_{ij,\gamma}^{(\infty)}(\gamma, Q_\text{g}, R_\text{o}) = \alpha_{ij,\gamma}^{(\infty)}(\gamma, Q_\text{g}, R) \delta_{ij}\).

Define principal polarizability axes for the vibration \(s\) fixed in the molecule such that they coincide with the space-fixed axes for \(R = R_\text{o}\).

In general, these axes will not coincide with the principal axes of inertia or the principal axes for the vibration-independent part of the polarizability \(\alpha_{ij}^{(\infty)}(\gamma, Q_\text{g}, R)\) although they may for symmetrical molecules. Let the cosine of the angle between the \(i'\) molecule-fixed axis and the \(j\)
space-fixed axis for the value $R$ of the rotational coordinates be $c_{j_l}(R)$, so that $c_{j_l}(R_0) = 1$. Then

$$\alpha_{ij,s}^{\infty}(\gamma, Q_0, R) = \sum_{i',s} \alpha_{i'i',s}^{\infty}(\gamma, Q_0, R_0) c_{i'i}(R) c_{j_i}(R)$$

and

$$[\alpha_{ij,s}^{\infty}(\gamma, Q_0, R)]_{rr'} = \sum_{i',s} \alpha_{i'i,s}^{\infty}(\gamma, Q_0, R) [c_{i'i}(R) c_{j_i}(R)]_{rr'}$$

where $r$ and $r'$ represent the rotational quantum numbers for the initial and final states, respectively.

By comparison with the preceding classical discussion, the intensity of the Raman radiation along the $x$ space-fixed axis with electric vector polarized along the $j = y$ or $z$ axis, for exciting radiation incident along the $y$ axis and polarized along the $i = z$ or $x$ axis, and resulting from the fundamental transition for $Q_s$ is

$$I_{ij,s} = A_o^2 \sum_{\nu} \sum_{r} N_r [\alpha_{ij,s}^{\infty}(\gamma, Q_0, R)]^2$$

where $N_r$ is the number of molecules initially in the rotational state $r$ and the sum extends over all initial and final rotational states for which the matrix element is non-vanishing. The rotational quantum numbers $r$ always include a magnetic quantum number $M$ which specifies the projection of the total angular momentum of the molecule on an arbitrary direction in space (i.e., the $z$ space-fixed axis relative to which the Eulerian angles $R$ and the rotational wave functions are defined). Let $\rho$ represent the rotational quantum numbers other than $M$. For given $\rho$, $M$ takes $2J + 1$ values, where $J$ is the quantum number for total angular momentum (included in the set $\rho$). Each of these $2J + 1$ levels represents a single quantum state having the same statistical weight and equal
population. Therefore if $N_\phi$ is the number of molecules in any one of the initial rotational states $r = (\rho, M)$,

$$I_{ij, s} = A_0 s^2 \sum_{\rho'} \sum_{M'} N_\phi \sum_{M''} \left[ \alpha_{ij, s}^{\rho'} (\nu, Q_0, R) \right]^2 \rho M, \rho' M'$$

As a result of the summation over $M$ and $M'$ the observed intensity will be independent of the absolute orientation in space of the $i$ and $j$ axes relative to which the experimental observations are made. The expression for the intensity may therefore be averaged over all orientations of these axes (this is equivalent to the classical average over all orientations of a molecule, but is adopted here as the rotational wave functions depend on the orientation of the molecule and must be maintained constant during the averaging process). On substituting the expression previously given for $\left[ \alpha_{ij, s}^{\rho} (\nu, Q_0, R) \right]_{rr}$ in the expression for $I_{ij, s}$, indicating the average over all orientation of $i, j$ axes by a horizontal bar, and noting that the principal polarizability components for the vibration $Q_s$, $\alpha_{i', i'}^{\rho} (\nu, Q_0, R_0)$, are independent of the orientation of the $i, j$ axes, there is obtained

$$I_{ij, s} = A_0 s^2 \sum_{\rho'} \sum_{M'} N_\phi \sum_{M''} \left[ \alpha_{i', i'}^{\rho'} (\nu, Q_0, R) \alpha_{j', j'}^{\rho} (\nu, Q_0, R_0) \right]$$

$$\times \sum_{\rho'} \sum_{M'} N_\phi \sum_{M''} \left[ c_{ii'}^{(R)} c_{jj'}^{(R)} \right] \rho M, \rho' M', \rho M, \rho' M'$$

An exact discussion of the averages of the products of matrix elements of direction cosines in this expression is complicated. However, for molecules with reasonably large moments of inertia and therefore relatively large mean values of the rotational quantum numbers in the initial
state at ordinary temperature, the following approximation is plausible

\[
\sum_{c, M, e} \left[ c_{i11}^{(R)} c_{j11}^{(R)} \right]_{e, M, e'} \sum_{c', M'} \left[ c_{ij}^{(R)} c_{j11}^{(R)} \right]_{e, M, e'} \approx c_{i11}^{(R)} c_{j11}^{(R)} c_{ij}^{(R)} c_{j11}^{(R)} \delta_{e e'} \delta_{M M'}
\]

The numerical values of the average of products of direction cosines appearing on the second line of this equation have been given in connection with the preceding classical discussion. With this approximation the quantum theory expression for the scattered intensities reduce to

\[
I_{i1, s} = N A_0 a_s^2 \left\{ (1/5) \sum_{l=1}^{3} \left[ \alpha_{i1, s}^{(l)} (v, q_0, R_0) \right]^2 + (2/15) \sum_{l' \neq i} \alpha_{i1, s}^{(l')} (v, q_{0}, R_0) \alpha_{j1, s}^{(l')} (v, q_{0}, R_0) \right\}
\]

and for \( i \neq j \),

\[
I_{ij, s} = N A_0 a_s^2 \left\{ (1/15) \sum_{l=1}^{3} \left[ \alpha_{ij, s}^{(l)} (v, q_0, R_0) \right]^2 - (1/15) \sum_{l' \neq j} \alpha_{ij, s}^{(l')} (v, q_{0}, R_0) \alpha_{ji, s}^{(l')} (v, q_{0}, R_0) \right\}
\]

where

\[
N = \sum_{e e'} N_e \sum_{M M'} \delta_{e e'} \delta_{M M'} = \sum_{e e'} N_e (2J + 1)
\]

is the total number of molecules in all rotational states of the initial vibrational state.

Before comparing these equations with the classical equations previously derived it should be noted that the latter were given in the form applicable for Rayleigh scattering. The classical theory of Raman scattering is obtained by expanding the components of the molecular polarizability used there in powers of the normal coordinates \( Q_s \), or

\[
\alpha_{ij} = \alpha_{ij, 0} + \sum_{s} \alpha_{ij, s} Q_s + \sum_{s} \sum_{t} \alpha_{ij, st} Q_s Q_t + \ldots
\]

As in the quantum treatment, the fundamental Raman bands are due to the
terms in $Q_s$, and overtone and combination bands to the higher order terms. As $\alpha_{ij,s}$ is a symmetric second-order tensor it can be diagonalized by a rotation to axes characteristic of the vibrational coordinate $Q_s$, reducing it to its principal components $\alpha_{ii,s}^0$. The latter are to be substituted for $\alpha_{ii,s}^0$ in the classical theory of Rayleigh scattering to obtain the classical theory of Raman scattering. On comparing the classical theory thus obtained with the approximate quantum theoretical expression for Raman scattering obtained in the preceding paragraph, it is clear that they are equivalent if $\alpha_{ii,s}^0$ is identified with $a_s \alpha_{ii,s}^{oo}(\nu,Q_0,R_0)$. One can therefore define a spherical part, $\alpha_s$, and an anisotropic part, $\beta_s$, of the polarizability tensor associated with the vibration $Q_s$ in the quantum treatment as follows:

$$\alpha_s = (1/3)a_s \sum_{i<j} \alpha_{ii,s}^{oo}(\nu,Q_0,R_0) :$$

$$\beta_s^2 = (1/2)(a_s^2 \sum_{i<j} [\alpha_{ii,s}^{oo}(\nu,Q_0,R_0) - \alpha_{ij,s}^{oo}(\nu,Q_0,R_0)]^2) .$$

Then in the same way as shown in the classical treatment the depolarization ratio observed in the Edsall-Wilson method is

$$\rho_s = 6 \beta_s^2/(45 \alpha_s^2 + 7 \beta_s^2) .$$

In many cases, including the present investigation, the molecule in question will possess the symmetry of one of the point groups. Then, as is well known, its normal vibrations $Q_s$ can be classified as belonging to definite irreducible representations of the point group. In this case certain rigorous deductions regarding the behavior of $\alpha_s$, $\beta_s$, and $\rho_s$ can be drawn (for proofs of these statements reference should be
made to Placzek\textsuperscript{31} or the simplified discussion of Herzberg\textsuperscript{32}):  

(1) For non-totally symmetric vibrations $\alpha_s = 0$, and therefore $\rho_s = 6/7$;  

(2) For totally symmetric vibrations of isotropic (i.e., tetrahedral, cubic, or icosahedral) molecules, $\alpha_s \neq 0$, $\beta_s = 0$, and therefore $\rho_s = 0$;  

(2') For totally symmetric vibrations of non-isotropic molecules, $\alpha_s \neq 0$, $\beta_s \neq 0$, and therefore $0 < \rho_s < 6/7$.  

Of course, these statements apply also to molecules lacking any symmetry other than the trivial $C_1$, but then all vibrations are totally symmetric and case (2') applies. The preceding rules apply to fundamental Raman bands. The corresponding rules for overtone and combination bands can be inferred from the symmetries of the initial and final vibrational states involved. For example, the first overtones of non-degenerate vibrations follow the rules for totally symmetric fundamentals, and a combination between a totally symmetric and any other vibration follows the rule for the fundamental of the second vibration. Raman bands for which $\rho_s < 6/7$ are described as polarized and correspond in the case of fundamentals to totally symmetric vibrations; if $\rho_s = 6/7$ they are depolarized and correspond to non-totally symmetric vibrations.  

In the polarization method of Edsall and Wilson $\rho_s$ as defined above is equal to the ratio of the scattered intensities for incident

\textsuperscript{31} Placzek, \textit{op. cit.}  

radiation polarized parallel and perpendicular to the axis of the Raman tube. The polarization of the incident light was accomplished by encircling the Raman tube with a sheet of Polaroid film with the electric vector parallel to the axis for the first exposure, and perpendicular for the second. Both exposures were made for the same length of time as is the general practice, although it would perhaps be preferable to have the exposures in the ratio 7/6. Because of the stigmatic character of the spectrograph it was possible to record both polarization spectra in adjacent positions on the same film, as well as the argon spectrum for wavelength calibration. Partial collimation of the incident radiation in planes perpendicular to the axis of the Raman tube was achieved by placing around the Raman tube a device consisting of thin parallel annular discs of I. D. 3/4 inch and O. D. 2 inch. The original spacing of the discs was 1/8 inch but to increase the intensity this was increased to 3/8 inch in the present investigation. Thus the depolarization ratios may be subject to a larger convergence error than in the measurements of Taylor et al.\(^3\) on \(\text{B}_9\) where the same collimator was used with the smaller spacing.

5. Measurement of Intensities

The Raman film used for \(\text{B}_9\) was Eastman Kodak Company Tri-X-Pan film, developed according to the manufacturer's specifications. An attempt was made to obtain Eastman 103-0 Spectroscopic film which is highly sensitive to low levels of illumination in the spectral region

\(^{33}\) Taylor, Beckett, Tung, Holden, and Johnston, op. cit.
used. However, delays in delivery made it necessary to proceed with the other film. The Raman spectrum of B$_5^4$H$_9$ was recorded by Taylor et al. using Eastman 103-F film which is similar to the newer 103a-0 film. This may be in part responsible for the greater apparent intensity of the spectra for B$_5^4$H$_9$.

As in the earlier investigation of B$_5^4$H$_9$, density tracings of the films were made on a Leeds and Northrup Company Knorr-Albers Microphotodensitometer equipped with a photocell and Speedomax recorder. This instrument yields a large tracing with optical density as ordinate and linear distance on the film (the d of section 3) as abscissa.

For the purposes of photographic photometry$^{34}$ the essential characteristics of the photographic emulsion (film or plate) are contained in a plot of optical density versus the common logarithm of the exposure. The optical density $D$ is by definition the common logarithm of the reciprocal of the fraction $T$ of light transmitted by the emulsion, $$D = \log(1/T).$$

The exposure $E$ is defined as the total radiant energy per unit area incident on the film, and is usually expressed as the product of an intensity per unit area $I$ multiplied by the time of exposure $t$ in appropriate units, or $E = It$. The calculation of exposure from this relation assumes the validity of the reciprocity law, which may be significantly in error for very low or very high intensities. The characteristic

curve of the emulsion, or plot of $D$ versus $\log E$, is known to be of a
sigmoid type. For $E = 0$, or $\log E = -\infty$, of course $D = 0$. For suffi-
ciently small values of $E$ the characteristic curve (with $D$ as ordinate)
is concave upward; this portion is known as the "toe" of the curve or
region of "underexposure" in ordinary photography. With increasing $E$
there usually occurs a range in which the characteristic curve is
approximately linear. This is the region of "normal" exposure for
photography, but is also of importance in quantitative photometry as in
this region the theoretical equations assume a simple form. The slope
of the linear part of the curve is denoted by $\gamma = \frac{dD}{d\log E}$, where $\gamma$
is sometimes called the "development factor." Clearly in this range of
exposure $D$ may be represented by an equation

$$D = \gamma \log(E/i)$$

$i$ is the exposure for which $D$ would vanish if the linear relation were
valid in the region of "underexposure," and is called the "inertia" of
the emulsion. The "speed" of the film is usually defined as $1/\log i$, the
units being chosen so that $\log i$ is positive. Thus for high-speed film
$i$ is relatively small; furthermore $\gamma$ is relatively small for such
film. For exposures greater than "normal," or in the region of "over-
exposure," the characteristic curve becomes concave downward and may
even go through a maximum (the region beyond the maximum is that of
"reversal" or "solarization"). Finally it should be noted that the
characteristic curve of a given emulsion and the value of $\gamma$ depend on
the wavelength of the incident radiation and the conditions of develop-
ment of the film. The latter effect is eliminated by developing under
fixed conditions, and the dependence on wavelength may be ignored for
film of approximately constant speed in the Raman region used.
From the preceding discussion the desirability of maintaining exposures in the normal or linear region of the characteristic curve is clear. In working with very low light intensities, as in some phases of Raman spectroscopy, this may not always be practicable and exposures in the "underexposure" region may sometimes be encountered. The following formulation enables the effects of underexposure (or overexposure) to be conveniently incorporated in the theoretical analysis in a form qualitatively similar to that for the normal region. Let $D_1$ and $D_2$ be the optical densities for two arbitrary exposures, $E_1$ and $E_2$, respectively. We may then write the identity,

$$D_2 - D_1 = \gamma_{12} \log \left( \frac{E_2}{E_1} \right),$$

where

$$\gamma_{12} = \frac{(D_2 - D_1)}{(\log E_2 - \log E_1)}$$

is the slope of the chord connecting the two points on the characteristic curve. In the normal region $\gamma_{12} = \gamma =$ constant. In the region of underexposure, $0 < \gamma_{12} < \gamma$; in that of overexposure, $\gamma > \gamma_{12} \geq 0$; and in the reversal region $\gamma_{12} < 0$. Unless otherwise specified it will be assumed hereafter that the two exposures being compared both lie in the normal region so that $\gamma_{12} = \gamma$.

The first aspect of the Raman intensity measurements to be considered will be the determination of the characteristic curve and the value of $\gamma$. The application to the determination of relative intensities and depolarization ratios will be considered subsequently. The ideal procedure in photographic photometry is, of course, the determination of the characteristic curve over the entire range of exposures and wavelengths to be utilized. In the conventional determination of
such curves two procedures for the variation of exposure, \( E = E(I, t) \), are used: (1) exposure for a fixed time \( t \) to varying intensities \( I \), for example, by varying the distance of the source from the emulsion; or (2) exposure to a fixed intensity \( I \) for varying times \( t \), for example by means of a rotating sector. However, because of the limitations imposed by the reciprocity law a characteristic curve determined by either method is of dubious applicability in Raman spectroscopy unless the intensities used in the calibration approximate the often extremely low intensities of the Raman bands themselves. In the present investigation exposures of nearly 400 hours were required, and even longer exposure would have been useful but were made impossible due to failure of the mercury arcs. The difficulty of obtaining calibrating sources of these low intensities is obvious, and becomes even more so if the characteristic curve is to be determined over a range of wavelengths. This suggests the desirability of determining the characteristic curve in the course of the Raman exposures themselves. Although this seems to involve a simple and straightforward procedure, the possibility of such a procedure does not seem to be discussed in the standard sources on Raman techniques and did not become entirely evident until the later phases of the present investigation. For this reason, but also as a result of experimental difficulties, the data obtained makes possible only a limited application of the method.

For the determination of the characteristic curve of the emulsion by "internal" calibration during the course of the Raman exposures it is only necessary to take a series of exposures for times \( t_1, t_2, \ldots \).
with all other conditions (sample arrangement, source intensity, filters, and slit width) maintained as nearly constant as possible. The intensity $I(\lambda)$ of a Raman line at wavelength $\lambda$ will then be essentially constant, and the exposures $E_1$, $E_2$, ..., at this $\lambda$ will therefore be proportional to $t_1$, $t_2$, ... . A plot of the peak optical density for this versus $\log t$ will therefore yield the characteristic curve as previously defined except that the curve obtained by the present procedure will be translated by $-\log I(\lambda)$ along the axis of $\log E$. This translation will not affect the value of $\gamma(\lambda)$ obtained from the slope of the linear portion of the curve.

In the present investigation a simplified procedure was used for the calculation of $\gamma$, because as a result of experimental difficulties only two good Raman exposures (other than polarization measurements) were obtained with all conditions other than time of exposure identical. Let the exposures for these two spectra be $t_1$ and $t_2$. If the optical densities, $D_1$ and $D_2$, for two corresponding features (e.g., peak line or background densities) both lie on the linear part of the characteristic curve, then

$$D_1 = -\gamma \log i + \gamma \log (It_1),$$

$$D_2 = -\gamma \log i + \gamma \log (It_2),$$

and

$$\gamma = (D_2 - D_1)/\log (t_2/t_1).$$

A complication which usually arises is the occurrence of significant background radiation of an apparently continuous character throughout the Raman region, consisting of Rayleigh radiation, weak unresolve Raman radiation, and scattering of the strong exciting radiation within the spectrograph (although the latter is minimized by
anti-reflection coatings on the optical elements and baffles). From
the optical densities of the background, interpolated to the wavelength
\( \lambda \) of the given line, one may construct a characteristic curve in a
similar fashion which will be translated by \(-\log I^o(\lambda)\), where \(I^o(\lambda)\) is
the intensity of background at \( \lambda \). As these two curves refer to the
same \( \lambda \) they must evidently be identical except for the translations
indicated and correspond to the same \( \gamma \) (discounting experimental error).
The translation of the second curve relative to the first yields
\( \log(I/I^o) \). However, of more interest is the calculation of a corrected
optical density, \( D' \), at the peak of the line which would be observed in
the absence of background. Let \( T \) be the observed transmission at the
line peak, \( T^o \) that of the background, and \( T' \) the peak transmission which
would obtain if background were absent. The basic assumption made is
that \( T = T^oT' \), or \( T' = (T/T^o) \). Then \( D' \), defined as the difference of
optical densities observed for the peak and background, or
\[
D' = D - D^o = \log(T^o/T) = \log(1/T')
\]
is evidently the corrected peak density.

The determination of the relative intensities of two spectral
lines at wavelengths sufficiently separated so that the characteristic
curves and values of \( \gamma \) differ significantly is relatively complex and
requires the methods of heterochromatic photographic photometry.\(^{35}\) As
the spectral range of the vibrational Raman lines of a given compound
using a given exciting line is small relative to the spectral range of
sensitivity of most emulsions, and highly accurate relative intensities

\(^{35}\) Ibid.
of different Raman lines are not usually required, it is generally sufficient to assume a single characteristic curve and \( \gamma \) for the emulsion in Raman work. Let \( D'_1 = D_1 - D'_1 \) and \( D'_2 = D_2 - D'_2 \) be the peak optical densities for two Raman lines, corrected for background as discussed in the preceding paragraph, for the same exposure time \( t \) (i.e., on the same film). Then assuming the densities \( D'_1 \) and \( D'_2 \) both lie on the linear portion of the characteristic curve,

\[
D'_1 = -\lambda \log i + \gamma \log(I'_1 t)
\]

\[
D'_2 = -\lambda \log i + \gamma \log(I'_2 t).
\]

and

\[
D'_2 - D'_1 = \gamma \log(I'_2/I'_1).
\]

Here \( I'_1 \) and \( I'_2 \) are the peak intensities of the two lines, exclusive of background. Thus, the relative intensities of the two lines corrected for background is

\[
(I'_2/I'_1) = \text{antilog} \left[ (D'_2 - D'_1)/\gamma \right]
\]

If \( D'_1 \) and \( D'_2 \) do not both lie on the linear portion of the curve then must be replaced by the slope of the chord, \( \gamma_{12} \), previously defined.

The preceding relation may be adapted immediately to the calculation of depolarization ratios as measured, for example, by the Edsall-Wilson method used in this investigation and discussed in section 4. In this method two spectra are photographed with the same exposure time \( t \), one with light polarized parallel, the other with light polarized perpendicular to the axis of the Raman tube. The depolarization ratio for a given line is defined by

\[
\rho = (I''_2/I''_1),
\]

where the primes on the intensities indicates background is excluded.
The corrected optical densities are \( D''_n = D_n - D''_n \) and \( D'_\perp = D_\perp - D'_\perp \).

Then, as in the preceding paragraph,
\[
\rho = \left( \frac{I'_n}{I'_\perp} \right) \text{ antilog} \left[ \frac{(D''_n - D'_\perp)}{\gamma} \right],
\]
providing both densities fall on the linear part of the characteristic curve. If this is not the case \( \gamma \) must be replaced by the slope of the chord \( \gamma_{n,\perp} \). This places a definite limitation on the determination of \( \rho \) for sufficiently weak Raman lines if only \( \gamma \), and not the complete characteristic curve, is known. As the intensity of a line approaches zero \( D'_n \to 0 \). But \( 0 \leq D''_n < D'_n \), and therefore \( (D''_n - D'_\perp)/\gamma \to 0 \), for fixed \( \gamma \), and \( \rho \) as calculated from the preceding equation approaches unity. Thus, sufficiently weak lines will appear to be depolarized if treated by means of the preceding equation. The resolution of this seeming paradox lies in the fact that as \( D''_n \) and \( D'_\perp \) approach zero one moves further and further into the "toe" of the characteristic curve, and \( \gamma_{n,\perp} \) also approaches zero in such a way that \( (D''_n - D'_\perp)/\gamma_{n,\perp} \) is non-vanishing, and \( 0 \leq \rho \leq 6/7 \).

The discussions in the three preceding paragraphs assume that a background curve for the line or lines in question can be drawn with sufficient accuracy to be meaningful. This is often not the case for closely-spaced lines between which the intensity does not fall to background level, or where the irregularity or "noise" in the densitometer tracing of the background is too great. In these cases the background correction has been omitted, and peak line intensities alone used.

6. **Failure of the Reciprocity Law**

One of the fundamental generalizations of photographic photometry is the reciprocity law of Bunsen and Roscoe which states that optical density \( D \) is a function of exposure, defined as \( E = It \), so that a
reciprocal relation exists between variations of intensity $I$ and time $t$. This law was enunciated a century ago, but has been shown by subsequent workers not to be exact even though a useful idealization. Departures from the reciprocity law were apparently first observed in stellar photography by Scheiner, and were confirmed by Abney using sensitometric methods. The present discussion is based for the most part on an excellent review by Berg\(^{36}\) although it involves some extensions of the theory.

If the reciprocity law were strictly valid, the exposure $E = It$ required to produce a given optical density would be independent of the intensity of illumination. In studies with real emulsions over a wide range of intensities it is found that there is in fact an optimum intensity $I_0$ for which a minimum exposure is required to produce any given optical density. This optimum intensity seems to be effectively independent of the density considered. For lesser and greater intensities the exposure required to produce a given density increases monotonically with the (absolute) difference between $I$ and $I_0$. Kron made detailed studies and introduced a convenient method of plotting the data with $\log(It)$ as ordinate and $\log I$ as abscissa. As stated, the curves of $\log(It)$ for constant density show a minimum at $I = I_0$. Kron represented the functional relation between $\log(It)$ and $\log I$ in hyperbolic form. However, he also suggested a catenary-type relation which was further tested by Halm, and in an extensive series of investigations by Jones

and coworkers, and found to give the best representation of the data. The catenary relation is

$$\text{It} = (I_o t_o/2)[(I/I_o)^a + (I/I_o)^{-a}]$$

where $I_o t_o$ is the minimum or optimum exposure for the given density, and $a$ is a pure number characterizing the emulsion. For the present discussion of the relation of reciprocity failure to Raman spectroscopy the limiting form of this relation for very low intensities is of primary interest. For $I << I_o$, there is obtained

$$\log(\text{It}) = \log(I_o t_o) + \log(I_o^a/2) - a \log I$$

if a term of order $(I/I_o)^{2a}$ is discarded.

Even though the optical density is accumulated at a very low intensity, as in Raman spectroscopy, the final density may still lie in the region of normal exposure. It is therefore useful to consider the effect of reciprocity failure on the equation for the linear part of the characteristic curve as discussed in section 5,

$$D = -\gamma \log i + \gamma \log(\text{It})$$

It seems justified to assume that when the reciprocity law fails this relation is still applicable for the optimum intensity of exposure, or

$$D = -\gamma \log i + \gamma \log(I_o t_o)$$

However, for exposures at other intensities $\log(\text{It})$ must be replaced by the equivalent logarithm of exposure at optimum intensity, which is

$$\log(I_o t_o) = \log(\text{It}) - \log(I_o^a/2) + a \log I$$

in the limit of low intensities. Therefore in the linear region

$$D = -\gamma \log(iI_o^a/2) + \gamma (1 + a) \log I + \gamma \log t$$
It follows from this relation that for two exposures at the same intensity I but differing times, \( t_1 \) and \( t_2 \),

\[
D_2 - D_1 = \gamma \log(t_2/t_1)
\]

This is identical with the relation obtained in section 5 in the discussion of the determination of \( \gamma \). Therefore reciprocity failure has no effect on measurements carried out at constant intensity. On the other hand, for two exposures with differing intensities, \( I_1 \) and \( I_2 \), but for the same time \( t \),

\[
D_2 - D_1 = \gamma (1 + a) \log(I_2/I_1)
\]

This differs from the corresponding relation obtained in section 5 by the replacement of \( \gamma \) by \( \gamma (1 + a) \). As \( a \) is a positive constant this is equivalent to an increase in the effective development factor from its true value \( \gamma \) to \( \gamma (1 + a) \) as a result of reciprocity failure. Thus, in the analyses in section 5 applicable to two exposures at different intensities but equal times, \( \gamma \) is to be replaced by \( \gamma (1 + a) \). In particular, the relative intensities of two lines on the same film is given by

\[
(I_2/I_1) = \text{antilog} \left[ (D_2 - D_1)/\gamma (1 + a) \right]
\]

and the depolarization ratio is to be calculated as

\[
\rho = (I_{II}/I_{\perp}) = \text{antilog} \left[ (D_{II} - D_{\perp})/\gamma (1 + a) \right]
\]

The preceding results have been established for the region of normal exposures for which the development factor \( \gamma \) is constant. The experimental data to be presented in the next section indicate that most of the present measurements are in the region of underexposure or on the toe of the characteristic curve. As discussed in section 5 the preceding relations may still be utilized if \( \gamma \) is replaced by a mean value \( \overline{\gamma} \) corresponding to the slope of a chord of the characteristic curve. In
the limit in which the termini of the chord approach one another, or 
\( t_2 \to t_1 \), \( \gamma \) becomes the slope of the characteristic curve. In any case, 
on the toe of the curve, \( \gamma < \gamma \). The following simple analysis indi-
cates that even in the region of underexposure the effective development 
factor for exposures at different intensities is greater than that for 
exposures at constant intensity by a factor \((1 + a)\). If \( D \) is an 
arbitrary differentiable function of \( I \) and \( t \),

\[
\left( \frac{\partial D}{\partial \log I} \right)_t / \left( \frac{\partial D}{\partial \log t} \right)_I = - \left( \frac{\partial \log t}{\partial \log I} \right)_D \\
= 1 - \left[ \frac{\partial \log (It)}{\partial \log I} \right]_D \\
= (1 + a)
\]

where the last line has been obtained by substituting the limiting low 
intensity form of the catenary relation. But the left-hand side of this 
equation is simply the ratio of the effective development factors for 
constant time and constant intensity exposures.

From a physical point of view the failure of the reciprocity law 
at low intensities of illumination seems to be the result of thermally 
activated decay of the latent image, as shown by the fact that as the 
temperature is lowered \( I_0 \) decreases. At sufficiently low temperatures 
\((-186^\circ C.)\) the reciprocity law seems to become valid. As shown by the 
preceding discussion the decay of the latent image is relatively greater 
the lower the intensity, so that optical density differences are accentu-
ated. Thus, intensity differences will be overestimated unless cor-
rection is made for reciprocity failure.
7. **Experimental Data**

In photographing the Raman spectrum of $B_5H_9$, Taylor et al.\(^ {37}\) obtained spectra of good density with exposures in the range 20 to 50 hours, using a current of only 15 amperes in each of the two mercury arcs. In their polarization spectra the exposure time was 50 hours for each spectrum with arc currents increased to 25 amperes to compensate for the absorption by the polaroid. The volume of the $B_5H_9$ sample used by these investigators was 20-25 ml., as compared with the much smaller sample of 4 ml. of $B_5D_9$ available for the present measurements. Thus it would be anticipated that exposures about 5 times as long would be necessary for $B_5D_9$ at the same arc current of 15 amperes. Since each increase of 5 amperes in arc current approximately doubles their intensity, it was hoped that satisfactory Raman spectra for $B_5D_9$ could be obtained in about 50 hours at a current of 25 amperes, which is the maximum current which does not seriously shorten the life of the arcs.

The first attempt to obtain the Raman spectrum of $B_5D_9$ was made with an exposure of 27 hours at 20 amperes, using Wratten 2A, Rhodamine 5GDN, and saturated praseodymium chloride solution filters (see section A). The slit width in this as in all but one of $B_5H_9$, was 100 microns. Eastman Tri-X Pan film was used in the present investigation. This first exposure gave a weak spectrum, showing lines only at 639, 737, 959, 1944, and 1979 cm.\(^{-1}\) A second spectrum was then taken with an exposure of 274 hours, of which the first 106 were at a current of 20 amperes and the balance of the time at 25 amperes. The same filters

were used. The spectrum was still of very low density in spite of the long exposure time, although it showed in addition to the preceding lines weaker lines at 682 and 975 cm\(^{-1}\), and very faint activity at \(\sim\)1400 cm\(^{-1}\).

At this point it was decided it would be advantageous to discard the praseodymium filter, which was known to increase exposure times by a considerable factor through absorption of the exciting radiation. As previously mentioned the need for this filter is not very great with the present arcs because of their relatively low continuous background. The next exposure was for 160 hours, using only the first two filters mentioned and a current of 25 amperes. This spectrum was more satisfactory, giving the previously mentioned lines with greater strength and an indication of several lines or bands in the region 1300-1500 cm\(^{-1}\).

The final and best Raman spectrum (other than the polarization spectra) was obtained by exposing for 393 hours at 25 amperes. During the final 193 hours of this exposure the lower half of the slit which is used for the argon calibration spectra (section 3) was uncovered. This spectrum taken under identical conditions except for exposure time was used to estimate the constant \(\gamma\) for the film as described later. The calibration spectrum was later superimposed on the latter Raman spectrum. In these exposures the intensity of incident light was further increased by using a wider spacing (5/8 inch) for the collimator (see section 4). This, combined with the extremely long exposure time, relatively high arc current, and the abandonment of the praseodymium filter, is probably responsible for the rather high background on this film, which is much greater relative to line strength than in the spectra for \(^5\text{B}_9\). In spite of the high background, the 393 hour exposure showed additional
weak lines at 425, 507, 537, 846, 1274, 1333, 1393, and 1492 cm$^{-1}$, or a total of 15 Raman bands inclusive of those previously listed. This is considerably smaller than the total of 25 predicted Raman active fundamentals for pentaborane, but of course a number of the latter would be expected to have low intensity or to approximately coincide. Taylor et al. observed 25 to 30 Raman lines for B$_5$H$_9$, but several of these are overtone or combination bands.

No attempt to make longer Raman exposures on B$_5$D$_9$ was undertaken for two reasons. In the first place the exposure of 393 hours, or more than 16 days, was already excessively long and placed an abnormal strain on the arcs and cooling system, in addition to constituting an appreciable fraction of the estimated arc life. Exposures of this length seem to have been made rarely if ever, at least in modern Raman work. In the second place the 393 hour exposure itself was terminated by the accidental breakage of both mercury arcs, caused by an attempt to drain excess water from the cooling system with the arcs in operation (a leak developed permitting tap water used for cooling to mix with distilled water circulating through the arcs). As this type of arc is no longer commercially available it was impossible to obtain replacements in a reasonable time.

Fortunately spectra with polarized incident light for the determination of depolarization ratios had been taken immediately prior to the 393 hour exposure in which the arcs were broken. As discussed in section 4, the two polarization spectra based on the method of Edsall and Wilson are photographed successively on the same film under identical conditions except that for one the light is polarized parallel to, and for the other perpendicular to, the axis of the Raman tube by means of
polaroid film (these spectra will be denoted by the symbols $\parallel$ and $\perp$, respectively). Each spectrum was photographed for 170 hours at a current of 25 amperes, with Wratten 2A and Rhodamine 5GDN filters and a collimator spacing of 3/8 inch. Unfortunately the polaroid film absorbs an estimated 75 to 80 percent of the exciting radiation, so that the polarization spectra have effective exposures of the order of one-tenth that of the 393 hour exposure with unpolarized light. As a result only the lines at 639, 682, 737, 959, 975, 1393, 1944, and 1979 cm$^{-1}$, are observed with sufficient strength to make possible the calculation of depolarization ratios. The depolarization ratio for a line is defined as the ratio of its intensity in the parallel to that in the perpendicularly polarized spectrum.

Figure 7 shows the densitometer tracing of the 393 hour Raman spectrum of $\text{B}_2\text{D}_9$ obtained in the present investigation, and for comparison a tracing of the spectrum of $\text{B}_2\text{H}_9$ obtained by Taylor et al. with an exposure of 20 hours (their film No. 64). Other conditions are indicated in the figure. The abscissas in the figures are proportional to distances on the film and are not linear in wavelength. The wavelengths were determined directly from comparator measurements on the film (see section 3) and are given on the tracings for each important feature of the spectra. However, the two tracings are offset, so that points aligned vertically on the two scales correspond to the same wavelength. The ordinates represent optical density on a relative scale. For an absolute optical density scale, the top and bottom of the scales, $D = \infty$ and $D = 0$, would represent transmissions of $T = 0$ and $T = 1$, respectively. The tracing for $\text{B}_2\text{H}_9$ is on an absolute basis in a particular
Figure 7

**Raman Spectrum of Pentaborane (B$_5$H$_9$)**

Sample: liquid, 15 mL
Exposure: 2.0 hrs, $1/4$, 50 $\mu$m slit
Arcs: 2 low-pressure Hg, 15 amp
Filters: Wratten 2A, Rhodamine 5GDN

**Raman Spectrum of Deuterated Pentaborane (P$_5$D$_9$)**

Sample: liquid, 3 mL
Exposure: 395 hrs, $1/3$, 100 $\mu$m slit
Arcs: 2 low-pressure Hg, 25 amp
Filters: Wratten 2A, Rhodamine 5GDN
sense, as the point \( D = 0 \) represents the transmission of the film outside the region where the spectrum is focused. In this region of "clear" film the transmission is reduced below unity only by the inherent absorption of the film and the slight fogging which always occurs. From the analysis in section 5 it follows that in the \( B\text{H}_9 \) tracing the optical densities are the optical densities which would be observed if the film were perfectly transparent and there were no fogging. As previously discussed the background in the 393 hour exposure for \( B\text{D}_9 \) was relatively high. This background is due either to a weak continuum in the radiation from the arcs which undergoes Rayleigh scattering in the sample, or possibly to a weak continuous Raman spectrum arising from the interchange of energy between the strong monochromatic exciting radiation and complex dynamical modes in the liquid. The high background on the \( B\text{D}_9 \) film makes the absolute optical densities so high that the entire tracing would be compressed into a small range at the top of the scale if it were placed on an absolute basis. As a consequence the optical density scale has been expanded as much as possible by means of an adjustment on the Knorr-Albers densitometer. This expansion is such that transmissions are multiplied by an approximately constant factor less than unity. Therefore a constant amount is subtracted from optical densities, placing them lower on the scale, but the ratio of two transmissions or the difference of two optical densities are unaffected. Only these ratios or differences occur in the calculations described in section 5 or carried out in the present section.

As previously discussed the polarization measurements are based on separate exposures, and the depolarization ratios to be described are
obtained from separate tracings of these films. These tracings are not reproduced as visual examination yields little of value and quantitative conclusions must be based on careful measurement of the originals combined with the methods of section 5. However, the intervals between the solid and dashed curves in Figure 7 give a qualitative indication, transferred from the other tracings, of the differences in optical density observed with incident light polarized perpendicular and parallel, respectively, to the axis of the Raman tube. When treated quantitatively the decrease in optical density, or ratio of the intensities, yields the depolarization ratio \( \rho \). The lines for which it is considered that \( \rho < 6/7 \), and which are therefore regarded as polarized, are marked (p) in the figure.

The Raman spectra were examined for false lines due to scattering of the two mercury lines at 4347 and 4339 \( \AA \), which have intensities about 5 percent of that of the principal exciting line at 4358 \( \AA \). These produce satellites of each Raman band displaced to lower frequencies by 57 and 101 cm\(^{-1} \), respectively, but these are likely to be observed only for the strongest Raman lines if at all. In the Raman spectrum of \( \text{B}_2\text{H}_9 \) there is little doubt that the weak polarized lines at 929 and 944 cm\(^{-1} \) are satellites of the two polarized lines at 986 and 1001 cm\(^{-1} \), which are the strongest lines in the spectrum. Similarly, in the spectrum of \( \text{B}_2\text{D}_9 \) the weak line at 902 cm\(^{-1} \) is almost certainly a satellite of the 959 cm\(^{-1} \) line, again the strongest in the spectrum. In the preceding cases the displacement of the satellite is by 57 cm\(^{-1} \). The satellites displaced by 101 cm\(^{-1} \) if present are obscured by the moderately strong line of \( \text{B}_2\text{H}_9 \) at 884 cm\(^{-1} \) and the weak Raman activity
centered at 846 cm.\textsuperscript{-1} for $B_5D_9$. The higher frequency component of the latter may be due to the satellite at 858 cm.\textsuperscript{-1} However, this may also represent true Raman activity as an infrared band of $B_5D_9$ is observed with maxima at 844, 850, and 856 cm.\textsuperscript{-1}

The Raman frequencies observed for $B_5D_9$ in the present investigation, and for $B_5H_9$ by Taylor et al. are listed in the first columns of Tables 4 and 5, respectively. The remaining columns in these tables refer to the relative intensities and depolarization ratios for the lines. Before discussing these it is desirable to discuss the information which may be extracted from the observations regarding the effective values of the parameter $\Upsilon$ which determines the relation between exposure and optical density. Values of $\Upsilon$ for the 103-F film used for $B_5H_9$ were calculated from tracings of their films No. 63 and 64, with exposure ratio 5:1, using the simplified two-exposure procedure described in section 5. This procedure yields the slopes of chords of the characteristic curve, or mean values of $\Upsilon$,

$$\Upsilon = \frac{(D_2 - D_1)}{\log(t_2/t_1)}$$

from corresponding optical densities, $D_1$ and $D_2$, for the two exposures. If $D_1$ and $D_2$ are both in the normal or linear region of the characteristic curve, $\Upsilon$ would be expected to be constant and equal to the slope $\gamma$ in this region. However, the values of $\Upsilon$ are found to show a marked dependence on the magnitudes of the densities $D_1$ and $D_2$. This is shown by the upper curve in Figure 8, in which several values of $\Upsilon$ are plotted versus the mean optical densities, $\bar{D} = (D_1 + D_2)/2$, used in the calculation. The values given were obtained from the prominent lines in
the spectrum as well as three background ratios. The middle curve in Figure 8 represents values of $\chi$ obtained in the same way from the 193 and 393 hour exposures with $B_5D_9$, and the lower curve was calculated from the 27 and 274 hour exposures with $B_5D_9$. The optical densities are

### Table 4

**Raman Spectrum of Deuterated Pentaborane**

<table>
<thead>
<tr>
<th>Displacement (cm.(^{-1}))</th>
<th>Relative Intensity ((T_1/T') (T_1'/T')^{1/\chi})</th>
<th>Depolarization ((T_2/T_{11}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>425</td>
<td>.29</td>
<td>.17</td>
</tr>
<tr>
<td>507</td>
<td>.25</td>
<td>.14</td>
</tr>
<tr>
<td>537</td>
<td>.25</td>
<td>.14</td>
</tr>
<tr>
<td>639</td>
<td>.55</td>
<td>.43</td>
</tr>
<tr>
<td>682</td>
<td>.38</td>
<td>.25</td>
</tr>
<tr>
<td>737</td>
<td>.89</td>
<td>.83</td>
</tr>
<tr>
<td>846</td>
<td>.25</td>
<td>.14</td>
</tr>
<tr>
<td>959</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>975</td>
<td>.50</td>
<td>.37</td>
</tr>
<tr>
<td>1274</td>
<td>.27</td>
<td>.15</td>
</tr>
<tr>
<td>1333</td>
<td>.29</td>
<td>.17</td>
</tr>
<tr>
<td>1393</td>
<td>.34</td>
<td>.22</td>
</tr>
<tr>
<td>1492</td>
<td>.29</td>
<td>.17</td>
</tr>
<tr>
<td>1944</td>
<td>.64</td>
<td>.53</td>
</tr>
<tr>
<td>1979</td>
<td>.73</td>
<td>.64</td>
</tr>
</tbody>
</table>

For explanation of column headings, see text.

low for the latter two exposures because of the absorption by the praseodymium filter used. The effective exposure ratio for the latter pair of exposures is estimated as 1:16, when account is taken of the differences in the arc currents. The optical density scales for the upper and lower curves are on an essentially absolute basis, but that for the middle curve is indeterminate to an additive constant because of the expansion of the transmission scale for the corresponding tracings
### TABLE 5

RAMAN SPECTRUM OF NORMAL PENTABORANE*

<table>
<thead>
<tr>
<th>Displacement (cm.(^{-1}))</th>
<th>Relative Intensity ((T_1/T'))</th>
<th>Relative Intensity ((T_1'/T))^{1/\gamma})</th>
<th>Depolarization ((T_L/T_H))</th>
</tr>
</thead>
<tbody>
<tr>
<td>470</td>
<td>.08</td>
<td>.04</td>
<td>1.00 dp</td>
</tr>
<tr>
<td>566</td>
<td>.11</td>
<td>.06</td>
<td>1.08 dp</td>
</tr>
<tr>
<td>596</td>
<td>.08</td>
<td>.04</td>
<td>1.00 dp</td>
</tr>
<tr>
<td>616</td>
<td>.14</td>
<td>.08</td>
<td>.81 p</td>
</tr>
<tr>
<td>700</td>
<td>.17</td>
<td>.11</td>
<td>1.01 dp</td>
</tr>
<tr>
<td>738</td>
<td>.50</td>
<td>.42</td>
<td>.40 p</td>
</tr>
<tr>
<td>803</td>
<td>.39</td>
<td>.30</td>
<td>.44 p</td>
</tr>
<tr>
<td>884</td>
<td>.10</td>
<td>.06</td>
<td>.91 dp</td>
</tr>
<tr>
<td>986</td>
<td>1.00</td>
<td>1.00</td>
<td>.29 p</td>
</tr>
<tr>
<td>1001</td>
<td>.41</td>
<td>.33</td>
<td>.47 p</td>
</tr>
<tr>
<td>1120</td>
<td>.21</td>
<td>.14</td>
<td>.58 p</td>
</tr>
<tr>
<td>1170</td>
<td>.08</td>
<td>.04</td>
<td></td>
</tr>
<tr>
<td>1193</td>
<td>.08</td>
<td>.04</td>
<td></td>
</tr>
<tr>
<td>1350</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1390</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1435</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1495</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1600</td>
<td>.08</td>
<td>.04</td>
<td>1.06 dp</td>
</tr>
<tr>
<td>1730</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1800</td>
<td>.12</td>
<td>.07</td>
<td>.99 dp</td>
</tr>
<tr>
<td>1830</td>
<td>.22</td>
<td>.15</td>
<td>.43 p</td>
</tr>
<tr>
<td>1895</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1950</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1970</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2010</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2040</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2077</td>
<td>.09</td>
<td>.05</td>
<td>.64 p</td>
</tr>
<tr>
<td>2105</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2120</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2152</td>
<td>.09</td>
<td>.05</td>
<td>.74 p</td>
</tr>
<tr>
<td>2196</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2240</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2280</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2600</td>
<td>.91</td>
<td>.89</td>
<td></td>
</tr>
</tbody>
</table>

For explanation of column headings, see text.

$T = \frac{D_2 - D_1}{\log(t_2/t_1)}$

Mean Optical Density, $(D_1 + D_2)/2$

**FIG. 8**
discussed previously. To place the middle curve on an absolute basis it should be translated toward higher optical densities by 0.2 to 0.3. If this is done fair agreement of the lower two curves which refer to Tri-X Pan film is obtained in the range of low optical densities. The higher values of $\gamma$ obtained for the 103-F film (upper curve) indicate that it has greater contrast at any given density than the Tri-X Pan film. The large scattering of the points on which the middle curve is based is probably connected with the graininess of this emulsion. For both films $\gamma$ drops off sharply at low densities, but shows some indication at leveling off at about 0.9 for 103-F and about 0.3 for Tri-X Pan film at high optical densities. Presumably the latter limits are the values of $\gamma$ characteristic of the normal or linear region for each film, and the range of the present measurements is on the "toe" or underexposure region of the characteristic curve. As discussed in section 6, failure of the reciprocity law does not affect the determination of $\gamma$ (or $\overline{\gamma}$) as carried out here.

The calculation of relative intensities of spectral lines and of depolarization ratios as described in section 5 are both based on the optical densities, $D_1$ and $D_2$, of two images produced by two different intensities of illumination, $I_1$ and $I_2$, with the same exposure time $t$ for both images. Primes are used as in section 5 to indicate the peak optical densities are corrected for background; for the polarization measurements the subscripts 1 and 2 are to be replaced by $\parallel$ and $\perp$, respectively. The results of the preceding paragraph indicate that in the region of underexposure $\gamma$ is to be replaced by an effective value $\overline{\gamma}$, and the discussion of reciprocity failure in section 6 indicates
that the effective overall development factor will be \( \gamma(1 + a) \). With these modifications the relation for relative intensities given in section 5 may be put in the following form:

\[
\frac{I_1'}{I_1^1} = \left( \frac{T_1'}{T_1^1} \right)^{1/\gamma}(1 + a),
\]

\[
\frac{T_1'}{T_1^1} = \text{antilog}(D' - D_1'),
\]

where the subscript 1 refers to a suitably chosen reference line in the spectrum. Depolarization ratios may be expressed similarly as

\[
\varphi = \frac{I_2'}{I_2^1} = \left( \frac{T_2'}{T_2^1} \right)^{1/\gamma}(1 + a),
\]

\[
\frac{T_2'}{T_2^1} = \text{antilog}(D_2' - D_2^1).
\]

The second columns of Tables 4 and 5 give the relative transmissions \( \frac{T_1'}{T_1^1} \) for the Raman lines of \( B_5D_9 \) and \( B_5H_9 \), respectively. In each case the reference line is the most intense in the spectrum, 959 cm\(^{-1}\) for \( B_5D_9 \) and 986 cm\(^{-1}\) for \( B_5H_9 \). These values are calculated from the 393 hour exposure for \( B_5D_9 \), and a 20 hour exposure (Film No. 64) for \( B_5H_9 \). Relative intensities are omitted for a number of weak lines of \( B_5H_9 \) for which the calculation is too inaccurate to be of significance. For the remaining lines the mean optical densities, \( (D' + D_1')/2 \), were sufficiently high so that it appeared from the upper two curves in Figure 8 that \( \gamma \) could be approximated by constant values of 0.7 for the Tri-X Pan film used for \( B_5D_9 \) and 0.8 for the 103-F film used for \( B_5H_9 \).

The third columns of Tables 4 and 5 give values of

\[
\frac{(I_1'/I_1^1)(1 + a)}{(T_1'/T_1^1)^{1/\gamma}},
\]

which may be regarded as apparent relative intensities uncorrected for reciprocity failure. As \( a \) is positive the true relative intensities are somewhat greater than the apparent intensities. Because of the uncertainty in the value of \( a \) it is not possible to make a significant
correction of the relative intensities for reciprocity failure. As far as is known such a correction has not been applied in previous Raman work. Fortunately, highly accurate relative intensities are not required for the purposes of the present investigation. The principal reason for introducing a discussion of the reciprocity effect is because it may be of considerable importance in the depolarization measurements to be discussed next.

The fourth columns of Tables 4 and 5 give values of

\[
\left( \frac{T'_1}{T''_1} \right) = \text{antilog}(D'_{11} - D'_{1})
\]

for those Raman lines of \(B_2D_9\) and \(B_2H_9\), respectively, which were observed in the polarization spectra. The latter were the two 170 hour exposures for \(B_2D_9\), and two 50 hour exposures (Film No. 65) for \(B_2H_9\). From a preceding equation depolarization ratios are to be calculated by raising \(\left( \frac{T'_1}{T''_1} \right)\) to the power \(1/\gamma(1 + a)\). For \(B_2H_9\) \(\gamma\) may be assigned the approximate value 0.8 used in reducing the relative intensities, as the range of optical densities is similar. Values of the reciprocity coefficient \(a\) in the literature seem to lie in the range 0.2 to 0.5. Thus, \(1/\gamma(1 + a)\) should not differ greatly from unity for \(B_2H_9\), and the values of \(\left( \frac{T'_1}{T''_1} \right)\) may be accepted as approximate depolarization ratios. An inspection of these values in Table 5 shows that the Raman lines of \(B_2H_9\) marked \(p\) are definitely polarized (\(\rho < 6/7\)), with the exception of the line at 700 cm.\(^{-1}\) which is only slightly polarized (\(\rho = .805\)). The remaining lines for \(B_2H_9\) have values of the approximate depolarization ratio \(\left( \frac{T'_1}{T''_1} \right)\) which are greater than the theoretical maximum for

38. Berg, op. cit.
depolarized lines, $\varphi = 6/7$. These deviations from the theoretical value must be assigned to experimental error as no reasonable value of the exponent $1/\sqrt[3]{(1 + a)}$ is capable of removing them. There is no doubt that these lines are depolarized because sufficient polarized lines are observed to account for the totally-symmetric fundamental vibrations of $B_{5}H_{9}$. The interpretation of the polarization measurements for $B_{5}D_{0}$ in Table 4 is less satisfactory. Because of the absorption by the polaroid these films were of fairly low optical density, in about the same range as the 27 and 27$^{4}$ hour exposures using the praseodymium filter for which $\gamma$ is indicated by the lower curve in Figure 9. Thus, it would appear from an objective evaluation that $\gamma$ is about 0.2 for the polarization films, corresponding to considerable underexposure. With $a = 0.2$ to 0.5, the calculated value of the exponent $1/\gamma(1 + a)$ is then 3 to 4. If depolarization ratios are calculated by applying powers of this magnitude to the values of $(T_{1} / T_{2})$ then all the lines for which polarization data are available appear to be highly polarized. This is a possibility, as when account is taken of $B^{10} - B^{11}$ isotope splitting the number of lines observed in the polarization spectra is seven, or equal to the number of totally-symmetric vibrations. However, in the subsequent discussion of the assignment for $B_{5}D_{0}$ and $B_{5}H_{9}$ a convincing argument based on the product rule will be given which indicates that it is virtually impossible for both of the two lines at 639 and 682 cm.$^{-1}$ which have the largest values of $(T_{1} / T_{2})$ to be totally symmetric, and that it is unlikely that either is totally symmetric. It is therefore felt that for reasons which are not understood the exponent to be applied to the values of $(T_{1} / T_{2})$ for $B_{5}D_{0}$ is much closer to unity than the value of 3 or 4 estimated above.
Possibly there is an exaggerated reciprocity failure with Tri-X Pan film for these exceptionally low intensities. The 103-F film used for $B_{5H_9}$ with more satisfactory results was specially developed for use at low intensities and thus presumably is less subject to the reciprocity effect. As previously explained delays in obtaining 103 film made it necessary to use Tri-X Pan.
IV. SYMMETRY AND SELECTION RULES

The pentaborane molecule, whose structure has been discussed in chapter II, belongs to the point group $C_{4v}$. It has a four-fold rotation axis, two planes of symmetry, $\sigma_v$, passing through the diagonals of the square base, and two planes of symmetry, $\sigma_d$, passing through the midpoints of opposite sides of the square base. The normal vibrations can be classified into five symmetry types (irreducible representations) $A_1, A_2, B_1, B_2,$ and $E$, depending on their behavior with respect to the symmetry operations. The $A_1$ vibrations are totally symmetric, i.e., they are symmetric with respect to all the symmetry operations. The $A_2$ vibrations are symmetric with respect to rotations about the four-fold axis, but are antisymmetric with respect to reflection in the symmetry planes. The $B_1$ and $B_2$ vibrations are antisymmetric with respect to a $90^\circ$ rotation about the four-fold axis; hence they are symmetric with respect to a $180^\circ$ rotation. The $B_1$ vibrations are symmetric with respect to reflection in $\sigma_v$ and antisymmetric to $\sigma_d$, while the $B_2$ vibrations are symmetric to $\sigma_d$ and antisymmetric to $\sigma_v$ reflections. The $E$ vibrations are doubly degenerate, and thus are not simply symmetric or antisymmetric with respect to all the symmetry operations. A vibration which is a member of a degenerate set of vibrations is transformed into a linear combination of the members of the degenerate set by a symmetry operation. In the present case, each degenerate set contains two normal vibrations.
The symmetry behavior is summarized in the character table of the group,\(^1\) which is given in Table 6. The headings of the columns are the classes of symmetry elements in the \(C_{4v}\) point group. \(E\) is used for the identity operation. The headings of the rows are the irreducible representations. The characters are the trace or sum of the diagonal elements of the irreducible representation matrices. For the non-degenerate representations, the characters give immediately the behavior of each type of vibration with respect to the symmetry operations. A character of +1 corresponds to symmetric behavior, while a character of -1 indicates antisymmetric behavior.

**TABLE 6**

CHARACTER TABLE FOR \(C_{4v}\) POINT GROUP

<table>
<thead>
<tr>
<th></th>
<th>(E)</th>
<th>(2C_4)</th>
<th>(C_2)</th>
<th>(2\sigma_v)</th>
<th>(2\sigma_d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A_1)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>(A_2)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>(B_1)</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>(B_2)</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>(E)</td>
<td>2</td>
<td>0</td>
<td>-2</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

From the character table, it is possible to predict the number of vibrations of each symmetry type in a particular molecule, and the infrared and Raman activity of each symmetry type. In order to do this, it is

---

necessary to calculate the characters of the coordinates of the molecule. The character \( \chi(R) \) for the symmetry operation \( R \) is given by \((u_r - 2)(1 + 2\cos\phi)\) for proper rotations and by \((u_r)(-1 + 2\cos\phi)\) for an improper rotation, where \( u_r \) is the number of atoms that are not changed by the symmetry operation, and \( \phi \) is the angle of rotation. The number \( n_y \) of normal coordinates in each symmetry species can be found by application of the following reduction formula, which can be proved by means of the orthogonality theorem for group characters,

\[
m_y = \frac{1}{g} \sum_{R} g_R \chi_y(R) \chi(R),
\]

where \( g \) is the number of symmetry operations or order of the group, \( g_R \), the number of symmetry operations in the class \( R \), \( Y \) is the irreducible representation, \( \chi_y(R) \) is the character of the \( Y \) irreducible representation for the class \( R \), and the sum is over all classes of symmetry operations. The results obtained by the use of this formula are given in Table 7. Calculations were made not only for the pentaborane molecule,

<table>
<thead>
<tr>
<th>Symmetry Species</th>
<th>( A_1 )</th>
<th>( A_2 )</th>
<th>( B_1 )</th>
<th>( B_2 )</th>
<th>( E )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Entire Molecule</td>
<td>7</td>
<td>2</td>
<td>5</td>
<td>4</td>
<td>9</td>
</tr>
<tr>
<td>Boron Skeleton</td>
<td>2</td>
<td>0</td>
<td>2</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Bridge Hydrogen</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Non-bridge Hydrogen</td>
<td>3</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>Apex Hydrogen</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

but also for the boron skeleton, the bridge hydrogens, the non-bridge hydrogens, and the apex hydrogen. The translations and rotations of the
molecule were subtracted from the boron skeleton and not from the other parts of the molecule.

The optical activity is obtained in a similar manner. Only those vibrations which change the dipole moment of the molecule are active in the infrared, while only those which change the polarizability of the molecule are Raman active. In a first order approximation, the transition probability between two vibrational states is proportional to the square of the integrals $\int \Psi_v. M_{\hat{1}}. \Psi_{v'}. d\tau$ where $\Psi_v$ and $\Psi_{v'}$ are the time independent vibrational eigenfunctions of the two states, and $M_{\hat{1}}$ is one of the components $M_x, M_y, M_z$ of the dipole moment. This integral must be invariant to any symmetry operation. Thus the non-vanishing integrals must be totally symmetric with respect to all symmetry operations. In group theory terminology, a vibration will be infrared active only if the representation of $\Psi_v. \bar{M} \Psi_{v'}$ contains the totally symmetric $A_1$ irreducible representation. The ground state of the molecule is always totally symmetric, while the fundamental levels (first excited state) have the same symmetry as the corresponding normal coordinates. Thus, for fundamental vibrations, a vibration will be infrared active only if the symmetry species to which the vibration belongs contains the irreducible representation of $M_x, M_y, M_z$. Similarly, a vibrational mode will be Raman active as a fundamental only if its symmetry is the same as the symmetry of at least one component of the polarizability tensor. It can be shown that the components of the dipole moment $M_x, M_y, M_z$ transform under symmetry operations exactly as $x, y, z$. The components of the polarizability tensor $\alpha_{xx}, \alpha_{xy}$, etc. transform in the same way as $x^2, xy$, etc.
In order to determine the selection rules it is necessary to calculate the characters of the dipole moment $\chi_m(R)$ and of the polarizability $\chi_{\alpha}(R)$. These characters can be calculated from the following formulas,$^2$

$$\chi_m(R) = \pm 1 + 2 \cos \phi,$$

$$\chi_{\alpha}(R) = 2 \pm 2 \cos \phi + 2 \cos(2\phi),$$

where the plus sign is used for proper rotations and the minus sign for improper rotations. The representation formed by $m$ and $\alpha$ is in general reducible and the reduced representation can be found by the application of the orthogonality theorem for group characters, as in finding the number of vibrations of each symmetry type. When the above procedure is carried out, it is found that the reduced representations of the dipole moment and the polarizability tensor are $A_1 + E$ and $2A_1 + B_1 + B_2 + E$, respectively. Therefore the $A_1$ and $E$ modes are infrared active, while the $A_1$, $B_1$, $B_2$, and $E$ vibrations are Raman active. Only the $A_2$ vibrations are inactive in both the Raman and infrared. The symmetry species of the dipole moment and the polarizability components, as well as the translations and rotations of the molecule, are given to the right of the character table in Table 6.

Just as for fundamentals, the activity of a combination or overtone band depends on the non-vanishing of an integral $\int \psi_v \cdot P \psi_{v''} \, d\tau$ where $\psi_v$ and $\psi_{v''}$ are the vibrational wave functions of the initial and final states, and $P$ is a component of the dipole moment or

---

polarizability. Binary combinations are either sum or difference bands. In the first case $\psi_v$ is the totally-symmetric ground state, while the excited state has the direct product representation, $\Gamma = \Gamma_a \times \Gamma_f$, where $\Gamma_a$ and $\Gamma_f$ are the irreducible representations of two different normal modes each excited with one vibrational quantum. In the second case $\psi_v$ and $\psi_{v''}$ belong to the representations $\Gamma_a$ and $\Gamma_f$, respectively, of the two distinct normal modes which are singly excited in the initial and final states. Therefore, in either case the representation of the product $\psi_v \psi_{v''}$ is $\Gamma = \Gamma_a \times \Gamma_f$. It follows that if the binary combination is to be allowed in a given spectrum, the generally reducible representation $\Gamma = \Gamma_a \times \Gamma_f$ must contain the irreducible representation of at least one component of $P$. In the case of the first overtone $\psi_v$ will again be the totally-symmetric ground state, while $\psi_{v''}$ will be the state in which the given vibration belonging to irreducible representation $\Gamma_a$ is excited with two quanta. The representation of $\psi_{v''}$ is then given by the symmetric square of $\Gamma_a$, or $[\Gamma_a^2]$, as first shown by Tisza. If the vibration is non-degenerate, so that $\Gamma_a$ is one-dimensional, then $[\Gamma_a^2]$ is identical with the ordinary direct product, $\Gamma_a \times \Gamma_a$, and is easily seen to be the identity representation for all non-degenerate $\Gamma_a$. If the vibration is doubly degenerate, the character of $[\Gamma_a^2]$ for the operation $R$ is

$$[\chi_a^2(R)] = \frac{1}{2} \left\{ [\chi_a(R)]^2 + \chi_a(R^2) \right\}$$

The representation $[\Gamma_a^2]$ may be reduced in the usual manner by means of the characters and the orthogonality theorem. The symmetry species of

all binary combinations and first overtones for a molecule having symmetry $C_{4v}$ are given in Table 8. The infrared and Raman activity of these combinations and overtones are obtained by using Table 6 in conjunction with Table 8.

**TABLE 8**

**SYMMETRY TYPE OF COMBINATIONS AND OVERTONES**

<table>
<thead>
<tr>
<th>Binary Combinations</th>
<th>$A_1$</th>
<th>$A_2$</th>
<th>$B_1$</th>
<th>$B_2$</th>
<th>$E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>$A_1$</td>
<td>$A_2$</td>
<td>$B_1$</td>
<td>$B_2$</td>
<td>$E$</td>
</tr>
<tr>
<td>$A_2$</td>
<td>$A_2$</td>
<td>$A_1$</td>
<td>$B_2$</td>
<td>$B_1$</td>
<td>$E$</td>
</tr>
<tr>
<td>$B_1$</td>
<td>$B_1$</td>
<td>$B_2$</td>
<td>$A_1$</td>
<td>$A_2$</td>
<td>$E$</td>
</tr>
<tr>
<td>$B_2$</td>
<td>$B_2$</td>
<td>$B_1$</td>
<td>$A_2$</td>
<td>$A_1$</td>
<td>$E$</td>
</tr>
<tr>
<td>$E$</td>
<td>$E$</td>
<td>$E$</td>
<td>$E$</td>
<td>$E$</td>
<td>$(A_1 + A_2 + B_1 + B_2)$</td>
</tr>
</tbody>
</table>

**FIRST OVERTONES**

$$[A_1^2] = [A_2^2] = [B_1^2] = [B_2^2] = A_1$$

$$[E^2] = A_1 + B_1 + B_2$$
V. MOMENTS OF INERTIA AND BAND TYPES

The moments of inertia of a molecule are of importance in the interpretation of the infrared and Raman spectra because they determine the rotational energy levels, and therefore the rotational fine structure of the vibrational bands or the contours of unresolved bands. Pentaborane is a symmetric rotor as a result of the existence of a four-fold symmetry axis. The unique moment of inertia about this axis will be designated $I_z$, and the two equal moments of inertia about axes perpendicular to the symmetry axis by $I_x$ and $I_y$. The values of the moments of inertia of pentaborane can be calculated from the structural data given in Table 1 or from the microwave data of Hrostowski and Myers.\(^1\) The values of the moments of inertia are given in Table 9 for normal and deuterated pentaborane. The values for $B_5^\text{H}_9$ and $B_5^\text{D}_9$ are taken from the microwave data. For $B_5^\text{H}_9$, two sets of values in close agreement are obtained by considering different rotational transitions. The values for $B_5^{10.822}\text{H}_9$ and $B_5^{10.822}\text{D}_9$ have been calculated from the structural parameters as given in the final column of Table 1 with the B-H bond length assumed to be 1.22 Å. These mean values calculated with the chemical atomic weight of boron are required for the statistical calculation of the thermodynamic properties of pentaborane. Since $I_z$ is greater than $I_x$ and $I_y$, pentaborane is an oblate symmetric top.

---

TABLE 9
MOMENTS OF INERTIA OF PENTABORANE

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$I_z$</th>
<th>$I_x, I_y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_{11}^5H_9$</td>
<td>$104.3 \pm 1.3$</td>
<td>$72.1773 \pm 0.0003$</td>
</tr>
<tr>
<td></td>
<td>$103.3 \pm 0.2$</td>
<td>$72.1769 \pm 0.0002$</td>
</tr>
<tr>
<td>$B_{11}^5D_9$</td>
<td>$134.6 \pm 3.5$</td>
<td>$96.9895 \pm 0.0009$</td>
</tr>
<tr>
<td>$B_{10.822}^5H_9$</td>
<td>$101.9$</td>
<td>$91.30$</td>
</tr>
<tr>
<td>$B_{10.822}^5D_9$</td>
<td>$133.7$</td>
<td>$96.64$</td>
</tr>
</tbody>
</table>

The rotational energy levels of a symmetric top are given approximately by

$$F_v(J,K) = B_vJ(J + 1) + (A_v - B_v)K^2,$$

where $J$ and $K$ are quantum numbers for the total and z-component of the angular momentum, respectively, $A = \frac{h}{8\pi^2 c I_z}$, $B = \frac{h}{8\pi^2 c I_x}$, and $A_v$ and $B_v$ indicate average values of $A$ and $B$ in the $v$th vibrational state. The above formula is valid only for non-degenerate vibrational states; for degenerate vibrational states it is necessary to take account of the influence of Coriolis forces. The rotational energy levels are then approximately given by

$$F_v(J,K) = B_vJ(J + 1) + (A_v - B_v)K^2 \pm 2A_vJ_1K\sqrt{1 - J_1^2}, (0 \leq J_1 \leq 1)$$

where $J_1$, the Coriolis parameter, is a measure of the vibrational angular momentum about the symmetry axis.

The infrared absorption bands of a symmetric top molecule are conveniently classified as parallel or perpendicular. For a parallel band, the change in dipole moment during a vibration is parallel to the symmetry axis, while for a perpendicular band it is perpendicular to the symmetry axis. For pentaborane the $A_1$ vibrations give rise to parallel bands, and the $E$ vibrations yield perpendicular bands. The selection rules for parallel bands are as follows: $\Delta K = 0$ and $\Delta J = 0$ or $\pm 1$, if $K \neq 0$; $\Delta K = 0$ and $\Delta J = \pm 1$, if $K = 0$. For perpendicular bands $\Delta K = \pm 1$ and $\Delta J = 0$ or $\pm 1$.

A discussion of the band contours of unresolved parallel and perpendicular bands is given by Gerhard and Dennison. The parallel bands have P, Q, and R branches; the band shows a strong central maximum with a weaker maximum on each side. The separation of the maxima of the P and R branches can be calculated from the following formula of Gerhard and Dennison.

$$\Delta \nu = S(\beta) \left(1/\pi\right) \left(kT/I_x\right)^{\frac{1}{4}},$$

where

$$\log S(\beta) = \frac{.721}{(\beta + 4)^{1.13}},$$

and

$$\beta = (I_x/I_z) - 1.$$

For pentaborane $\beta = -0.3$, $S(\beta) = 1.46$, and the separation of the P and R branches is 28.7 cm.$^{-1}$ and 24.8 cm.$^{-1}$ for normal and deuterated pentaborane, respectively. The treatment of perpendicular bands is more complex. Gerhard and Dennison have plotted the band contours for various values of $\beta$ with the neglect of Coriolis interactions. They give a plot for $\beta = -(1/3)$ which is very close to the value for

---

pentaborane ($\beta = -0.3$). The band contour is very similar to that of a parallel band with a central maximum and a weaker maximum on both sides. The $P$ and $R$ spacing is slightly smaller than for a parallel band, however. In general, for larger values of $\beta$ (in particular for $\beta > 0$), perpendicular bands will consist of simply a central maximum without any maxima corresponding to $P$ and $R$ branches. However for pentaborane, this is not the case, and parallel and perpendicular bands are very similar. Therefore, the band contour is of little if any aid in distinguishing between $A_1$ and $E$ vibrational modes in pentaborane at least with the low resolution of a small prism spectrometer. Hrostowski and Pimentel$^4$ did not seem to recognize this fact in making their (partial) assignment of vibrational modes for $B_9^9$ and $B_9^{13}$. 

---

VI. NORMAL COORDINATE ANALYSIS

A. Introduction

If the force constants and geometry of a molecule are known, it is possible to calculate the vibrational frequencies, \( \nu_i \), of the molecule from the following matrix equation

\[
| g f - \lambda I | = 0 \quad \lambda_i = 4 \pi^2 \nu_i^2
\]

\( f \) is the square symmetric potential energy matrix with elements which are the force constants of the molecule. \( g \) is a square symmetric matrix which depends only on the geometry and masses of the atoms in the molecule. The \( g \) matrix was first used by Wilson\(^1\) and is the reciprocal of the kinetic energy or mass matrix. In the harmonic approximation, the internal potential and kinetic energy of the molecule can be expressed as quadratic forms,

\[
2V = \sum_{i,j} f_{ij} s_i s_j,
\]

\[
2T = \sum_{i,j} (g^{-1})_{ij} \dot{s}_i \dot{s}_j,
\]

where \( s_i \) is an internal coordinate and \( \dot{s}_i \) is the time derivative of the coordinate \( s_i \). The above expressions can be written in matrix form as

\[
2V = (s)'f(s)
\]

\[
2T = (\dot{s})'g^{-1}(\dot{s})
\]

where \( (s) \) and \( (\dot{s}) \) are column vectors of the internal coordinates, and

the prime indicates the transposed or row vectors. The secular equation arises because it is desired to transform the original internal coordinates to normal coordinates, q, for which the kinetic and potential energy are reduced to sums of squares, or diagonal form,

\[ 2V = (q)' \Lambda (q) \]
\[ 2T = (\dot{q})' (\dot{q}) \]

where \( \Lambda \) is a diagonal matrix with elements \( \lambda_i = 4\pi^2 \nu_i^2 \). Thus it is necessary to find a linear transformation matrix \( L^{-1} \) which transforms the internal coordinates to normal coordinates \( (q) = L^{-1}(s) \), or \( (s) = L(q) \). Substitution in the above equations yields as the required conditions on \( L \),

\[ 2V = (q)'L'fL(q) = (q)'\Lambda (q) \]
\[ 2T = (\dot{q})'L'^{-1}L(\dot{q}) = (\dot{q})' (\dot{q}) \]

or

\[ L'fL = \Lambda \]
\[ L'^{-1}L = E \]

where \( E \) is the unit matrix. Solving the second equation for \( L' \) and substituting in the first

\[ L' = L^{-1} \]
\[ L^{-1}gfL = \Lambda \]

and

\[ gfL = L \Lambda \]

The last equation shows that the columns of \( L \) are eigenvectors of the matrix \( gf \) with eigenvalues \( \lambda_i \). The permissible values of \( \lambda_i \) are the roots, \( \lambda \), of

\[ |gf - \lambda I| = 0 \]
which is the secular equation. The existence of a transformation \( L \)
which diagonalizes the potential and kinetic energy matrices is assured
by the fact that the potential and kinetic energy matrices are symmetric
and positive definite.

The order \( N \) of the above matrix equation is the same as the number
of internal degrees of freedom of the molecule, \( 3n - 5 \) for a linear
molecule, and \( 3n - 6 \) for a non-linear molecule, where \( n \) is the number of
atoms in the molecule. The secular equation is equivalent to a poly-
nomial of degree \( N \) in \( \lambda \). This equation has \( N \) roots, but all are not
necessarily distinct as there may be multiple roots, corresponding to
degenerate eigenvalues.

In the most general case it is necessary to solve an \( N \times N \)
secular equation for the vibrational frequencies of the molecule.
However, if the molecule has symmetry it is possible to reduce the order
of the equations. This requires taking linear combinations of the
original coordinates of the molecule in such a way that the new coor-
dinates, called symmetry coordinates, transform according to the
irreducible representations or symmetry species of the molecular point
group. The orthogonality theorem of group theory shows that there can
be no cross-terms in the kinetic or potential energies between coordinates
transforming according to different representations or different rows in
the same representations. The \( g, f, \) and \( gf \) matrices therefore have non-
vanishing elements only within sub-matrices or "blocks" on their principal
diagonals connecting coordinates belonging to the same row of the
same representation. Therefore the roots, \( \lambda \), may be obtained by
solving the secular equation of each block separately. Furthermore, blocks corresponding to different rows of the same representation are identical, and yield the same roots. Table 7 shows that in the case of pentaborane the original 36 degree secular equation can be factored into equations of degree 7, 2, 5, 4, and 9 (two identical equations) for the frequencies of \( A_1, A_2, B_1, B_2, \) and \( E \) modes, respectively. The roots of the second degree equation are readily expressed analytically, but numerical methods are preferable for equations of higher degree, and are in general unavoidable for equations of the fifth or higher degree.

Since the number of steps required to obtain the roots of an equation by numerical methods increases rapidly with the degree of the equation (or order of the matrices), this amounts to a great simplification.

In most cases it is the frequencies which are known and not the force constants. Ordinarily, it is not possible to solve the secular equation explicitly for the force constants in terms of the frequencies. The usual procedure has been one of trial and error, in which the roots calculated for estimated values of the force constants are compared with the observed frequencies, and the force constants then readjusted as indicated. If there are molecules which are similar in structure and bonding to the molecule of interest, it may be possible to transfer some force constants from these molecules to the one of interest. However, except in a few exceptional cases where data on a number of isotopic molecules are available, the number of force constants in the complete potential function is greater than the number of observed frequencies, and there is no guarantee that a set of force constants obtained by the
above procedure is unique. The best one can hope for is that the force constants obtained in this way are physically more reasonable than any other set which yields approximately the same frequencies. Frequently, also, the problem is simplified and made less indeterminate by assuming that many off-diagonal force constants in the complete potential function are unimportant. Although the results of such force constant determinations may depend on the judgment used in selecting the initial or trial values, it is possible to set up computational procedures which proceed automatically to the best set of force constants starting from a given initial set. In the present investigation a procedure of this type has been devised, and programmed for the IBM 704 computer, based on the minimization of the sum of the squares of the errors in the calculated frequencies. This minimization is accomplished by a method of steepest descents. This procedure, which appears to be the first application of the method of steepest descents to this problem, has proved to be entirely practicable and reduces greatly the labor of such calculations. This has the effect of enabling the investigator to devote more time to the effect of varying the initial or trial force constants inserted into the program.

In the following pages, the secular equation will be set up for pentaborane. As the first step a suitable set of internal coordinates will be defined. The s-vectors of Wilson, which depend only on the geometry of the molecule and the internal coordinates will then be calculated. Following this a transformation to symmetry coordinates and the corresponding symmetry S-vectors will be carried out. After eliminating certain redundant coordinates, the F matrix will be set up

2. Ibid.
In terms of force constants for the original internal coordinates. The G matrices are easily calculated from the S-vectors. The solution of the secular equation by the IBM 704 computer will be described and the results given.

B. **Definition of Coordinates**

One of the first steps in any normal coordinate or force constant analysis is to choose coordinates which uniquely describe the internal motions of the molecule. The potential and kinetic energy of the molecule are then expressible as quadratic forms in terms of these coordinates, in the harmonic approximation. The kinetic energy of the molecule is most simply expressed in terms of the Cartesian coordinates of each atom. The potential energy is however relatively complex when expressed in Cartesian coordinates, and is simplified by using internal coordinates, such as the distances between atoms and the angles between bonds (valence coordinates).

In the Wilson\textsuperscript{3} G-matrix method, the linear relationship existing between Cartesian and internal coordinates for the case of small displacements is expressed by certain vectors, the s-vectors. The elements of the G-matrix, which is the reciprocal of the kinetic energy matrix, are easily calculated from the s-vectors. The major advantage of the use of the G-matrix, rather than the kinetic energy matrix itself, is the fact that it is not necessary to consider explicitly the orthogonalization of internal coordinates to overall translation and rotation of the molecule.

---

3. Ibid.
For describing the potential energy, the changes in angles between bonds and the changes in the distance between bonded atoms are utilized in the so-called valence bond method. The change in distance between non-bonded atoms may also be important if appreciable forces exist between them and is taken account of in the Urey-Bradley method. Certain torsion coordinates or angles between two planes each defined by three atoms (or two adjoining bonds) may sometimes be useful. Examples of all these types will occur in the present calculation.

The final \( N \) coordinates used in treating the vibration problem must be a complete and independent set. However, in symmetrical molecules it is frequently convenient in the initial formulation of the problem to treat a set of valence or other coordinates which are equivalent by symmetry in an equivalent manner, rather than arbitrarily excluding one or more of the set. Otherwise the valence force constants obtained are likely to be falsified and the interaction constants abnormally large. This symmetrical procedure may result in the initial set of coordinates not being independent, and exceeding in number the coordinates in a complete set by \( r \), say. In this case there must exist \( r \) independent functional relations between the initial coordinates. In the limit of small vibrations, or to the first order in the coordinates, these relations are linear and have the form

\[
\sum_{s=1}^{\infty} a_{ij} s_j = 0; \quad i = 1, 2, \ldots, r;
\]

where the \( a_{ij} \) are constants dependent on the equilibrium configuration of the molecule. That is, the \( N + r \) initial coordinates in such a case are linearly dependent (to the first order). Conditions of this type are called redundancy conditions, and \( r \) of the coordinates are dependent or
redundant. It is essential that the \( r \) redundancy conditions themselves be linearly independent; the necessary and sufficient condition for this is that the rank of the \( r \) by \( N + r \) matrix \( (a_{ij}) \) equal \( r \), so that the order of its highest-order non-vanishing minor be \( r \). Formal methods for finding the redundancy conditions are known and will be described later. These conditions are then utilized at a convenient point in the calculation to eliminate the dependent coordinates.

Since pentaborane has the symmetry \( C_{4v} \), several sets of 4 or 8 equivalent valence or other internal coordinates occur in the molecule. These sets have been treated symmetrically, leading to the inclusion of an exceptional number of redundancy conditions. The coordinates chosen, and the number in each equivalent set are \( B_0 - H_0 \), 4 \( B - H' \), 4 \( B_0 - B \), 4 \( B - B \), and 8 \( B - H' \) bond lengths, and 4 \( B - B_0 - H \), 4 \( B - H' - B \), 4 \( B_0 - B - H \), 8 \( B_0 - B - H' \), 4 \( H' - B - H' \), and 8 \( H' - B - H \) angles (see Fig. 1). It should be clearly understood that the coordinates used in the treatment of the vibrations are the changes or increments of these bond lengths and angles from their equilibrium values. It will also be recalled that in the discussion of bonding in pentaborane in section B of chapter II it was concluded that there is probably little direct bonding between base boron atoms. Thus the coordinate \( B - B \) is probably to be regarded as of the Urey-Bradley type between non-bonded atoms.

After the calculation was well under way, it was found necessary to add a coordinate \( \theta \), defined as the change in the angle between the plane defined by atoms \( B_0 \), \( B \), and \( B \) and the plane defined by atoms \( B \), \( B \), and \( H' \), in order to treat satisfactorily the motion of the bridge hydrogens perpendicular to the plane of the bridge. One reason for this
is the relative insensitivity of the $B_0$-$B$-$H'$ angle to this bridge bending motion as a result of the equilibrium configuration of the molecule, with the result that the force constant calculated for the $B_0$-$B$-$H'$ angle is abnormally large when $\theta$ is omitted. Since the coordinate $\theta$ was added late in the calculation it does not appear in some of the tables which follow. With the inclusion of $\theta$ there are a total of 57 coordinates, of which only 36 can be independent. Hence, there must be 21 redundancy conditions. The notations and definitions of the coordinates used are given in Table 10.

**C. $s$-Vectors**

The most convenient way to express the relationship between the Cartesian coordinates, in terms of which the kinetic energy is simply expressed, and the internal coordinates in terms of which the potential energy is expressed, is through the $s$-vectors of Wilson, which will now be defined. If $s_i$ is an internal coordinate and $x_t$, $y_t$, $z_t$ the Cartesian displacements of the $t$th atom, then to the first order of infinitesimals,

$$s_i = \sum_{k=q}^r a_{it} x_t + b_{it} y_t + c_{it} z_t$$

where the coefficients $a_{it}$, $b_{it}$, and $c_{it}$ are determined by the geometry of the molecule. This expression may be written in vector notation as

$$s_i = \sum_{k=q}^r s_{it} \cdot \vec{r}_t,$$

where $\vec{r}_t$ is the vector displacement of the $t$th atom, with components $x_t$, $y_t$, and $z_t$, and $\vec{s}_{it}$ is a vector with components $a_{it}$, $b_{it}$, and $c_{it}$.

---

4. Ibid.
TABLE 10
COORDINATES OF PENTABORANE

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bending coordinates (increments of following bond angles):</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_1$</td>
<td>$B_0 - B_1 - H_1$</td>
</tr>
<tr>
<td>$\alpha_2$</td>
<td>$B_0 - B_2 - H_2$</td>
</tr>
<tr>
<td>$\alpha_3$</td>
<td>$B_0 - B_3 - H_3$</td>
</tr>
<tr>
<td>$\alpha_4$</td>
<td>$B_0 - B_4 - H_4$</td>
</tr>
<tr>
<td>$\beta_1$</td>
<td>$B_0 - B_1 - H_3$</td>
</tr>
<tr>
<td>$\beta_2$</td>
<td>$B_0 - B_1 - H_5$</td>
</tr>
<tr>
<td>$\beta_3$</td>
<td>$B_0 - B_2 - H_5$</td>
</tr>
<tr>
<td>$\beta_4$</td>
<td>$B_0 - B_2 - H_6$</td>
</tr>
<tr>
<td>$\beta_5$</td>
<td>$B_0 - B_3 - H_6$</td>
</tr>
<tr>
<td>$\beta_6$</td>
<td>$B_0 - B_3 - H_7$</td>
</tr>
<tr>
<td>$\beta_7$</td>
<td>$B_0 - B_4 - H_7$</td>
</tr>
<tr>
<td>$\beta_8$</td>
<td>$B_0 - B_4 - H_8$</td>
</tr>
</tbody>
</table>

Bridge-bending coordinates (increment of angle between planes defined by following triplets of atoms):

<table>
<thead>
<tr>
<th>Angle</th>
<th>Bending coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta_1$</td>
<td>$B_0$, $B_1$, $B_2$ and $B_1$, $B_2$, $H_5$</td>
</tr>
<tr>
<td>$\theta_2$</td>
<td>$B_0$, $B_2$, $B_3$ and $B_2$, $B_3$, $H_6$</td>
</tr>
<tr>
<td>$\theta_3$</td>
<td>$B_0$, $B_3$, $B_4$ and $B_3$, $B_4$, $H_7$</td>
</tr>
<tr>
<td>$\theta_4$</td>
<td>$B_0$, $B_4$, $B_1$ and $B_4$, $B_1$, $H_8$</td>
</tr>
</tbody>
</table>
A given vector $\mathbf{s}_{it}$ is associated with the $ith$ internal coordinate and with the $tth$ atom. The $s$-vector procedure has the advantage that it is not necessary to specify the Cartesian axes. From the preceding equation the following physical interpretation of the $s$-vectors can be given. If all atoms except the $tth$ atom are held stationary, then the direction of $\mathbf{s}_{it}$ is the direction in which displacement of atom $t$ produces the largest rate of increase in the coordinate $s_i$ per linear distance moved. The magnitude of $\mathbf{s}_{it}$ is equal to this maximum rate of increase of $s_i$. That is, $\mathbf{s}_{it}$ is the projection of the gradient of $r_i$ in the $3n$ dimensional space $x_1, y_1, \ldots, z_n$, on the subspace spanned by $x_t, y_t$, and $z_t$. It is simple to derive the $s$-vectors for various internal coordinates from this interpretation.\(^5\)

Consider a bond stretching coordinate $r_i$ between atoms 1 and 2. For convenience we define a unit vector $\mathbf{e}_{tt}$, which is directed from atom $t$ to atom $t'$. If atom 1 is stationary, it is apparent that the direction of motion of atom 2 which causes the greatest increase in the bond length is along the bond or the direction of $\mathbf{e}_{12}$. Furthermore, the magnitude of this increase in bond length is equal to the displacement. Thus $\mathbf{s}_{12} = \mathbf{e}_{12}$. It is also evident that $\mathbf{s}_{11} = -\mathbf{e}_{12}$.

The $s$-vectors for angle bending coordinates can be derived from similar considerations. Let $\phi_i$ be the angle formed at a central atom 3 by two bonds of length $r_{31}$ and $r_{32}$ to two terminal atoms 1 and 2, and $\mathbf{e}_{31}$ and $\mathbf{e}_{32}$ be unit vectors along these bonds. Then the $s$-vectors for

the internal coordinate defined as the infinitesimal increment in the bond angle $\phi$ are given by

\[ s_{11} = (\cos \phi_1 \bar{e}_{31} - \bar{e}_{32})/r_{31} \sin \phi_1 \]

\[ s_{12} = (\cos \phi_1 \bar{e}_{32} - \bar{e}_{31})/r_{32} \sin \phi_1 \]

\[ s_{13} = \left[(r_{31} - r_{32} \cos \phi_1)\bar{e}_{31} + (r_{32} - r_{31} \cos \phi_1)\bar{e}_{32}\right]/r_{31}r_{32} \sin \phi_1 \]

In the above formulas the $s$-vectors are expressed in terms of unit vectors along the bonds. In carrying out the calculation of the $G$ matrices it is convenient although not essential to express all $s$-vectors in terms of three mutually orthogonal unit vectors, $\bar{I}$, $\bar{J}$, and $\bar{K}$, directed along the $x$, $y$, and $z$ axes. The $x$-axis is arbitrarily taken as directed from boron atom $B_3$ to boron atom $B_1$, the $y$-axis from boron atom $B_4$ to boron atom $B_2$, and the $z$-axis perpendicular to the plane of $B_1$, $B_2$, $B_3$, and $B_4$ and directed towards boron atom $B_0$. Thus, the origin of the $x$, $y$, and $z$ axes lies at the center of the square formed by the four base boron atoms (see Fig. 1). Table 11 lists the $\bar{I}$, $\bar{J}$, and $\bar{K}$ components of unit vectors along the bonds. They were calculated using the bond lengths and angles previously specified in section A, chapter II, and Table 1. For the $m$ and $r$ coordinates, the vectors are directed from the boron atoms to the hydrogen atoms, and for the $l$ coordinates from the base boron to the apex boron atom. For the $d_1$ coordinates, the vectors are directed from the $i$th boron atom to the other boron atom (see Table 10).

It is now possible by using the unit vectors along the bonds and the above formulas for the $s$-vectors for bond stretching and angle bending coordinates to express the $s$-vectors for each atom and each coordinate in terms of $\bar{I}$, $\bar{J}$, and $\bar{K}$. In Table 12, the $s$-vectors for
<table>
<thead>
<tr>
<th></th>
<th>$\mathbf{i}$</th>
<th>$\mathbf{j}$</th>
<th>$\mathbf{k}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$l_1$</td>
<td>-.7546</td>
<td>.7546</td>
<td>.6562</td>
</tr>
<tr>
<td>$l_2$</td>
<td>.7546</td>
<td>-.7546</td>
<td>.6562</td>
</tr>
<tr>
<td>$l_3$</td>
<td>.7546</td>
<td>.7546</td>
<td>.6562</td>
</tr>
<tr>
<td>$l_4$</td>
<td>.7546</td>
<td>.7546</td>
<td>.6562</td>
</tr>
<tr>
<td>$r_0$</td>
<td>.9988</td>
<td>.9988</td>
<td>1.0000</td>
</tr>
<tr>
<td>$r_1$</td>
<td>.9988</td>
<td>.9988</td>
<td>.0493</td>
</tr>
<tr>
<td>$r_2$</td>
<td>.9988</td>
<td>.9988</td>
<td>.0493</td>
</tr>
<tr>
<td>$r_3$</td>
<td>.9988</td>
<td>.9988</td>
<td>.0493</td>
</tr>
<tr>
<td>$r_4$</td>
<td>.9988</td>
<td>.9988</td>
<td>.0493</td>
</tr>
<tr>
<td>$d_1$</td>
<td>.7071</td>
<td>.7071</td>
<td>.7071</td>
</tr>
<tr>
<td>$d_2$</td>
<td>.7071</td>
<td>.7071</td>
<td>.7071</td>
</tr>
<tr>
<td>$d_3$</td>
<td>.7071</td>
<td>.7071</td>
<td>.7071</td>
</tr>
<tr>
<td>$d_4$</td>
<td>.7071</td>
<td>.7071</td>
<td>.7071</td>
</tr>
<tr>
<td>$m_1$</td>
<td>-.2647</td>
<td>.6732</td>
<td>-.6854</td>
</tr>
<tr>
<td>$m_2$</td>
<td>.6732</td>
<td>-.2647</td>
<td>-.6854</td>
</tr>
<tr>
<td>$m_3$</td>
<td>-.2647</td>
<td>.6732</td>
<td>-.6854</td>
</tr>
<tr>
<td>$m_4$</td>
<td>.2647</td>
<td>-.6732</td>
<td>-.6854</td>
</tr>
<tr>
<td>$m_5$</td>
<td>.2647</td>
<td>-.6732</td>
<td>-.6854</td>
</tr>
<tr>
<td>$m_6$</td>
<td>-.2647</td>
<td>.6732</td>
<td>-.6854</td>
</tr>
<tr>
<td>$m_7$</td>
<td>.6732</td>
<td>.2647</td>
<td>-.6854</td>
</tr>
<tr>
<td>$m_8$</td>
<td>.6732</td>
<td>.2647</td>
<td>-.6854</td>
</tr>
<tr>
<td>$m_9$</td>
<td>-.2647</td>
<td>.6732</td>
<td>-.6854</td>
</tr>
<tr>
<td>$m_{10}$</td>
<td>-.6732</td>
<td>.2647</td>
<td>-.6854</td>
</tr>
<tr>
<td>Atom</td>
<td>Coordinate</td>
<td>( \mathbf{I} )</td>
<td>( \mathbf{J} )</td>
</tr>
<tr>
<td>------</td>
<td>-----------</td>
<td>-----------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>( B_0 )</td>
<td>( l_1 )</td>
<td>-.7546</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( r_0 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \alpha_1 )</td>
<td>-.3891</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \beta_1 )</td>
<td>.2776</td>
<td>.4152</td>
</tr>
<tr>
<td></td>
<td>( \omega_1 )</td>
<td>1.2087</td>
<td></td>
</tr>
<tr>
<td>( B_1 )</td>
<td>( l_1 )</td>
<td>.7546</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( r_1 )</td>
<td>-.9938</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( m_1 )</td>
<td>.2647</td>
<td>.6732</td>
</tr>
<tr>
<td></td>
<td>( \alpha_1 )</td>
<td>.3437</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \beta_1 )</td>
<td>-.9056</td>
<td>-.5450</td>
</tr>
<tr>
<td></td>
<td>( \gamma_1 )</td>
<td>-.3618</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \Delta_1 )</td>
<td>.7424</td>
<td>-.7393</td>
</tr>
<tr>
<td></td>
<td>( \epsilon_1 )</td>
<td>.5274</td>
<td>-.2533</td>
</tr>
<tr>
<td></td>
<td>( d_1 )</td>
<td>.7071</td>
<td>-.7071</td>
</tr>
<tr>
<td></td>
<td>( \omega_1 )</td>
<td>-.3890</td>
<td></td>
</tr>
<tr>
<td>( H_0 )</td>
<td>( r_0 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \omega_1 )</td>
<td>-.3197</td>
<td></td>
</tr>
<tr>
<td>( H_1 )</td>
<td>( r_1 )</td>
<td>.9938</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \alpha_1 )</td>
<td>.0404</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \Delta_1 )</td>
<td>-.0285</td>
<td>.5824</td>
</tr>
<tr>
<td>( H_5 )</td>
<td>( m_2 )</td>
<td>-.2647</td>
<td>.6782</td>
</tr>
<tr>
<td></td>
<td>( \gamma_1 )</td>
<td>.1909</td>
<td>.5443</td>
</tr>
<tr>
<td></td>
<td>( \beta_2 )</td>
<td>.6280</td>
<td>-.1298</td>
</tr>
<tr>
<td></td>
<td>( \Delta_2 )</td>
<td>-.7139</td>
<td>-.1569</td>
</tr>
<tr>
<td></td>
<td>( \epsilon_1 )</td>
<td>-.2741</td>
<td>-.2741</td>
</tr>
</tbody>
</table>
pentaborane are resolved in this way. They are listed first by atoms and then by coordinates. In computing the s-vectors all bond lengths have been expressed in Angstrom units. Because of the symmetry of pentaborane, it is sufficient to list only one atom of each equivalent set of atoms. Under each atom it is sufficient to list only one coordinate of each set of coordinates equivalent under the subgroup of the molecular point group leaving that atom invariant. Of the remaining s-vectors many may vanish; thus, \( \bar{s}_i \) vanishes if the \( i \)th coordinate is unaffected by displacement of the \( \ell \)th atom. From the s-vectors listed all of the remaining non-vanishing s-vectors of the molecule may be obtained by applying the symmetry operations of the molecular point group. As an example consider the vector \( s_{m_2B_1} \) for the coordinate \( m_2 \) and atom \( B_1 \). \[ s_{m_2B_1} = 0.2647 \bar{T} - 0.6732 \bar{J} + 0.6854 \bar{k}. \]

By reflection in the plane of symmetry \( \sigma_v \), passing through atoms \( B_1 \) and \( B_2 \), \( m_2 \) is transformed into \( m_1 \), \( B_1 \) into itself, \( \bar{T} \) into \( \bar{I} \), \( \bar{J} \) into \( -\bar{J} \), and \( \bar{k} \) into \( \bar{k} \). Thus \[ \sigma_v s_{m_2B_1} = s_{m_1B_1} = 0.2647 \bar{T} + 0.6732 \bar{J} + 0.6854 \bar{k}. \]

For a rotation of 90° about the \( z \)-axis \( m_2 \) is transformed into \( m_4 \), \( B_1 \) into \( B_2 \), \( \bar{T} \) into \( \bar{J} \), \( \bar{J} \) into \( -\bar{I} \), and \( \bar{k} \) into \( \bar{k} \). Thus, \[ C_4^1 s_{m_2B_1} = s_{m_4B_2} = 0.6732 \bar{T} + 0.2647 \bar{J} + 0.6854 \bar{k}. \]

### D. Symmetry Coordinates

In order to factor the secular equation, it is necessary to take linear combinations of the original internal coordinates which transform under symmetry operations of the molecule according to one of the irreducible representations or symmetry species of the molecular point group. It is sufficient to form symmetry coordinates from equivalent
sets of internal coordinates. In general each set of equivalent coordinates forms the basis for a reducible representation of the molecular point group. The number of times a given irreducible representation occurs in the reducible representation may be obtained prior to the actual construction of the symmetry coordinates by the familiar method of reduction based on the orthogonality theorem for irreducible representations. There are several methods of finding the coefficients of the transformation from internal to symmetry coordinates. The following formula due originally to Wigner may be used to construct non-degenerate symmetry coordinates

\[ S_Y^* = N \sum_R \chi^Y(R) R s_1 \]

where \( S_Y^* \) is a symmetry coordinate belonging to the \( Y \) irreducible representation of the molecular point group, \( \chi^Y(R) \) is the character of the representation for the symmetry operation \( R \), \( s_1 \) is an internal coordinate or a linear combination of internal coordinates, and \( R s_1 \) is the coordinate or linear combination of coordinates into which \( s_1 \) is transformed by the symmetry operation \( R \). \( N \) is a normalizing factor chosen to maintain the orthogonality of the overall transformation from internal to symmetry coordinates. It is readily shown by means of the orthogonality theorem for group characters that \( S_Y^* \) transforms according

6. Ibid.
to the $r$th irreducible representation if it does not vanish identically.

If the preceding formula is applied to a degenerate irreducible representation $\mathbf{V}$, the coordinates $\mathbf{S}^V$ obtained will transform according to some one row of the representation if it does not vanish. For many applications, including the calculation of the reciprocal kinetic energy and potential energy matrices, it is sufficient to have a coordinate transforming according to one row of the representation, for reasons explained subsequently. If the "partners" of $\mathbf{S}^V$ transforming according to the other rows of the representation are required they can be obtained by varying $s_1$ until the required number of non-vanishing linearly-independent coordinates are obtained. A given set of equivalent internal coordinates may contribute more than one set of symmetry coordinates to a degenerate representation (but not a greater number than the dimension of the representation). If this occurs it is possible to form linear combinations of the original internal coordinates which split into two or more subsets such that each subset contributes not more than one symmetry coordinate to the representation. These subsets can then be treated separately by the preceding formula. In group theoretical terms this is equivalent to first carrying out a partial reduction of the reducible representation furnished by the coordinates within conjugate site or subgroups of the point group. The coordinates in each subset transform according to the same irreducible representation of the conjugate site groups. Another problem which may arise with degenerate coordinates is that of proper "orientation." This is of importance only when two or more sets of symmetry coordinates belonging to the same degenerate representation occur; these may arise
from a single set of equivalent coordinates as just discussed or from two different types of internal coordinates. Since irreducible matrix representations of a group of dimension greater than one are indeterminate to the extent of an arbitrary unitary transformation two \( S^Y \)'s calculated from the preceding formulas may transform according to particular rows of representations which are equivalent but not identical. In general the internal coordinate \( s_1 \) in one case or the other must be varied so that the two \( S^Y \)'s transform according to the same rows of identical representation matrices, if full factoring of the secular equation is to be obtained.

As an example of the above method, the symmetry coordinates formed from the \( r \) internal coordinates will be calculated. \( r_1 \) is taken as the generating coordinate. By applying the symmetry operations, \( E, C_4, C_2, \sigma_v, \sigma_d \), and \( \sigma_d' \) in that order to \( r_1 \), we obtain

\[
S_A = N(1r_1 + 1r_2 + 1r_3 + 1r_4 + 1r_1 + 1r_3 + 1r_2 + 1r_4) = \frac{1}{2}(r_1 + r_2 + r_3 + r_4)
\]

\[
S_B = N(1r_1 - 1r_2 - 1r_3 - 1r_4 + 1r_1 + 1r_3 - 1r_2 - 1r_4) = \frac{1}{2}(r_1 - r_2 + r_3 - r_4)
\]

\[
S_E = N(2r_1 + 0r_2 - 2r_3 + 0r_4 + 0r_1 + 0r_3 + 0r_2 + 0r_4) = \sqrt{2}(r_1 - r_3)
\]

A similar procedure is followed with the \( \beta \) internal coordinates, for example, after first forming linear combinations of the two \( \beta \)'s adjacent to each base boron which transform according to the symmetric and antisymmetric representations of the site group \( C_n \). The symmetry coordinates are given in Table 13 (see Table 10 for the definitions of internal coordinates).
TABLE 13
SYMMETRY COORDINATES

$A_1 : L = \frac{1}{2}(l_1 + l_2 + l_3 + l_4)$

$R = \frac{1}{2}(r_1 + r_2 + r_3 + r_4)$

$M = \frac{1}{\sqrt{8}}(m_1 + m_2 + m_3 + m_4 + m_5 + m_6 + m_7 + m_8)$

$A = \frac{1}{2}(\alpha_1 + \alpha_2 + \alpha_3 + \alpha_4)$

$B = \frac{1}{\sqrt{8}}(\beta_1 + \beta_2 + \beta_3 + \beta_4 + \beta_5 + \beta_6 + \beta_7 + \beta_8)$

$\Gamma = \frac{1}{2}(\gamma_1 + \gamma_2 + \gamma_3 + \gamma_4)$

$\Delta = \frac{1}{\sqrt{8}}(\Delta_1 + \Delta_2 + \Delta_3 + \Delta_4 + \Delta_5 + \Delta_6 + \Delta_7 + \Delta_8)$

$\Xi = \frac{1}{2}(\varepsilon_1 + \varepsilon_2 + \varepsilon_3 + \varepsilon_4)$

$\mathcal{W} = \frac{1}{2}(w_1 + w_2 + w_3 + w_4)$

$D = \frac{1}{2}(d_1 + d_2 + d_3 + d_4)$

$R_0 = r_0$

$A_2 : K = -\frac{1}{\sqrt{8}}(m_2 + m_4 + m_6 + m_8 - m_1 - m_3 - m_5 - m_7)$

$B = \frac{1}{\sqrt{3}}(\beta_1 + \beta_3 + \beta_5 + \beta_7 - \beta_2 - \beta_4 - \beta_6 - \beta_8)$

$\Delta = \frac{1}{\sqrt{8}}(\Delta_1 + \Delta_3 + \Delta_5 + \Delta_7 - \Delta_2 - \Delta_4 - \Delta_6 - \Delta_8)$

$B_1 : L = \frac{1}{2}(l_1 - l_2 + l_3 - l_4)$

$R = \frac{1}{2}(r_1 - r_2 + r_3 - r_4)$

$M = \frac{1}{\sqrt{8}}(m_2 - m_3 - m_4 + m_5 + m_6 - m_7 - m_8 + m_1)$

$A = \frac{1}{2}(\alpha_1 - \alpha_2 + \alpha_3 - \alpha_4)$

$B = \frac{1}{\sqrt{8}}(\beta_1 + \beta_2 - \beta_3 - \beta_4 + \beta_5 + \beta_6 - \beta_7 - \beta_8)$
\begin{align*}
\Gamma &= \frac{1}{\sqrt{8}} (\gamma_1 - \gamma_2 + \gamma_3 - \gamma_4) \\
\Delta &= \frac{1}{\sqrt{8}} (\Delta_1 + \Delta_2 - \Delta_3 - \Delta_4 + \Delta_5 + \Delta_6 - \Delta_7 - \Delta_8) \\
\omega &= \frac{1}{\sqrt{8}} (w_1 - w_2 + w_3 - w_4).
\end{align*}

\begin{align*}
B_2 : M &= \frac{1}{\sqrt{8}} (-m_2 + m_3 - m_4 + m_5 - m_6 - m_7 + m_8 + m_1) \\
B &= \frac{1}{\sqrt{8}} (\beta_1 - \beta_2 - \beta_3 + \beta_4 + \beta_5 - \beta_6 - \beta_7 + \beta_8) \\
\Delta &= \frac{1}{\sqrt{8}} (\Delta_1 - \Delta_2 - \Delta_3 + \Delta_4 + \Delta_5 - \Delta_6 - \Delta_7 + \Delta_8) \\
E &= \frac{1}{4} (\varepsilon_1 - \varepsilon_2 + \varepsilon_3 - \varepsilon_4) \\
D &= \frac{1}{4} (d_1 - d_2 + d_3 - d_4).
\end{align*}

\begin{align*}
B &= \sqrt{F} (1_1 - 1_3) \\
R &= \sqrt{F} (r_1 - r_3) \\
A &= \sqrt{F} (\alpha_1 - \alpha_3) \\
\Gamma &= \sqrt{F} (\gamma_1 - \gamma_3) \\
E &= \frac{1}{4} (\varepsilon_1 - \varepsilon_2 - \varepsilon_3 + \varepsilon_4) \\
D &= \frac{1}{4} (d_1 - d_2 - d_3 + d_4) \\
\omega &= \sqrt{F} (w_1 - w_3) \\
M &= \frac{1}{4} (m_1 + m_2 - m_5 - m_6) \\
M' &= \frac{1}{4} (m_3 - m_4 - m_7 + m_8) \\
B' &= \frac{1}{4} (\beta_1 + \beta_2 - \beta_5 - \beta_6) \\
B'' &= \frac{1}{4} (\beta_3 - \beta_4 + \beta_7 + \beta_8) \\
\Delta' &= \frac{1}{4} (\Delta_1 + \Delta_2 - \Delta_5 - \Delta_6) \\
\Delta'' &= \frac{1}{4} (\Delta_3 - \Delta_4 - \Delta_7 + \Delta_8).
\end{align*}
E. S-Vectors for Symmetry Coordinates

S-vectors may be defined for symmetry coordinates in a manner entirely analogous to the definition of s-vectors for internal coordinates in section C. That is, the value of the symmetry coordinate $S_k$ may be expressed as

$$S_k = \sum_t \bar{S}_{kt} \mathbf{r}_t,$$

where $\mathbf{r}_t$ is the vector displacement of the $t$th atom. If the symmetry coordinate $S_k$ is related to the internal coordinates by

$$S_k = \sum_i U_{ki} s_i,$$

substitution of the expression for $s_i$ in terms of the s-vectors and comparison with the preceding equation shows that

$$\bar{S}_{kt} = \sum_i U_{ki} \bar{s}_{it}.$$

That is, the vectors $\bar{S}_{kt}$ are obtained by applying to the vectors $\bar{s}_{it}$ the same linear (orthogonal) transformation which relates the symmetry coordinates $S_k$ to the internal coordinates $s_i$. Since the $U_{ki}$ and the $\bar{s}_{it}$ are known, it is easy to calculate the $\bar{S}_{kt}$.

The S-vectors for the symmetry coordinates are given in Table 14, where they are resolved in terms of the mutually orthogonal system of unit vectors defined in section C. The unit of length is the Angstrom. As was true in the case of the s-vectors, it is not necessary to list the S-vectors for each atom. For non-degenerate species, it is sufficient to give the vector for one atom of each equivalent set of atoms. The S-vectors for the other atoms can then be obtained by applying the symmetry operations, recalling that a non-degenerate symmetry coordinate transforms into itself or its negative under all operations of the group.
### Table 14: S-Vectors

<table>
<thead>
<tr>
<th>Atom</th>
<th>Coordinate</th>
<th>Vector Components</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( \mathbf{I} )</td>
</tr>
<tr>
<td>( H )</td>
<td>( R )</td>
<td>1.0000</td>
</tr>
<tr>
<td>( B^0 )</td>
<td>( L^0 )</td>
<td>( A )</td>
</tr>
<tr>
<td>( H )</td>
<td>( \Delta )</td>
<td>( \Gamma )</td>
</tr>
<tr>
<td>( B_1 )</td>
<td>( D )</td>
<td>.7071</td>
</tr>
<tr>
<td>( H_0 )</td>
<td>( R^1 )</td>
<td>( A^1 )</td>
</tr>
<tr>
<td>( H_5 )</td>
<td>( M )</td>
<td>( B )</td>
</tr>
<tr>
<td>( A_2 ) Symmetry Coordinates</td>
<td>( B_1 )</td>
<td>( M )</td>
</tr>
<tr>
<td>( H_1^{-} )</td>
<td>( \Delta )</td>
<td>( \Delta )</td>
</tr>
<tr>
<td>( H_5^{-} )</td>
<td>( M )</td>
<td>( B )</td>
</tr>
</tbody>
</table>

Note: The table lists the coordinates and vector components for various atoms, including \( H \), \( B \), \( A \), etc., with specific values for \( \mathbf{I} \), \( \mathbf{J} \), and \( \mathbf{K} \) components.
TABLE 14 (contd.)

<table>
<thead>
<tr>
<th>Atom</th>
<th>Coordinate</th>
<th>$\bar{1}$</th>
<th>$\bar{j}$</th>
<th>$\bar{k}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\bar{I}$</td>
<td>$\bar{J}$</td>
<td>$\bar{K}$</td>
</tr>
<tr>
<td>$B_1$ Symmetry Coordinates</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B_1$</td>
<td>L</td>
<td>.3773</td>
<td></td>
<td>-.3281</td>
</tr>
<tr>
<td></td>
<td>R</td>
<td>-.4994</td>
<td></td>
<td>-.0247</td>
</tr>
<tr>
<td></td>
<td>M</td>
<td>.1872</td>
<td></td>
<td>.4846</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>.1744</td>
<td></td>
<td>.6332</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>-.6403</td>
<td></td>
<td>.0366</td>
</tr>
<tr>
<td></td>
<td>$\Gamma$</td>
<td>-.1809</td>
<td></td>
<td>-.4686</td>
</tr>
<tr>
<td></td>
<td>$\Delta$</td>
<td>.5250</td>
<td></td>
<td>-.4924</td>
</tr>
<tr>
<td></td>
<td>W</td>
<td>-.1945</td>
<td></td>
<td>.2237</td>
</tr>
<tr>
<td>$H_1$</td>
<td>R</td>
<td>.4994</td>
<td>.0247</td>
<td></td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>.0202</td>
<td>-.4094</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\Delta$</td>
<td>-.0202</td>
<td>.4073</td>
<td></td>
</tr>
<tr>
<td>$H_5$</td>
<td>M</td>
<td>-.3334</td>
<td>.3334</td>
<td></td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>.2679</td>
<td>-.2679</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\Gamma$</td>
<td>-.1817</td>
<td>.1817</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\Delta$</td>
<td>-.1969</td>
<td>.1969</td>
<td></td>
</tr>
</tbody>
</table>

$B_2$ Symmetry Coordinates

| $B_1$ | D          | -.7071    |           |           |
|       | M          | .4796     |           |           |
|       | B          | -.3854    |           |           |
|       | $\Delta$   | -.5228    |           |           |
|       | E          | -.2533    |           |           |
| $H_1$ | $\Delta$   | .4118     |           |           |
| $H_5$ | M          | -.1462    | -.1462    | .4846     |
|       | B          | -.1761    | -.1761    | .2623     |
|       | $\Delta$   | .3079     | .3079     | -.0851    |
|       | E          | -.1371    | -.1371    | .4543     |
### Table 14 (contd.)

<table>
<thead>
<tr>
<th>Atom</th>
<th>Coordinate</th>
<th>Vector Components</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( \bar{i} )</td>
</tr>
<tr>
<td><strong>E Symmetry Coordinates</strong></td>
<td></td>
<td>( \bar{l} )</td>
</tr>
<tr>
<td>( B_0 )</td>
<td>L</td>
<td>-1.0672</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>-.5503</td>
</tr>
<tr>
<td></td>
<td>B'</td>
<td>.5552</td>
</tr>
<tr>
<td></td>
<td>B''</td>
<td>-.8304</td>
</tr>
<tr>
<td></td>
<td>W</td>
<td>1.7094</td>
</tr>
<tr>
<td>( B_1 )</td>
<td>D</td>
<td>.7071</td>
</tr>
<tr>
<td></td>
<td>L</td>
<td>.5336</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>-.7063</td>
</tr>
<tr>
<td></td>
<td>B'</td>
<td>.2466</td>
</tr>
<tr>
<td></td>
<td>B''</td>
<td>-.2558</td>
</tr>
<tr>
<td></td>
<td>E</td>
<td>.5274</td>
</tr>
<tr>
<td></td>
<td>M'</td>
<td>.5274</td>
</tr>
<tr>
<td></td>
<td>M''</td>
<td>-.2647</td>
</tr>
<tr>
<td></td>
<td>W</td>
<td>-.9056</td>
</tr>
<tr>
<td></td>
<td>( A' )</td>
<td>.7424</td>
</tr>
<tr>
<td></td>
<td>( A'' )</td>
<td>-.2751</td>
</tr>
<tr>
<td>( B_2 )</td>
<td>D</td>
<td>-.7071</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>.2533</td>
</tr>
<tr>
<td></td>
<td>M'</td>
<td>.6782</td>
</tr>
<tr>
<td></td>
<td>M''</td>
<td>.5450</td>
</tr>
<tr>
<td></td>
<td>( \Delta' )</td>
<td>1.7063</td>
</tr>
<tr>
<td></td>
<td>( \Delta'' )</td>
<td>.7393</td>
</tr>
<tr>
<td>( H_1 )</td>
<td>R</td>
<td>.0286</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>-.0285</td>
</tr>
<tr>
<td></td>
<td>( \Delta' )</td>
<td>-.5824</td>
</tr>
<tr>
<td></td>
<td>( \Delta'' )</td>
<td>.1279</td>
</tr>
<tr>
<td>( H_2 )</td>
<td>( \Gamma )</td>
<td>-.1371</td>
</tr>
<tr>
<td></td>
<td>E</td>
<td>-.1324</td>
</tr>
<tr>
<td></td>
<td>M'</td>
<td>.3391</td>
</tr>
<tr>
<td></td>
<td>M''</td>
<td>-.3140</td>
</tr>
<tr>
<td></td>
<td>B'</td>
<td>-.0649</td>
</tr>
<tr>
<td></td>
<td>B''</td>
<td>-.3570</td>
</tr>
<tr>
<td></td>
<td>( \Delta' )</td>
<td>-.0785</td>
</tr>
<tr>
<td>( H_0 )</td>
<td>( \Gamma )</td>
<td>.11592</td>
</tr>
</tbody>
</table>
For degenerate coordinates, the preceding is not valid since the symmetry coordinate does not necessarily transform into itself under the symmetry operations. However, for pentaborane it is sufficient to list the $S$-vectors for two adjacent atoms of each equivalent set of four atoms. The $S$-vectors for the other two atoms can be obtained by applying the symmetry operation $C_2$ which changes the sign of the degenerate symmetry coordinate.

F. Force Constant Matrices

The force constants for the original internal coordinates are the coefficients in the quadratic form for twice the potential energy,

$$2V = \sum_{i,j} f_{ij} s_i s_j$$

In matrix form this becomes

$$2V = (s)' f (s),$$

where $(s)$ is a column matrix and the prime indicates its transpose (a row matrix). In the general quadratic potential function there is a force constant for every combination $s_i s_j$. Since $f_{ij} = f_{ji}$, there are for $N$ coordinates $N(N-1)/2$ force constants of which $N$ are principal or diagonal force constants $f_{ii}$ and the remainder off-diagonal constants. Some of these constants may be equal as a result of molecular symmetry; others may be approximately equal because they refer to similar localized bonds.

In order to factor the secular equation, the original coordinates were transformed to symmetry coordinates. In matrix terminology this transformation may be written $(S) = U(s)$, where $U$ is the square transformation matrix, and $(S)$ is the column matrix of the symmetry
coordinates. \( U \) is assumed to be non-singular; thus \( (s) = U^{-1}(S) \). The quadratic forms for potential and kinetic energy may be transformed to symmetry coordinates by substitution of this expression in the preceding equations, yielding
\[
2V = (S)^\dagger (U^{-1})^\dagger f U^{-1}(S),
\]
\[
2T = (S)^\dagger (U^{-1})^\dagger g^{-1} U^{-1}(S).
\]
Define
\[
F = (U^{-1})^\dagger f U^{-1},
\]
and
\[
G^{-1} = (U^{-1})^\dagger g^{-1} U^{-1}
\]
or
\[
G = U g U'.
\]
Then
\[
2V = (S)^\dagger F(S),
\]
\[
2T = (S)^\dagger G^{-1}(S).
\]

Thus \( F \) is the force constant matrix and \( G^{-1} \) the kinetic energy matrix for the symmetry coordinates. If \( U \) is an orthogonal matrix, i.e., \( U^t = U^{-1} \), as is usually the case, then
\[
F = U f U'.
\]

The force constant \( F_{ij} \) connecting symmetry coordinates \( S_i \) and \( S_j \) is necessarily zero if \( S_i \) and \( S_j \) transform according to different irreducible representations. The proof of this for non-degenerate symmetry coordinates is simple. The potential energy is given by
\[
2V = \sum_{i,j} F_{ij} S_i S_j.
\]
If \( S_i \) and \( S_j \) belong to different representations, there exists at least one symmetry operation \( R \), which changes the sign of either \( S_i \) or \( S_j \), while leaving the other coordinate unchanged. Thus
\[
RF_{ij} S_i S_j = -F_{ij} S_i S_j.
\]
But the potential energy must be invariant to all symmetry operations of the molecular point group; hence, \( F_{ij} = 0 \). The proof for degenerate coordinates or representations is based on the
orthogonality theorem for group representations. In this case not only does $F_{ij}$ vanish if $S_i$ and $S_j$ belong to different representations, but also if $S_i$ and $S_j$ belong to different rows of the same representation. As discussed in section D the latter condition requires that the representation matrices for different types of coordinates belonging to the same irreducible representation be identical in form, corresponding to similar orientation of degenerate coordinates. As a result of the preceding theorems, it is clear that if the symmetry coordinates in the column matrix $\mathbf{S}$ are arranged in order according to irreducible representations, and within each representation according to the row of the representation, the $F$ matrix with rows and columns rearranged accordingly will have non-vanishing elements only within "blocks" or square sub-matrices on the principal diagonal corresponding to the same row of the same representation. The number of blocks for each representation is equal to the dimension or degeneracy of the representation. However, it may also be proved by the orthogonality theorem that these blocks or sub-matrices will be identical if the representation matrices are taken in identical form for all coordinates belonging to a given degenerate representation. That is, if $S_i$ and $S_j$ are symmetry coordinates formed from equivalent internal coordinates and transforming according to the $i$th and $j$th rows of a given irreducible representation, and $S_i'$ and $S_j'$ are symmetry coordinates having the same transformation

properties but formed from a distinct set of equivalent internal
coordinates, not only is \( F_{ij} = F_{ji} = 0 \), corresponding to the vanishing
of force constants for different rows, but also \( F_{ii} = F_{jj} \). Thus, for
pentaborane, with symmetry \( C_{4v} \), \( F \) has the form

\[
F = \begin{pmatrix}
F_{A_1} & 0 & 0 & 0 & 0 & 0 \\
0 & F_{A_2} & 0 & 0 & 0 & 0 \\
0 & 0 & F_{B_1} & 0 & 0 & 0 \\
0 & 0 & 0 & F_{B_2} & 0 & 0 \\
0 & 0 & 0 & 0 & F_{E} & 0 \\
0 & 0 & 0 & 0 & 0 & F_{E}
\end{pmatrix}
\]

where \( F_{A_1}, F_{A_2}, F_{B_1}, F_{B_2}, \) and \( F_{E} \) are the force constant matrices for
symmetry coordinates belonging to representations \( A_1, A_2, B_1, B_2, \) and \( E \)
and the two \( F_{E} \) are identical. Entirely equivalent results are obtained
for the matrix \( G^{-1} \) since the analysis depends only on the transforma-
tion properties of quadratic forms. Thus \( G^{-1} \) has an equivalent block
form, and therefore also \( G \), with \( (G_{A_1})^{-1} = (G^{-1})_{A_1} \), etc. The secular
equation therefore reduces to

\[
\begin{align*}
|GF - \lambda I| & = 0 \\
|G_{A_1}F_{A_1} - \lambda I| & = 0 \\
& \vdots \\
|G_{E}F_{E} - \lambda I| & = 0 
\end{align*}
\]

Thus, the secular equation may be formulated and solved for each
symmetry species separately.

The actual calculation of the symmetry force constant matrices
is not as difficult as it may appear. The number of valence coordinates
chosen to describe the configuration of pentaborane and defined in Table 10 is 57. The dimensions of the matrices \( f \), \( F \), and \( U \) are therefore \( 57 \times 57 \). This is greater than the number of internal degrees of freedom because of the redundancies which have not yet been removed. The multiplication of matrices of this size is a formidable task. However the symmetry coordinates are formed from linear combinations of internal coordinates which belong to the same equivalent set. Therefore, if the original internal coordinates are arranged with all members of equivalent sets together, the elements of the \( U \) matrix will vanish except within blocks along the diagonal. Furthermore, as discussed by Kilpatrick,\(^{11}\) the blocks of the \( U \) matrix of a given dimension can usually be assigned the same orthogonal form, although proper "orientation" of degenerate coordinates may require different forms. Since for pentaborane the largest number of coordinates in an equivalent set is eight, this will be the dimension of the largest blocks along the diagonal. In view of these simplifications the \( F \) matrix is conveniently obtained by multiplying the matrices in partitioned form, with each block playing the role of an element in ordinary matrix multiplication.

Before proceeding with the calculation of the \( F \) matrix, it is convenient to adopt a more concise notation for the force constants. Sets of internal coordinates which have exactly the same symmetry properties will be grouped together. \( l, r, \alpha, \gamma \), and \( w \) will be called class I coordinates; \( \varepsilon \) and \( d \), class II; \( m, \beta, \) and \( \Delta \), class III; and \( r_0 \), class IV. All class I coordinates may be associated with a

\(^{11}\) Kilpatrick, op. cit.
particular base boron atom or edge of the pyramid, and class II coordinates with a specific hydrogen bridge or the corresponding pair of base boron atoms. Class III coordinates are each associated with a particular base boron and one of the two bridge hydrogens adjacent to it. Each set of Class I or class II contains 4 equivalent internal coordinates, while III has 8 equivalent coordinates in each set. \( r_0 \) is an unique coordinate and is already an \( A_1 \) symmetry coordinate.

In Table 15, the valence force constant matrices for pentaborane are given in terms of general coordinates \( v \) and \( v' \). To obtain that part of the partitioned force constant matrix corresponding to two particular sets of equivalent coordinates, for example \( \alpha \) and \( \beta \), it is sufficient to substitute \( \alpha \) for \( v \) and \( \beta \) for \( v' \) in the force constant matrix in this table for the classes of \( \alpha \) and \( \beta \). The expression for that part of the potential energy involving terms \( vv' \) is also given in the table. The general rule, that two force constants \( f_{ij} \) and \( f_{kl} \) are equal if there exists some symmetry operation which transforms \( s_is_j \) into \( s_ks_l \), has been used in setting up the valence force constant matrices. The symbols used in the force constant matrices are completely defined by their position in the force constant matrix.

In Table 16 the matrices \( U \) used for the transformations from valence to symmetry coordinates are given. The methods of finding such transformations has already been discussed. It should be noted that the transformation matrices are orthogonal. Different matrices are required for class I and II coordinates to give proper "orientation" of the


**TABLE 15**

**DEFINITION OF VALENCE FORCE CONSTANTS**

---

**Class I - Class I Coordinates**

\[ v = 1, r, \alpha, \gamma, \text{ or } w \]

\[ v' = 1, r, \alpha, \gamma, \text{ or } w \]

\[
\begin{pmatrix}
  v_1' \\
  v_2 \\
  v_3 \\
  v_4
\end{pmatrix}
= 
\begin{pmatrix}
  k & h & n & h \\
  n & k & h & n \\
  n & h & k & h \\
  h & n & h & k \\
\end{pmatrix}
\begin{pmatrix}
  v_1' \\
  v_2' \\
  v_3' \\
  v_4'
\end{pmatrix}
\]

---

**Class II - Class II Coordinates**

\[ v = \epsilon \text{ or } d \]

\[ v' = \epsilon \text{ or } d \]

\( V_{vv'} \) is the same as for Class I - Class I coordinates

---

**Class III - Class III Coordinates**

\[ v = m, \beta, \text{ or } \Delta \]

\[ v' = m, \beta, \text{ or } \Delta \]

\[
\begin{pmatrix}
  v_1' \\
  v_2' \\
  v_3' \\
  v_4' \\
  v_5' \\
  v_6' \\
  v_7' \\
  v_8'
\end{pmatrix}
= 
\begin{pmatrix}
  p & q & r & s & t & u & r & v \\
  q & p & v & r & u & t & s & r \\
  r & v & p & q & r & s & t & u \\
  s & r & q & p & v & r & u & t \\
  t & u & r & v & p & q & r & s \\
  u & t & s & r & q & p & v & r \\
  r & s & t & u & r & v & p & q \\
  v & r & u & t & s & r & q & p \\
\end{pmatrix}
\begin{pmatrix}
  v_1' \\
  v_2' \\
  v_3' \\
  v_4' \\
  v_5' \\
  v_6' \\
  v_7' \\
  v_8'
\end{pmatrix}
\]
TABLE 15 (contd.)

Class I - Class II Coordinates*
\( v = 1, r, \alpha, \gamma, \text{ or } w \)
\( v' = \epsilon \text{ or } d \)

\[
V_{vv'} =
\begin{pmatrix}
  v_1' \\
v_2' \\
v_3' \\
v_4'
\end{pmatrix}
= 
\begin{pmatrix}
e & g & e & g & e \\
e & e & g & g & e \\
g & e & e & g & e \\
g & g & e & e & e
\end{pmatrix}
\begin{pmatrix}
v_1 \\
v_2 \\
v_3 \\
v_4
\end{pmatrix}
\]

Class I - Class III Coordinates*
\( v = 1, r, \alpha, \gamma, \text{ or } w \)
\( v' = m, \beta, \text{ or } \Delta \)

\[
V_{vv'} =
\begin{pmatrix}
  v_1' \\
v_2' \\
v_3' \\
v_4'
\end{pmatrix}
= 
\begin{pmatrix}
a & a & b & c & 'd & d & c & b \\
c & b & a & a & b & c & d & d \\
d & d & c & b & a & a & b & c \\
b & c & d & d & c & b & a & a
\end{pmatrix}
\begin{pmatrix}
v_1 \\
v_2 \\
v_3 \\
v_4
\end{pmatrix}
\]
**TABLE 15 (contd.)**

Class II - Class III Coordinates*

\[ v = \varepsilon \text{ or } d \]
\[ v' = m, \beta, \text{ or } \Delta \]

\[
\begin{pmatrix}
    v_1' \\
    v_2 \\
    v_3 \\
    v_4
\end{pmatrix}
= 
\begin{pmatrix}
    b & a & a & b & c & d & d & c \\
    d & c & b & a & a & b & c & d \\
    c & d & d & c & b & a & a & b \\
    a & b & c & d & d & c & b & a
\end{pmatrix}
\begin{pmatrix}
    v_1' \\
    v_2' \\
    v_3' \\
    v_4'
\end{pmatrix}
\]

Class IV Coordinate - \( r_0 \)

\[ V_{r_0r_0} = r_0 (f_{r_0r_0}) r_0 \]

For interactions of \( r_0 \) with any coordinate,

\[ V_{r_0v} = r_0 (f_{r_0v}, f_{r_0v}, ..., f_{r_0v}) \begin{pmatrix}
    v_1 \\
    v_2 \\
    \vdots \\
    v_n
\end{pmatrix} \]

*Each element in the force constant matrix should have the subscript \( vv' \). For \( v = v' \) the constants \( k \) and \( p \) are diagonal or principal force constants, as is \( f_{p} \) also. All other force constants are interaction constants between \( r_0r_0 \) different internal coordinates.
TABLE 16
TRANSFORMATION MATRICES, $\mathbf{U}$, FROM VALENCE TO SYMMETRY COORDINATES

### Class I Coordinates
$v = 1, r, \alpha, \gamma, \text{ or } w$

\[
\begin{pmatrix}
S^A_1 \\
S^B_1 \\
S^E \\
S^E
\end{pmatrix} =
\begin{pmatrix}
\frac{1}{2} & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\
\frac{1}{2} & -\frac{1}{2} & \frac{1}{2} & -\frac{1}{2} \\
\frac{1}{2} & 0 & -\frac{1}{2} & 0 \\
0 & \frac{1}{2} & 0 & -\frac{1}{2}
\end{pmatrix}
\begin{pmatrix}
v_1 \\
v_2 \\
v_3 \\
v_4
\end{pmatrix}
\]

### Class II Coordinates
$v = d \text{ or } \epsilon$

\[
\begin{pmatrix}
S^A_1 \\
S^B_2 \\
S^E \\
S^E
\end{pmatrix} =
\begin{pmatrix}
\frac{1}{2} & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\
\frac{1}{2} & -\frac{1}{2} & \frac{1}{2} & -\frac{1}{2} \\
\frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & \frac{1}{2} \\
\frac{1}{2} & 0 & \frac{1}{2} & \frac{1}{2}
\end{pmatrix}
\begin{pmatrix}
v_1 \\
v_2 \\
v_3 \\
v_4
\end{pmatrix}
\]

### Class III Coordinates
$v = m, \beta, \text{ or } \Delta$

\[
\begin{pmatrix}
S^A_1 \\
S^B_1 \\
S^E \\
S^E \\
S^A_2 \\
S^B_2 \\
S^E \\
S^E
\end{pmatrix} =
\begin{pmatrix}
\frac{1}{\sqrt{8}} & \frac{1}{\sqrt{8}} & \frac{1}{\sqrt{8}} & \frac{1}{\sqrt{8}} & \frac{1}{\sqrt{8}} & \frac{1}{\sqrt{8}} & \frac{1}{\sqrt{8}} & \frac{1}{\sqrt{8}} \\
\frac{1}{\sqrt{8}} & \frac{1}{\sqrt{8}} & -\frac{1}{\sqrt{8}} & -\frac{1}{\sqrt{8}} & \frac{1}{\sqrt{8}} & \frac{1}{\sqrt{8}} & -\frac{1}{\sqrt{8}} & -\frac{1}{\sqrt{8}} \\
\frac{1}{2} & \frac{1}{2} & 0 & 0 & \frac{1}{2} & \frac{1}{2} & 0 & 0 \\
0 & 0 & \frac{1}{2} & \frac{1}{2} & 0 & 0 & -\frac{1}{2} & -\frac{1}{2} \\
\frac{1}{\sqrt{8}} & -\frac{1}{\sqrt{8}} & \frac{1}{\sqrt{8}} & -\frac{1}{\sqrt{8}} & \frac{1}{\sqrt{8}} & \frac{1}{\sqrt{8}} & -\frac{1}{\sqrt{8}} & -\frac{1}{\sqrt{8}} \\
\frac{1}{\sqrt{8}} & -\frac{1}{\sqrt{8}} & -\frac{1}{\sqrt{8}} & \frac{1}{\sqrt{8}} & \frac{1}{\sqrt{8}} & -\frac{1}{\sqrt{8}} & -\frac{1}{\sqrt{8}} & \frac{1}{\sqrt{8}} \\
0 & 0 & \frac{1}{2} & -\frac{1}{2} & 0 & 0 & \frac{1}{2} & \frac{1}{2} \\
-\frac{1}{2} & \frac{1}{2} & 0 & 0 & \frac{1}{2} & -\frac{1}{2} & 0 & 0
\end{pmatrix}
\begin{pmatrix}
v_1 \\
v_2 \\
v_3 \\
v_4 \\
v_5 \\
v_6 \\
v_7 \\
v_8
\end{pmatrix}
\]
degenerate E symmetry coordinates. The class III matrix is the direct product of the class I matrix and the 2 x 2 orthogonal matrix

$$\begin{pmatrix} \sqrt{t} & \sqrt{t} \\ \sqrt{t} & -\sqrt{t} \end{pmatrix}$$

except for rearrangement of rows and some unimportant changes of sign. Applying the complete symmetry transformation matrix $U$ to the valence force constant matrix $f$ yields the symmetry force constant matrix $F = UfU'$; the latter is given in partitioned form in Table 17. By rearranging rows and columns of the complete symmetry force constant matrix, it is possible to bring it to a form in which non-vanishing elements occur only in blocks along the principal diagonal. Each of these blocks corresponds to a different symmetry species, except that the block for the doubly-degenerate E representation occurs twice, as previously discussed. The force constant matrices for each symmetry species are given in Table 18. As an illustration of the interpretation of these matrices, the element $J_{dw}$ in the $A_1$ matrix, which is the force constant connecting the $A_1$ symmetry coordinates formed from internal coordinates of type $d$ and $\omega$, respectively, is equal to $2(e_{dw} + g_{dw})$. The meaning of the latter two constants is established by the Class I - Class II matrix in Table 15, which shows that $e_{dw}$ and $g_{dw}$ are the interaction constants for adjacent and opposite $d$ and $\omega$ internal coordinates, as defined in Table 10.
**TABLE 17**

**SYMMETRY FORCE CONSTANT MATRICES**

### Class I - Class I Coordinates

<table>
<thead>
<tr>
<th></th>
<th>$S = L, R, A, \Gamma$ or $W$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S' = L, R, A, \Gamma$ or $W$</td>
<td></td>
</tr>
</tbody>
</table>

\[
V_{SS'} = \begin{pmatrix}
S_{A1}^A \\
S_{B1}^B \\
S_{E1}^E \\
S_{E2}^E
\end{pmatrix}
\begin{pmatrix}
(k + n + 2h) & 0 & 0 & 0 \\
0 & (k + n - 2h) & 0 & 0 \\
0 & 0 & (k - n) & 0 \\
0 & 0 & 0 & (k - n)
\end{pmatrix}
\begin{pmatrix}
S_{A1}^{S'} \\
S_{B1}^{S'} \\
S_{E1}^E \\
S_{E2}^E
\end{pmatrix}
\]

### Class II - Class II Coordinates

$S = E$ or $D$

$S' = E$ or $D$

The results are the same as for Class I - Class I coordinates except that the second symmetry coordinate is $B_2$ instead of $B_1$.

### Class III - Class III Coordinates

$S = M, B, \text{ or } \Delta$

$S' = M, B, \text{ or } \Delta$

\[
V_{SS'} = \begin{pmatrix}
S_{A1}^A \\
S_{B1}^B \\
S_{E1}^E \\
S_{E2}^E \\
S_{A2}^A \\
S_{B2}^B \\
S_{E1}^E \\
S_{E2}^E
\end{pmatrix}
\begin{pmatrix}
A & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & B & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & C & 0 & 0 & 0 & D & 0 \\
0 & 0 & 0 & C & 0 & 0 & 0 & D \\
0 & 0 & 0 & 0 & E & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & F & 0 & 0 \\
0 & 0 & D & 0 & 0 & 0 & G & 0 \\
0 & 0 & 0 & D & 0 & 0 & 0 & G
\end{pmatrix}
\begin{pmatrix}
S_{A1}^{S'} \\
S_{B1}^{S'} \\
S_{E1}^E \\
S_{E2}^E \\
S_{A2}^A \\
S_{B2}^B \\
S_{E1}^E \\
S_{E2}^E
\end{pmatrix}
\]
Table 17 (contd.)

Class III - Class III (contd.)

\[
A = p + q + 2r + s + t + u + v \\
B = p + q - 2r - s + t + u - v \\
C = p + q - t - u \\
D = v - s \\
E = p - q + 2r - s + t - u - v \\
F = p - q - 2r + s + t - u + v \\
G = p - q - t + u
\]

Class I - Class II Coordinates*  
\(S = L, R, A, \Gamma, \) or \(\bar{W}\)  
\(S' = D\) or \(E\)

\[
V_{SS'} = \begin{pmatrix}
S^{A_1} \\
S^{B_1} \\
S^{E} \\
S^{E}
\end{pmatrix}
\begin{pmatrix}
2(e + g) & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & \sqrt{2}(e - g) & 0 \\
0 & 0 & 0 & \sqrt{2}(e - g)
\end{pmatrix}
\begin{pmatrix}
S^{A_1} \\
S^{B_1} \\
S^{E} \\
S^{E}
\end{pmatrix}
\]

Class I - Class III Coordinates*  
\(S = L, R, A, \Gamma, \) or \(\bar{W}\)  
\(S' = H, B,\) or \(\Delta\)

\[
V_{SS'} = \begin{pmatrix}
S^{A_1} \\
S^{B_1} \\
S^{E} \\
S^{E}
\end{pmatrix}
\begin{pmatrix}
\sqrt{2A} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & \sqrt{2B} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & \sqrt{2C} & 0 & 0 & 0 & \sqrt{2D} \\
0 & 0 & 0 & \sqrt{2C} & 0 & 0 & 0 & \sqrt{2D}
\end{pmatrix}
\begin{pmatrix}
S^{A_1} \\
S^{B_1} \\
S^{E} \\
S^{E}
\end{pmatrix}
\]

\[
A = a + b + c + d \\
B = a - b - c + d \\
C = a - d \\
D = b - c
\]


**TABLE 17 (contd.)**

**Class II - Class III Coordinates**

\[
S = D \text{ or } E \\
S' = N, B, \text{ or } \Delta
\]

\[
V_{SS'} = \begin{pmatrix}
S_{A1}' \\
S_{B2}' \\
S_E' \\
S_E'
\end{pmatrix}
\begin{pmatrix}
\sqrt{2A} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & \sqrt{2C} & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & D \\
0 & 0 & 0 & 0 & 0 & 0 & 0
\end{pmatrix}
\begin{pmatrix}
S_{A1}' \\
S_{B1}' \\
S_E' \\
S_{A2}' \\
S_{B2}' \\
S_E'
\end{pmatrix}
\]

- \( A = a + b + c + d \)
- \( B = a - b - c + d \)
- \( C = a - d \)
- \( D = b - c \)

**Class IV Coordinate - \( r_0 \)**

\[
V_{r_0 r_0} = R_0 f_{r_0 r_0} R_0
\]

For interactions of \( R_0 \) with any coordinate

\[
V_{R_0 S} = R_0 \begin{pmatrix}
\sqrt{n} f_{r_0 S} & 0 & \ldots & 0
\end{pmatrix}
\begin{pmatrix}
S_{A1}' \\
\vdots \\
S_E'
\end{pmatrix}
\]

*Each element in the symmetry force constant matrix should have the subscripts \( SS' \).*
### TABLE 18

**FORCE CONSTANT MATRIX**

<table>
<thead>
<tr>
<th>A\textsubscript{1} Symmetry Class</th>
</tr>
</thead>
<tbody>
<tr>
<td>All elements of matrix should have a superscript A\textsubscript{1}</td>
</tr>
</tbody>
</table>

\[
\begin{array}{cccccccccccccc}
K_{DD} & J_{DA} & J_{DW} & J_{DL} & H_{DB} & J_{DR}^\Delta & K_{DE} & H_{DM} & J_{DR} & 2f_{Dr_o} \\
J_{DA} & K_{AA} & K_{AW} & K_{AL} & N_{AB} & K_{AR} & N_{A\Delta} & J_{AE} & N_{AM} & K_{AR} & 2f_{Ar_o} \\
J_{DW} & K_{AW} & K_{\Delta N} & K_{AL} & N_{WB} & K_{WR} & N_{W\Delta} & J_{WE} & N_{WM} & K_{WR} & 2f_{wr_o} \\
J_{DL} & K_{AL} & K_{WL} & K_{LL} & N_{LB} & K_{LR} & N_{L\Delta} & J_{LE} & N_{LM} & K_{LR} & 2f_{Lr_o} \\
K_{DE} & J_{AE} & J_{WE} & J_{LE} & H_{BE} & J_{EF} & H_{AE} & K_{EE} & H_{EM} & J_{ER} & 2f_{Er_o} \\
K_{DM} & N_{AM} & N_{WM} & N_{LM} & C_{BM} & N_{M\Delta} & C_{\Delta M} & H_{EM} & C_{MM} & N_{MR} & 2f_{Mr_o} \\
J_{DR} & K_{AR} & K_{WR} & K_{LR} & N_{BR} & K_{TR} & N_{A\Delta} & J_{ER} & N_{MR} & K_{RR} & 2f_{Rr_o} \\
2f_{Dr_o} & 2f_{Ar_o} & 2f_{wr_o} & 2f_{Lr_o} & 2f_{Er_o} & 2f_{Mr_o} & 2f_{Rr_o} & f_{r_r_o} \\
\end{array}
\]

where

\[
\begin{align*}
K_{SS'} &= k_{ss'} + 2h_{ss'} + n_{ss'} \\
C_{SS'} &= p_{ss'} + q_{ss'} + 2r_{ss'} + s_{ss'} + t_{ss'} + u_{ss'} + v_{ss'}
\end{align*}
\]
A1 Symmetry Class (contd.)

\[ J_{ss'} = 2(e_{ss'} + g_{ss'}) \]

\[ H_{ss'} = \sqrt{2} (a_{ss'} + b_{ss'} + c_{ss'} + d_{ss'}) \]

\[ N_{ss'} = \sqrt{2} (a_{ss'} + b_{ss'} + c_{ss'} + d_{ss'}) \]

\[ f_{roS} = f_{roS} \]

A2 Symmetry Class

All elements in matrix should have a superscript \( A_2 \).

\[
\begin{array}{ccc}
C_{12} & C_{13} & C_{14} \\
C_{13} & C_{23} & C_{24} \\
C_{14} & C_{24} & C_{34} \\
C_{1D} & C_{3D} & C_{4D}
\end{array}
\]

where

\[ C_{ss'} = p_{ss'} - a_{ss'} + 2r_{ss'} - s_{ss'} + t_{ss'} - u_{ss'} - v_{ss'} \]
### TABLE 18 (contd.)

**B\_1 Symmetry Class**

All elements of matrix should have a superscript $B_1$.

<table>
<thead>
<tr>
<th>$K_{AA}$</th>
<th>$N_{AM}$</th>
<th>$K_{AW}$</th>
<th>$N_{AB}$</th>
<th>$K_{AR}$</th>
<th>$K_{AL}$</th>
<th>$N_{AD}$</th>
<th>$K_{AR}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_{AM}$</td>
<td>$C_{MM}$</td>
<td>$N_{MW}$</td>
<td>$C_{MB}$</td>
<td>$N_{MR}$</td>
<td>$N_{ML}$</td>
<td>$C_{MA}$</td>
<td>$N_{MR}$</td>
</tr>
<tr>
<td>$K_{AW}$</td>
<td>$N_{MW}$</td>
<td>$K_{WW}$</td>
<td>$N_{WB}$</td>
<td>$K_{WG}$</td>
<td>$K_{WL}$</td>
<td>$N_{WA}$</td>
<td>$K_{WR}$</td>
</tr>
<tr>
<td>$N_{AB}$</td>
<td>$C_{MB}$</td>
<td>$N_{WB}$</td>
<td>$C_{BB}$</td>
<td>$N_{BR}$</td>
<td>$N_{BL}$</td>
<td>$C_{BA}$</td>
<td>$N_{BR}$</td>
</tr>
<tr>
<td>$K_{AR}$</td>
<td>$N_{MR}$</td>
<td>$K_{WG}$</td>
<td>$N_{BG}$</td>
<td>$K_{G}$</td>
<td>$K_{LR}$</td>
<td>$N_{DA}$</td>
<td>$K_{RG}$</td>
</tr>
<tr>
<td>$K_{AL}$</td>
<td>$N_{ML}$</td>
<td>$K_{W}$</td>
<td>$N_{EL}$</td>
<td>$K_{GL}$</td>
<td>$K_{LL}$</td>
<td>$N_{DA}$</td>
<td>$K_{LR}$</td>
</tr>
<tr>
<td>$N_{AA}$</td>
<td>$C_{AA}$</td>
<td>$N_{WA}$</td>
<td>$C_{BA}$</td>
<td>$N_{DA}$</td>
<td>$N_{DA}$</td>
<td>$C_{AA}$</td>
<td>$N_{DA}$</td>
</tr>
<tr>
<td>$K_{AR}$</td>
<td>$N_{DA}$</td>
<td>$K_{WR}$</td>
<td>$N_{BR}$</td>
<td>$K_{R}$</td>
<td>$K_{LR}$</td>
<td>$N_{DA}$</td>
<td>$K_{RR}$</td>
</tr>
</tbody>
</table>

where

$$K_{ss'} = k_{ss'} - 2h_{ss'} + n_{ss'}$$

$$C_{ss'} = p_{ss'} + q_{ss'} - 2r_{ss'} - s_{ss'} + t_{ss'} + u_{ss'} - v_{ss'}$$

$$N_{ss'} = \sqrt{2} (a_{ss'} - b_{ss'} - c_{ss'} + d_{ss'})$$
TABLE 18 (contd.)

$B_2$ Symmetry Class

All elements of matrix should have a superscript $B_2$.

\[
\begin{array}{cccccc}
K_{DD} & H_{DX} & H_{DB} & H_{D\Delta} & K_{DE} \\
H_{DX} & C_{MX} & C_{MB} & C_{M\Delta} & H_{ME} \\
H_{DB} & C_{MB} & C_{BB} & C_{B\Delta} & H_{BE} \\
H_{D\Delta} & C_{M\Delta} & C_{B\Delta} & C_{\Delta\Delta} & H_{AE} \\
K_{DE} & H_{ME} & H_{BE} & H_{NE} & K_{EE} \\
\end{array}
\]

where

\[
K_{SS'} = k_{SS'} - 2h_{SS'} + n_{SS'}
\]

\[
C_{SS'} = p_{SS'} - q_{SS'} - 2r_{SS'} + s_{SS'} + t_{SS'} - u_{SS'} + v_{SS'}
\]

\[
H_{SS'} = \sqrt{2} \left( -a_{SS'} + b_{SS'} + c_{SS'} - d_{SS'} \right)
\]
### TABLE 18 (contd.)

#### E Symmetry Class

All elements of matrix should have a superscript $E$.

```
<table>
<thead>
<tr>
<th>K_{DD}</th>
<th>J_{AD}</th>
<th>H_{DM}</th>
<th>K_{DE}</th>
<th>H_{DB}</th>
<th>J_{DR}</th>
<th>I_{DB}</th>
<th>I_{DM}</th>
<th>J_{DL}</th>
<th>H_{DA'}</th>
<th>J_{DR}</th>
<th>J_{DW}</th>
<th>I_{DA''}</th>
</tr>
</thead>
<tbody>
<tr>
<td>J_{AD}</td>
<td>K_{AA}</td>
<td>N_{AM}</td>
<td>J_{AB}</td>
<td>N_{AB}</td>
<td>K_{AR}</td>
<td>P_{AB}</td>
<td>P_{AM}</td>
<td>K_{AL}</td>
<td>N_{AA'}</td>
<td>K_{AR}</td>
<td>K_{AW}</td>
<td>P_{AA''}</td>
</tr>
<tr>
<td>H_{DM}</td>
<td>N_{AM}</td>
<td>C_{MM}</td>
<td>H_{ME}</td>
<td>C_{MB}</td>
<td>N_{MR}</td>
<td>Q_{MM}</td>
<td>Q_{MB}</td>
<td>N_{ML}</td>
<td>C_{MA'}</td>
<td>N_{MR}</td>
<td>N_{MW}</td>
<td>Q_{MA''}</td>
</tr>
<tr>
<td>K_{DE}</td>
<td>J_{AB}</td>
<td>H_{ME}</td>
<td>K_{EE}</td>
<td>H_{EB}</td>
<td>J_{ER}</td>
<td>I_{EB}</td>
<td>I_{EM}</td>
<td>J_{EL}</td>
<td>H_{EA'}</td>
<td>J_{ER}</td>
<td>J_{EW}</td>
<td>I_{EA''}</td>
</tr>
<tr>
<td>H_{DB}</td>
<td>N_{AB}</td>
<td>C_{MB}</td>
<td>H_{EB}</td>
<td>C_{B3}</td>
<td>N_{BR}</td>
<td>Q_{BB}</td>
<td>Q_{BM}</td>
<td>N_{BL}</td>
<td>C_{B'A'}</td>
<td>N_{BR}</td>
<td>N_{B''W}</td>
<td>Q_{B'A''}</td>
</tr>
<tr>
<td>J_{DR}</td>
<td>K_{AR}</td>
<td>N_{MR}</td>
<td>J_{ER}</td>
<td>N_{BR}</td>
<td>K_{FR}</td>
<td>P_{BR}</td>
<td>P_{LM}</td>
<td>K_{L}</td>
<td>N_{LA'}</td>
<td>K_{FR}</td>
<td>K_{fw}</td>
<td>P_{RA''}</td>
</tr>
<tr>
<td>I_{DB}</td>
<td>P_{AB}</td>
<td>Q_{MB}</td>
<td>I_{EB}</td>
<td>Q_{B3}</td>
<td>P_{BR}</td>
<td>G_{BB}</td>
<td>G_{BM}</td>
<td>P_{BL}</td>
<td>Q_{B'A'}</td>
<td>P_{BR}</td>
<td>P_{BW}</td>
<td>G_{BA''}</td>
</tr>
<tr>
<td>I_{DM}</td>
<td>P_{AM}</td>
<td>Q_{MM}</td>
<td>I_{EM}</td>
<td>Q_{B'M}</td>
<td>P_{MR}</td>
<td>G_{BM}</td>
<td>G_{MM}</td>
<td>P_{ML}</td>
<td>Q_{MA'}</td>
<td>P_{MR}</td>
<td>P_{MW}</td>
<td>G_{MA''}</td>
</tr>
<tr>
<td>J_{DL}</td>
<td>K_{AL}</td>
<td>N_{ML}</td>
<td>J_{EL}</td>
<td>N_{BL}</td>
<td>K_{LL}</td>
<td>P_{BL}</td>
<td>P_{ML}</td>
<td>K_{L}</td>
<td>N_{LA'}</td>
<td>K_{LR}</td>
<td>K_{fw}</td>
<td>P_{LA''}</td>
</tr>
<tr>
<td>H_{DA'}</td>
<td>N_{A'}</td>
<td>C_{H'A'}</td>
<td>H_{E'A'}</td>
<td>C_{B'A'}</td>
<td>N_{GA'}</td>
<td>Q_{B'A'}</td>
<td>Q_{MA'}</td>
<td>N_{LA'}</td>
<td>C_{A'A'}</td>
<td>N_{AR}</td>
<td>N_{A''W}</td>
<td>Q_{A'A''}</td>
</tr>
<tr>
<td>J_{DR}</td>
<td>K_{AR}</td>
<td>N_{MR}</td>
<td>J_{ER}</td>
<td>N_{BR}</td>
<td>K_{FR}</td>
<td>P_{BR}</td>
<td>P_{MR}</td>
<td>K_{LR}</td>
<td>N_{AR}</td>
<td>K_{RR}</td>
<td>K_{FW}</td>
<td>P_{RA''}</td>
</tr>
<tr>
<td>J_{DW}</td>
<td>K_{AW}</td>
<td>N_{MW}</td>
<td>J_{EW}</td>
<td>N_{B''W}</td>
<td>K_{TW}</td>
<td>P_{BW}</td>
<td>P_{MW}</td>
<td>K_{LW}</td>
<td>N_{A''W}</td>
<td>K_{RW}</td>
<td>K_{WW}</td>
<td>P_{WA''}</td>
</tr>
<tr>
<td>I_{DA'}</td>
<td>P_{AA''}</td>
<td>Q_{MA''}</td>
<td>I_{EA''}</td>
<td>Q_{B'A''}</td>
<td>P_{DA''}</td>
<td>G_{BA''}</td>
<td>G_{MA''}</td>
<td>P_{LA''}</td>
<td>Q_{A'A''}</td>
<td>P_{RA''}</td>
<td>P_{WA''}</td>
<td>G_{DA''}</td>
</tr>
</tbody>
</table>
```
TABLE 18 (contd.)

E Symmetry Class (contd.)

where

\[ K_{SS'} = k_{ss'} - n_{ss'} \]
\[ C_{ss'} = p_{ss'} + q_{ss'} - t_{ss'} - u_{ss'} \]
\[ G_{ss'} = p_{ss'} - q_{ss'} - t_{ss'} + u_{ss'} \]
\[ J_{ss'} = \sqrt{2} \left( e_{ss'} - g_{ss'} \right) \]
\[ H_{ss'} = a_{ss'} + b_{ss'} - c_{ss'} - d_{ss'} \]
\[ I_{ss'} = a_{ss'} - b_{ss'} + c_{ss'} - d_{ss'} \]
\[ N_{ss'} = \sqrt{2} \left( a_{ss'} - d_{ss'} \right) \]
\[ P_{ss'} = \sqrt{2} \left( b_{ss'} - c_{ss'} \right) \]
\[ Q_{ss'} = v_{ss'} - g_{ss'} \]
G. Redundancy Conditions

Before proceeding to the calculation of the final $G$ and $F$ matrices, it is necessary to eliminate the redundancies in the symmetry coordinates. Eleven $A_1$, three $A_2$, eight $B_1$, five $B_2$, and thirteen $E$ symmetry coordinates have been defined. Since there are only seven $A_1$, two $A_2$, five $B_1$, four $B_2$, and nine $E$ internal degrees of freedom, it follows that there are four $A_1$, one $A_2$, three $B_1$, one $B_2$, and four $E$ redundancy conditions. One method of finding the redundancy conditions, i.e., the coefficients $a_i$ in the equations, \( \sum a_i S_i = 0 \), expressing the linear dependency of certain symmetry coordinates $S_i$, is to derive the relationships from the geometry of the molecule. However, a more direct procedure may be used if the $S$-vectors are known. It is easily seen that the $S$-vectors for a redundant coordinate are zero for all atoms. If $R_k$ is a redundant coordinate then $R_k = \sum a_{ki} S_i = 0$. The $S$-vectors for $R_k$ are given by $S_{kt} = \sum a_{ki} S_{it} = 0$, where $S_{it}$ is the $S$-vector for the symmetry coordinate $S_i$ and atom $t$. There will be a vector equation of the latter type for each atom, although some of the equations may be identical if there is symmetry. The solution of this set of linear homogeneous equations will give the ratios of the $a_{ki}$'s and therefore the redundancy conditions (the remaining indeterminancy may be removed by normalization). If there are $r$ redundancy conditions in a given symmetry species, there will be $r$ linearly independent solutions to the set of equations. However, for $r > 1$ the redundancy conditions are not unique, as any other set of $r$ linearly independent redundancies related to them by a linear transformation is equally satisfactory. In general an attempt is made to choose the conditions
in as simple a form as possible (e.g., that choice which makes as many as possible of the $a_{kl}$'s vanish), or geometrical considerations may be used to pick the linear combinations. In any case, the particular linear combinations chosen do not affect the frequencies and eigenvectors obtained from the solution of the secular equation.

As an example of this method, the $B_2$ redundancy condition will be derived. The $B_2$ coordinates are $\kappa, \beta, \Delta, E$, and $D$. The redundancy condition can be written

$$R_k = a_D D + a_M M + a_B B + a_\Delta \Delta + a_E E = 0$$

The $S$-vectors for $R_k$ are

$$\vec{S}_{kt} = a_D \vec{S}_D + a_M \vec{S}_M + a_B \vec{S}_B + a_\Delta \vec{S}_\Delta + a_E \vec{S}_E = 0$$

Referring to Table 14 for the $S$-vectors, the linear homogeneous equations obtained are:

$$-0.7071 a_D + 0.4796 a_M - 0.3854 a_B - 0.5228 a_\Delta - 0.2533 a_E = 0,$$

$$0.4118 a_\Delta = 0,$$

$$-0.1462 a_M - 0.1761 a_B + 0.3079 a_\Delta - 0.1371 a_E = 0,$$

and

$$0.4846 a_M + 0.2623 a_B - 0.0851 a_\Delta + 0.4543 a_E = 0,$$

where the first equation refers to atom $B_1$, the second to $H_1$, and the third and fourth to two components of the $S$-vectors for $H_2$ on orthogonal axes. These equations can be solved by standard algebraic methods. Taking $a_D = 1.0000$, then $a_\Delta = 0, a_B = 0, a_M = 0.9431$, and $a_E = -1.0062$. The redundancy condition is

$$D + 0.9431 M - 1.0062 E = 0.$$
Another method for finding the redundancies has been given by Sun, Parr, and Crawford,\textsuperscript{12} based on the fact that the $G$-matrix elements for redundant coordinates, or the interaction of redundant and non-redundant coordinates must vanish identically, as such elements depend linearly on the $S$-vectors for the redundant coordinate (see section H). This method was tried but involved more effort than the method described here.

The redundancy conditions for the various symmetry species are listed in Table 19. For the $E$ redundancies it is sufficient to give only one member of each degenerate pair. Some of the redundancy conditions were checked by deriving them from geometric considerations. The redundancies involving the $\Theta$ coordinate, which was added late in the calculation, have been included in the table although they are not included in the preceding discussion. The addition of the $\Theta$ coordinate adds four redundancy conditions, one $A_1$, one $B_2$, and a degenerate $E$ pair. The $\Theta$ redundancies are derived in the same way as the other redundancies. It was possible in all symmetry species to retain the previously derived redundancies unchanged and simply add the linearly independent redundancies.

H. Elimination of Redundancies and Final Form of $F$ and $G$ Matrices

As discussed in sections B and G the number of coordinates taken initially in each symmetry class exceeds the number of degrees of freedom.\textsuperscript{12} C. E. Sun, R. G. Parr, and B. L. Crawford, J. Chem. Phys., 17, 840 (1949).
### TABLE 19

**REDUNDANCY CONDITIONS**

<table>
<thead>
<tr>
<th>Symmetry Class</th>
<th>Equation</th>
</tr>
</thead>
</table>
| \( A_1 \)       | \( \begin{align*} 
L & = 2.0699 E - 1.4544 B + .2801 \Gamma - .3839 M = 0 \\
\Theta & = 2.5344 M - 3.93903 B + 2.03584 L - 4.5928 D = 0 
\end{align*} \) |
| \( A_2 \)       | \( \begin{align*} 
M & + 1.2444 B = 0 
\end{align*} \) |
| \( A_1 \)       | \( \begin{align*} 
A & + .9911 B + .3719 \Gamma + 1.0051 \Delta = 0 \\
M & + .1909 \Gamma - .9914 B - .7683 E = 0 \\
L & = 2.0699 E - 1.4544 B + .2801 \Gamma - .3839 M = 0 \\
\Theta & = 2.5344 M - 3.93903 B + 2.03584 L - 4.5928 D = 0 
\end{align*} \) |
| \( A_2 \)       | \( \begin{align*} 
M & + 1.2444 B = 0 
\end{align*} \) |
| \( B_2 \)       | \( \begin{align*} 
D & + .9431 M - 1.0062 E = 0 \\
\Theta & = 2.5344 M + 3.93903 B - 4.5948 D = 0 
\end{align*} \) |
| \( E \)         | \( \begin{align*} 
M' & + .6669 M'' + 1.0062 E - D = 0 \\
A & + .9911 B' + .3719 \Gamma + 1.0051 \Delta' = 0 \\
M' & = M'' + 1.2446 B' - 1.2446 B'' + 1.6159 L = 0 \\
E & = .5972 L - .2439 \Gamma + .4041 M'' + .2993 B' + .9677 B'' = 0 \\
\Theta & = 1.7911 M' - 1.7911 M'' - 2.78346 B' - 2.78346 B'' + 1.43839 L - 4.5919 D = 0 
\end{align*} \) |
freedom. It is necessary, therefore, to eliminate certain coordinates until the number of linearly independent coordinates remaining equals the number of degrees of freedom, and conditions of linear dependency or redundancy are used for this purpose. Each redundancy condition may be used to remove one coordinate, but the choice of coordinates to be eliminated is not necessarily unique. Coordinates which are completely independent, i.e., not involved in any of the redundancy conditions, cannot be eliminated. However, if a coordinate is involved in a redundancy condition, it may be eliminated from the kinetic and potential energy expressions (and therefore from the G and F matrices) by the use of that redundancy condition. As many of the coordinates in pentaborane are involved in redundancy conditions, the choice of which to eliminate is arbitrary in many cases. In general, the coordinates eliminated were those which simplified the calculations to the greatest possible extent. Of course the choice of coordinates to be eliminated does not affect the final calculated frequencies or eigenvectors. It does however affect the final forms of the F and G matrices.

The mathematical equations used in eliminating coordinates may be derived in the following way. Let $S_i$ ($i = 1, 2, \ldots, n + r$) be the initial $(n + r)$ symmetry coordinates of a particular species. Here $n$ is the number of internal degrees of freedom and $r$ the number of redundancy conditions for the species. It will be assumed that $S_1, S_2, \ldots, S_r$ are to be eliminated by use of the redundancy conditions. The $r$ redundancies may be written $\sum L a_{ji} S_i = 0; j = 1, 2, \ldots, r$. It is convenient to rewrite this equation as

$$\sum_{L \neq i} a_{ji} S_i = \sum_{i \neq r} a_{ji} S_i; \quad j = 1, 2, \ldots, r.$$
Such a set of equations can be solved for

\[ S_j = \sum_{i=1}^{n-r} b_i S_i \quad ; \quad j = 1, 2, \ldots, r; \]

provided the determinant of the coefficients \( a_{ij} \) on the left-hand side of the equation does not vanish. The coordinates to be eliminated have been chosen in such a way that this condition is satisfied. The preceding equations can be expressed more conveniently in matrix form.

The redundancy conditions become

\[ A S = 0 \]

where \( A \) is the \( r \times (n + r) \) matrix of the \( a_{ij} \)'s, and \( S \) is the column matrix of the \( n + r \) symmetry coordinates of the given species. Introduce the partitioned matrices,

\[ S = \begin{pmatrix} S_r \\ S_n \end{pmatrix}, \quad A = \begin{pmatrix} A_{rr} & A_{rn} \\ A_{nr} & A_{nn} \end{pmatrix}, \]

where \( S_r \) is a column matrix of the coordinates to be eliminated, and \( S_n \) is a column matrix of the remaining coordinates. \( A \) is partitioned correspondingly into \( A_{rr} \) and \( A_{rn} \) (note that in using partitioned matrices conformability for multiplication must be maintained). The redundancy condition yields

\[ A_{rr} S_r + A_{rn} S_n = 0 \]

or

\[ S = -A_{rr}^{-1} A_{rn} S_n \]

provided \( A_{rr} \) is non-singular. The column matrix \( S \) can now be written

\[ S = \begin{pmatrix} S_r \\ S_n \end{pmatrix} = \begin{pmatrix} A_{rr}^{-1} A_{rn} S_n \\ S_n \end{pmatrix} = \begin{pmatrix} A_{rr}^{-1} A_{rn} \\ I \end{pmatrix} S_n, \]

where \( I \) is the \( n \times n \) unit matrix. The potential energy is

\[ 2V = S' F S = S_n' (-A_{rn}^{-1} A_{rr}^{-1})' I F \begin{pmatrix} -A_{rr}^{-1} A_{rn} \\ I \end{pmatrix} S_n, \]

where \( F \) is the \( (n + r) \times (n + r) \) force constant matrix for the
coordinates \( S \). If the latter is partitioned conformably as

\[
F = \begin{pmatrix}
F_{rr} & F_{rn} \\
F_{rn} & F_{nn}
\end{pmatrix},
\]

Substitution in the preceding equation and multiplication of the matrices yields

\[
2V = S'^t F^* S_n,
\]

where

\[
F^* = Y^t Y,
\]

\[
Y = \begin{pmatrix}
-A^{-1}_{rr} & A_{rn} \\
0 & I
\end{pmatrix},
\]

or in expanded form

\[
F^*_{nn} = F_{nn} - A_{rn}^t (A^{-1}_{rr})^t F_{rn} - A_{rn}^t A_{rr}^{-1} A_{rn} + A_{rn}^t (A^{-1}_{rr})^t F_{rr} A_{rr}^{-1} A_{rn}.
\]

The matrix \( F^*_{nn} \) is a symmetric square matrix of dimension \( n \times n \), and is the reduced or effective force constant matrix for the \( n \) coordinates \( S_n \) retained in the calculation.

The \( G \) matrix or reciprocal of the kinetic energy matrix is conveniently calculated from the \( s \)-vectors of Wilson, which were originally introduced for this purpose. The advantage of using the \( G \) matrix has been discussed in section B. The \( G \) matrix for the original valence-type internal coordinates will be denoted by \( g \), while the symbol \( G \) will be retained for the form the matrix takes after transformation to symmetry coordinates. Wilson showed that the elements of the matrix \( g \) are given by

\[
E_{ij} = \sum_{k=1}^{N} (\mathbf{s}_{it} \cdot \mathbf{s}_{jt})/m_t,
\]

where the sum is over all atoms, \( m_t \) is the mass of the \( t \)th atom, and \( \mathbf{s}_{it} \) is Wilson's vector for coordinate \( s_i \) and atom \( t \) introduced in section C. The \( G \) matrix for the symmetry coordinates can be calculated by direct
transformation of the g matrix in the same manner the F matrix for the
symmetry coordinates was obtained from the f matrix for valence coo-
dinates as discussed in section F. That is,

\[ G = U g U' \]

where U is the transformation matrix from valence to symmetry coo-
dinates. However, if the S-vectors for the symmetry coordinates have
been calculated as in the present investigation (see section D), it is
simpler to calculate the elements of the G matrix directly from these
vectors, and omit entirely the calculation of the g matrix. Since the
preceding formula for g is not restricted to any particular form of
internal coordinates, it is equally applicable to the calculation of the
elements of the matrix G for the symmetry coordinates, so that

\[ G_{ij} = \sum_{t=1}^{N} (\bar{S}_{it} \cdot \bar{S}_{jt})/m_t \]

where \( \bar{S}_{it} \) is Wilson's vector for the symmetry coordinate \( S_i \) and atom \( t \).
This formula may also be obtained by direct transformation of the
formula for \( g_{ij} \), using the linear relation between the vectors, \( \bar{S}_{it} \) and
\( \bar{S}_{jt} \), as given in section E. An element \( G_{ij} \) of the G matrix connecting
two (internal) symmetry coordinates, \( S_i \) and \( S_j \), depends only on the
S-vectors for these two coordinates. It is therefore sufficient to
compute the matrix elements \( G_{ij} \) for the \( n \) coordinates retained in the
calculation. In the partitioned matrix notation introduced above these
coordinates are represented by the column matrix \( S_n \), and the correspond-
ing \( n \times n \) sub-matrix of G is denoted by \( G_{nn} \). As shown in section A,
the secular equation for the \( n \) coordinates retained may be put in the
form

\[ |G_{nn} F^* - \lambda I| = 0 \]
where $F^{*}_{nn}$ is the effective force constant matrix for the coordinates $S_n$ as derived above. The roots or eigenvalues $\lambda$ of the secular equation give the squares of the frequencies of vibration of the molecule. These will be independent of the particular choice of coordinates $S_n$ provided the original force constant matrix $f$ correctly represents the potential energy of the molecule. The eigenvectors of $G_{nn} F^{*}_{nn}$ may be obtained in the course of the solution of the secular equation and yield the transformation matrix connecting $S_n$ and the normal coordinates, as discussed in section A.

There is another way of treating the redundancies that will be shown to give equivalent results. The original $n + r$ symmetry coordinates $S_1$ are subjected to a linear transformation such that the first $r$ coordinates are the redundancy conditions. This transformation may be written

$$Z = \begin{pmatrix} R \\ Z_n \end{pmatrix} = \begin{pmatrix} A_{rr} & A_{rn} \\ U_{nr} & U_{nn} \end{pmatrix} \begin{pmatrix} S_r \\ S_n \end{pmatrix} = U S,$$

where $Z$ is the column vector of the $n$ new coordinates, $R$ the column vector of the $r$ redundancies, $U_{nr}$ and $U_{nn}$ are $n \times r$ and $n \times n$ matrices whose form will be specified later, $S$ is the column vector of the symmetry coordinates, and $A_{rr}$ and $A_{rn}$ have been defined previously. In terms of the coordinates $Z$, the potential energy may be written

$$2V = Z'(U^{-1})'F U^{-1} Z = Z' F \overline{Z},$$

where $\overline{F} = (U^{-1})'F U^{-1}$. Recalling that the $S$-vectors for redundant coordinates are identically zero, it is apparent that the rows and columns of the $G$ matrix corresponding to the redundant coordinates
contain all zeroes. Thus in the present case \( G \) has the form

\[
G = \begin{pmatrix}
0 & 0 \\
0 & G_{nn}
\end{pmatrix}
\]

where \( G_{nn} \) is the \( n \times n \) matrix calculated for the coordinates \( Z_n \). The secular equation can be written

\[
|\bar{G} - \lambda I| = \begin{vmatrix}
F_{rr} & F_{rn} \\
F'_{rn} & F_{nn}
\end{vmatrix} \begin{pmatrix}
0 & 0 \\
0 & G_{nn}
\end{pmatrix} - \lambda I = 0
\]

This may be expanded to

\[
(-\lambda)^F |\bar{G}_{nn} - \lambda I| = 0
\]

or

\[
|\bar{G}_{nn} - \lambda I| = 0
\]

This secular equation is simply that obtained by calculating \( G_{nn} \) for the \( Z_n \) coordinates and neglecting the rows and columns of \( F \) which correspond to the redundant coordinates. The only remaining question is the choice of the coordinates \( Z_n \) or the equivalent choice of the matrices \( U_{nr} \) and \( U_{nn} \). The simplest choice of the matrices is to take \( U_{nr} = 0 \) and \( U_{nn} = 1 \). This corresponds to taking \( Z_n = S_n \), which is equivalent to the previous elimination of the coordinates \( S_r \). With this choice

\[
U = \begin{pmatrix}
A_{rr} & A_{rn} \\
0 & I
\end{pmatrix}, \quad U^{-1} = \begin{pmatrix}
A_{rr}^{-1} & -A_{rr}^{-1}A_{rn} \\
0 & I
\end{pmatrix}
\]

Partitioning \( F \) as was done previously

\[
F = \begin{pmatrix}
F_{rr} & F_{rn} \\
F'_{rn} & F_{nn}
\end{pmatrix}
\]

and substituting in the expression \( \bar{F} = (U^{-1})'FU^{-1} \), it is found that

\[
\bar{F}_{nn} = F_{nn} - A'_{rn} (A^{-1})'F_{rn} - F_{rn}A^{-1}A_{rn} + A'_{rn} (A^{-1})'F_{rr}A^{-1}_{rr}A_{rn}
\]
This is identical with the previous expression for the effective force constant matrix $F^*$ for the coordinates $S_n$. Furthermore, $G_{nn}$ is identical with the previous $G_{nn}$, as $Z_n = S_n$. The final secular equations are therefore identical, and both procedures are entirely equivalent.

It should be pointed out that the choice $U_{nr} = 0$ and $U_{nn} = I$ is not the only possible choice. Actually any matrices of the correct dimensions can be used for $U_{nr}$ and $U_{nn}$ as long as $|U| \neq 0$. This simply implies that any linearly independent linear combination of the original $S_i$ symmetry coordinates can be used to describe the vibrations of the molecule. Of course the linear combinations used cannot be a redundancy condition, but in this case $|U| = 0$. The choice of a different set of coordinates $Z_n$ will give a different $G$ matrix and a different $F^*$ matrix, but the roots of the secular equation will not be affected.

There is some advantage in taking $U$ as an orthogonal matrix, as $U^{-1}$ may then be obtained by simply transposing $U$, and this is the procedure which has been followed by most investigators. The orthogonalization of $U$ is easily carried out beginning with any particular non-singular form of $U$ such as that specified above, by orthogonalizing successive rows of $U$ by the Schmidt process. It is necessary to first mutually orthogonalize the redundant coordinates if these are not to be mixed with the final coordinates retained. The coordinates obtained by this procedure depend on the order in which the orthogonalization is carried out. There is in addition usually rather complete mixing of the original symmetry coordinates in each of the final coordinates, especially if there are several redundancies in the symmetry species. As a result the expressions relating the force constants for the final coordinates, or the elements
of $F_{nn}$, to the valence force constants or elements of $f$, become extremely cumbersome. It was decided that the disadvantages of this conventional procedure outweighed the difficulty of computing $U^{-1}$. In the present procedure $U$ has a great many elements equal to zero, and $U^{-1}$ is rather easily computed from a preceding formula which expressed it in partitioned form.

The matrices $U^{-1}$ for each symmetry species are given in Table 20. The original symmetry coordinates $S_i$ are listed to the left of, and the coordinates $Z_i$ are listed above, the $U^{-1}$ matrices. In the present procedure these are identical except for the redundant coordinates, which are denoted by $R_i^r$ to distinguish them from the symmetry coordinates $R_i^0$ and $R_i^1$. The relation of the redundant coordinates to the original symmetry coordinates is given in Table 19. From the preceding analysis, the final $n$ columns of $U^{-1}$ yield the $(n + r) \times n$ matrices,

$$Y = \begin{pmatrix} A^{-1}r & A \end{pmatrix},$$

required for the calculation of the effective force constant matrices $F_{nn}$, from the original symmetry force constant matrices $F$ for each species. The latter are given in Table 18.

The $G$ matrices for each symmetry species of normal and deuterated pentaborane are given in numerical form in Table 21. The coordinates $S_n$ are listed above and also to the left of each $G$ matrix. This indicates the coordinates to which each element of the $G$ matrix corresponds, i.e., the element $G_{ij}$ is found in the $S_i$ row and the $S_j$ column of the $G$ matrix. The following values of the mass of hydrogen, deuterium, and boron were used: $m_H = 1.0080$, $m_D = 2.0142$, and $m_B = 10.822$ (atomic
**TABLE 20**

**$U^{-1}$ MATRICES**

### $A_1$ Symmetry Class

<table>
<thead>
<tr>
<th></th>
<th>$R_1$</th>
<th>$R_2$</th>
<th>$R_3$</th>
<th>$R_4$</th>
<th>$B$</th>
<th>$r$</th>
<th>$\Delta$</th>
<th>$E$</th>
<th>$M$</th>
<th>$R_1$</th>
<th>$R_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.0062</td>
<td>.9431</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>A</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-1.2444</td>
<td>-1.2444</td>
<td>-1.0051</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>W</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>L</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1.4544</td>
<td>-1.2801</td>
<td>0</td>
<td>2.0699</td>
<td>.8839</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>r</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>E</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$M$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$R_1$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$R_0$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

### $A_2$ Symmetry Class

<table>
<thead>
<tr>
<th></th>
<th>$R'$</th>
<th>$B$</th>
<th>$\Delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M$</td>
<td>1</td>
<td>-1.2444</td>
<td>0</td>
</tr>
<tr>
<td>$B$</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>
### TABLE 20 (contd.)

#### $B_1$ Symmetry Class

<table>
<thead>
<tr>
<th></th>
<th>$R_1^1$</th>
<th>$R_2^1$</th>
<th>$R_3^1$</th>
<th>$B$</th>
<th>$\Gamma$</th>
<th>$L$</th>
<th>$\Delta$</th>
<th>$R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>-.9911</td>
<td>-.3719</td>
<td>0</td>
<td>-1.0051</td>
<td>0</td>
</tr>
<tr>
<td>$M$</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>-1.2446</td>
<td>0</td>
<td>0</td>
<td>-1.6159</td>
<td>0</td>
</tr>
<tr>
<td>$W$</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>.2722</td>
<td>.4014</td>
<td>.1389</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$B$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$L$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$R$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

#### $B_2$ Symmetry Class

<table>
<thead>
<tr>
<th></th>
<th>$R_1^1$</th>
<th>$M$</th>
<th>$B$</th>
<th>$\Delta$</th>
<th>$E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D$</td>
<td>1</td>
<td>-.9431</td>
<td>0</td>
<td>0</td>
<td>1.0062</td>
</tr>
<tr>
<td>$W$</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$B$</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>$E$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>
## TABLE 20 (contd.)

**E Symmetry Class**

<table>
<thead>
<tr>
<th>R₁</th>
<th>R₂</th>
<th>R₃</th>
<th>R₄</th>
<th>B'</th>
<th>Γ</th>
<th>B''</th>
<th>M''</th>
<th>L</th>
<th>Δ'</th>
<th>R</th>
<th>W</th>
<th>Δ''</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>A</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-1.0051</td>
</tr>
<tr>
<td>M'</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-1.2446</td>
<td>1.2446</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>E</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B'</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Γ</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B''</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>M''</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>L</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Δ'</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>R</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>W</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Δ''</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>$A_1$ Symmetry Species</td>
<td>$B_{5d9}$</td>
<td>$B_{5h9}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------</td>
<td>------------------------</td>
<td>----------</td>
<td>-----------</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A$</td>
<td></td>
<td>$B$</td>
<td>$\Gamma$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\beta$</td>
<td>.7465</td>
<td>.0555</td>
<td>-.6498</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>.0555</td>
<td>2.0081</td>
<td>-.6776</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta$</td>
<td>-.6498</td>
<td>-.6776</td>
<td>1.6326</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E$</td>
<td>-.7954</td>
<td>.4937</td>
<td>.6735</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Xi$</td>
<td>$.6710</td>
<td>$.0555</td>
<td>-.6776</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_1$</td>
<td>$.1179</td>
<td>.03767</td>
<td>-.09241</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_0$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$B_{5d9}$</th>
<th>$B$</th>
<th>$\Gamma$</th>
<th>$\Delta$</th>
<th>$E$</th>
<th>$\Xi$</th>
<th>$R_1$</th>
<th>$R_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B$</td>
<td>.4872</td>
<td>.04599</td>
<td>-.3906</td>
<td>-.4635</td>
<td>.3169</td>
<td>.1179</td>
<td>-.08342</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>.04599</td>
<td>1.0516</td>
<td>-.3141</td>
<td>.2687</td>
<td>-.3369</td>
<td>.03767</td>
<td>0</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>-.3906</td>
<td>-.3141</td>
<td>.9127</td>
<td>.4295</td>
<td>-.3126</td>
<td>-.09241</td>
<td>0</td>
</tr>
<tr>
<td>$E$</td>
<td>-.4635</td>
<td>.2687</td>
<td>.4295</td>
<td>.6636</td>
<td>-.5617</td>
<td>-.09320</td>
<td>0</td>
</tr>
<tr>
<td>$\Xi$</td>
<td>.3169</td>
<td>-.3369</td>
<td>-.3126</td>
<td>-.5617</td>
<td>.6510</td>
<td>-.03898</td>
<td>0</td>
</tr>
<tr>
<td>$R_1$</td>
<td>$.1179</td>
<td>.03767</td>
<td>-.09241</td>
<td>-.09320</td>
<td>-.03898</td>
<td>.5889</td>
<td>0</td>
</tr>
<tr>
<td>$R_0$</td>
<td>-.08342</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>.5889</td>
<td>0</td>
</tr>
</tbody>
</table>
### Table 21 (contd.)

#### $A_2$ Symmetry Species

<table>
<thead>
<tr>
<th></th>
<th>$B_{5H}$</th>
<th>$\Delta$</th>
<th>$B_{5D}$</th>
<th>$\Delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>.6245</td>
<td>-.3442</td>
<td>B</td>
<td>.3400</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>-.3442</td>
<td>1.0816</td>
<td>$\Delta$</td>
<td>-.1350</td>
</tr>
</tbody>
</table>

#### $B_1$ Symmetry Species

<table>
<thead>
<tr>
<th></th>
<th>$B_{5H}$</th>
<th>$\Gamma$</th>
<th>L</th>
<th>$\Delta$</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>.7216</td>
<td>-.3499</td>
<td>-.09373</td>
<td>-.5496</td>
<td>.1179</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>-.3499</td>
<td>.3553</td>
<td>.03160</td>
<td>.3341</td>
<td>.03767</td>
</tr>
<tr>
<td>L</td>
<td>-.09373</td>
<td>.03160</td>
<td>.09241</td>
<td>.1329</td>
<td>-.06665</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>-.5496</td>
<td>.3341</td>
<td>.1329</td>
<td>1.1591</td>
<td>-.09241</td>
</tr>
<tr>
<td>R</td>
<td>.1179</td>
<td>.03767</td>
<td>-.06665</td>
<td>-.09241</td>
<td>1.0845</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$B_{5D}$</th>
<th>$\Gamma$</th>
<th>L</th>
<th>$\Delta$</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>.4371</td>
<td>-.1569</td>
<td>-.09373</td>
<td>-.3404</td>
<td>.1179</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>-.1569</td>
<td>.2244</td>
<td>.03160</td>
<td>.1924</td>
<td>.03767</td>
</tr>
<tr>
<td>L</td>
<td>-.09373</td>
<td>.03160</td>
<td>.09241</td>
<td>.1329</td>
<td>-.06665</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>-.3404</td>
<td>.1923</td>
<td>.1329</td>
<td>.6757</td>
<td>-.09241</td>
</tr>
<tr>
<td>R</td>
<td>.1179</td>
<td>.03767</td>
<td>-.06665</td>
<td>-.09241</td>
<td>.5889</td>
</tr>
</tbody>
</table>
### TABLE 21 (contd.)

#### B$_2$ Symmetry Species

<table>
<thead>
<tr>
<th></th>
<th>M</th>
<th>B</th>
<th>Δ</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>1.1865</td>
<td>0.6404</td>
<td>-0.6136</td>
<td>0.9878</td>
</tr>
<tr>
<td>B</td>
<td>0.6404</td>
<td>0.5740</td>
<td>-0.4444</td>
<td>0.7006</td>
</tr>
<tr>
<td>Δ</td>
<td>-0.6136</td>
<td>-0.4444</td>
<td>1.5551</td>
<td>-0.4395</td>
</tr>
<tr>
<td>E</td>
<td>0.9878</td>
<td>0.7006</td>
<td>-0.4395</td>
<td>0.9919</td>
</tr>
</tbody>
</table>

#### B$_2$D$_9$

<table>
<thead>
<tr>
<th></th>
<th>M</th>
<th>B</th>
<th>Δ</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>0.6363</td>
<td>0.2864</td>
<td>-0.3536</td>
<td>0.4719</td>
</tr>
<tr>
<td>B</td>
<td>0.2364</td>
<td>0.3147</td>
<td>-0.1852</td>
<td>0.3686</td>
</tr>
<tr>
<td>Δ</td>
<td>-0.3536</td>
<td>-0.1852</td>
<td>0.3287</td>
<td>-0.1955</td>
</tr>
<tr>
<td>E</td>
<td>0.4719</td>
<td>0.3686</td>
<td>-0.1955</td>
<td>0.5082</td>
</tr>
</tbody>
</table>

#### E Symmetry Species

<table>
<thead>
<tr>
<th></th>
<th>B'</th>
<th>Γ</th>
<th>B''</th>
<th>M''</th>
<th>L</th>
<th>Δ'</th>
<th>R</th>
<th>W</th>
<th>Δ''</th>
</tr>
</thead>
<tbody>
<tr>
<td>B'</td>
<td>0.7251</td>
<td>-0.1472</td>
<td>-0.0678</td>
<td>0.7089</td>
<td>-0.1485</td>
<td>-0.5998</td>
<td>0.1179</td>
<td>0.1307</td>
<td>-0.05019</td>
</tr>
<tr>
<td>Γ</td>
<td>-0.1472</td>
<td>1.1819</td>
<td>-0.2927</td>
<td>-0.4808</td>
<td>0.0316</td>
<td>-0.1717</td>
<td>0.0377</td>
<td>0.0517</td>
<td>-0.5059</td>
</tr>
<tr>
<td>B''</td>
<td>-0.0678</td>
<td>0.2027</td>
<td>0.6631</td>
<td>-0.0683</td>
<td>0.0819</td>
<td>-0.0502</td>
<td>0</td>
<td>-0.1312</td>
<td>-0.3945</td>
</tr>
<tr>
<td>M''</td>
<td>0.7089</td>
<td>-0.4808</td>
<td>-0.0683</td>
<td>1.0769</td>
<td>0</td>
<td>-0.5210</td>
<td>0</td>
<td>0</td>
<td>-0.09266</td>
</tr>
<tr>
<td>L</td>
<td>-0.1485</td>
<td>0.0316</td>
<td>0.0819</td>
<td>0</td>
<td>0.1976</td>
<td>0.1329</td>
<td>0</td>
<td>-0.0667</td>
<td>-0.1686</td>
</tr>
<tr>
<td>Δ'</td>
<td>-0.5998</td>
<td>-0.1717</td>
<td>-0.0502</td>
<td>-0.5210</td>
<td>0.1329</td>
<td>1.3960</td>
<td>0</td>
<td>-0.0924</td>
<td>0.0030</td>
</tr>
<tr>
<td>R</td>
<td>0.1179</td>
<td>0.0377</td>
<td>0</td>
<td>0</td>
<td>-0.0667</td>
<td>-0.0924</td>
<td>1.0846</td>
<td>0.0380</td>
<td>0</td>
</tr>
<tr>
<td>W</td>
<td>0.1307</td>
<td>0.0517</td>
<td>-0.1312</td>
<td>0</td>
<td>-0.1686</td>
<td>0.0030</td>
<td>0.0380</td>
<td>1.6356</td>
<td>0</td>
</tr>
<tr>
<td>Δ''</td>
<td>0.0502</td>
<td>0.5059</td>
<td>-0.3945</td>
<td>0.0927</td>
<td>0</td>
<td>0.2368</td>
<td>0</td>
<td>0</td>
<td>1.3176</td>
</tr>
<tr>
<td>Symmetry Species</td>
<td>( \mathcal{B}_5 \mathcal{D}_9 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------------</td>
<td>-----------------</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( b' )</td>
<td>( \Gamma )</td>
<td>( b'' )</td>
<td>( \Delta'' )</td>
<td>( L )</td>
<td>( \Delta' )</td>
<td>( R )</td>
<td>( W )</td>
<td>( \Delta'' )</td>
</tr>
<tr>
<td>( b' )</td>
<td>.4530</td>
<td>-.0555</td>
<td>-.0552</td>
<td>.3548</td>
<td>-.1485</td>
<td>-.3656</td>
<td>.1179</td>
<td>.1307</td>
<td>-.02512</td>
</tr>
<tr>
<td>( \Gamma )</td>
<td>-.0555</td>
<td>.6381</td>
<td>.1015</td>
<td>-.2406</td>
<td>.0316</td>
<td>-.0609</td>
<td>.0377</td>
<td>.0517</td>
<td>-.2532</td>
</tr>
<tr>
<td>( b'' )</td>
<td>-.0552</td>
<td>.1015</td>
<td>.3911</td>
<td>-.0683</td>
<td>.0819</td>
<td>-.0251</td>
<td>0</td>
<td>-.1312</td>
<td>-.1602</td>
</tr>
<tr>
<td>( \Delta'' )</td>
<td>.3548</td>
<td>-.2406</td>
<td>-.0683</td>
<td>.5814</td>
<td>0</td>
<td>-.2607</td>
<td>0</td>
<td>0</td>
<td>-.0927</td>
</tr>
<tr>
<td>( L )</td>
<td>-.1485</td>
<td>.0316</td>
<td>.0819</td>
<td>0</td>
<td>.1976</td>
<td>.1329</td>
<td>-.0667</td>
<td>-.1686</td>
<td>0</td>
</tr>
<tr>
<td>( \Delta' )</td>
<td>-.3656</td>
<td>-.0609</td>
<td>-.0251</td>
<td>-.2607</td>
<td>.1329</td>
<td>.7943</td>
<td>-.0924</td>
<td>.0030</td>
<td>.1185</td>
</tr>
<tr>
<td>( R )</td>
<td>.1179</td>
<td>.0377</td>
<td>0</td>
<td>0</td>
<td>-.0667</td>
<td>-.0924</td>
<td>.5890</td>
<td>.0380</td>
<td>0</td>
</tr>
<tr>
<td>( W )</td>
<td>.1307</td>
<td>.0517</td>
<td>-.1312</td>
<td>0</td>
<td>-.1686</td>
<td>.0030</td>
<td>.0380</td>
<td>.9696</td>
<td>0</td>
</tr>
<tr>
<td>( \Delta'' )</td>
<td>-.0251</td>
<td>-.2532</td>
<td>-.1602</td>
<td>-.0927</td>
<td>0</td>
<td>.1185</td>
<td>0</td>
<td>0</td>
<td>.7103</td>
</tr>
</tbody>
</table>
weight units). The S-vectors used in the computation have been given in Table 14.

I. Program for Solution of the Secular Equation

The method by which the secular equation is solved will now be described. Because of the relatively large order of some of the matrices the solution was programmed for the IBM 704 computer. A subroutine was available from the Numerical Computation Laboratory of the Ohio State University for solving a symmetrical secular equation by the Jacobi method. However, the secular equation as written in the last section is not adapted to this method as the matrix GF is not symmetric even though G and F are symmetric. Therefore the following method of solving the secular equation by successive diagonalizations of the matrices G and F was used. The characteristic equation of G, or \(|G - \lambda I| = 0\) is solved, to obtain the eigenvalues and eigenvectors of the matrix G alone. The normalized and orthogonal eigenvectors form the columns of a matrix P which transforms G to the diagonal matrix \(\Gamma\). The elements on the diagonal of \(\Gamma\) are the eigenvalues of G, which are real as G is symmetric and positive as G is positive-definite. It follows that the square root of \(\Gamma\), or \(\Gamma^{1/2}\) is a real diagonal matrix, and \(\Gamma^{1/2}\) will be specified as the positive square root having the positive square roots of the eigenvalues on the diagonal. From the relation \(P'GP = \Gamma\) there is obtained \(G = P\Gamma P'\), and \(G^{-1} = P\Gamma^{-1}P'\). The secular equation given in

---

the preceding section can be written in the following form, as \( G \) is positive-definite and therefore non-singular

\[
|F^* - \lambda G^{-1}| = 0,
\]

where for simplicity the previous matrices \( F^*_{nn} \) and \( G_{nn} \) are denoted simply by \( F^* \) and \( G \). Substitution of the immediately preceding expression for \( G^{-1} \) yields

\[
|F^* - \lambda P \Gamma^{-1} \Gamma P'| = 0.
\]

This equation is next premultiplied by \( |\Gamma^{1/2}| \) and postmultiplied by \( |P||\Gamma^{1/2}| \). This is permissible as these matrices are all non-singular (\( \Gamma^{1/2} \) has been discussed above, and since \( P \) is orthogonal, \( |P| = |P'| = \pm 1 \)). Since the product of two or more determinants equals the determinant of the product of the matrices, the secular equation assumes the form

\[
|\Gamma^{1/2} P' F^* P \Gamma^{1/2} - \lambda I| = 0.
\]

This is in turn the characteristic equation of the real symmetric matrix \( \Gamma^{1/2} P' F^* P \Gamma^{1/2} \). The latter matrix is also positive-definite, as by the preceding theorem its determinant equals \( |\Gamma||P|^2 |F^*| \), and \( \Gamma \) and \( F^* \) are positive-definite while \( |P|^2 = 1 \). The eigenvectors and eigenvalues of this matrix are also calculated by the Jacobi method. The eigenvectors form the columns of an orthogonal matrix \( B \) which diagonalizes the matrix, or

\[
B' \Gamma^{1/2} P' F^* P \Gamma^{1/2} B = \Lambda,
\]

where \( \Lambda \) is the diagonal matrix of the positive eigenvalues. The latter are identical with the roots of the original secular equation, and are therefore of the form \( \lambda_i = 4n^2 \nu_i^2 \), where the \( \nu_i \)'s are the normal frequencies of vibration.
From the definitions of $P$ and $\Gamma$, and the orthogonality of $B$,
\[ B^t \Gamma^{-\frac{1}{2}} P^t \Gamma^{-\frac{1}{2}} B = I, \]
where $I$ is the unit matrix. Postmultiplication of this equation by the next preceding equation yields
\[ B^t \Gamma^{-\frac{1}{2}} P^t \Gamma^{-\frac{1}{2}} B = \Lambda. \]
This may be written
\[ GF^t L = L \Lambda, \]
where
\[ L = P \Gamma^{-\frac{1}{2}} B. \]
It follows that the columns of $L$ are the eigenvectors of the matrix $GF^*$, or of the original secular equation of the vibration problem as obtained in the preceding section. This is the eigenvector matrix $L$ introduced by Wilson, and yields the transformation relating the normal coordinates $Q$ to the final symmetry coordinates $S$ for the given species, or
\[ S = LQ, \]
where $S$ and $Q$ are column matrices. The element $L_{ij}$ of $L$ is the amplitude of $S_i$ when the normal coordinate $Q_j$ is excited with unit amplitude, and $Q_i = 0, i \neq j$. Also of interest is the inverse transformation,
\[ Q = L^{-1} S, \]
which may be transposed to obtain
\[ Q' = S'K, \]
where
\[ K = (L^{-1})' = P \Gamma^{-\frac{1}{2}} B, \]
and $Q'$ and $S'$ are row matrices. The elements of the $j$th column of $K$ yield the coefficients in the linear combination of the $S_i$'s which constitutes the $j$th normal mode. That is,
\[ Q_j = \sum_i K_{ij} S_j. \]
It should be noted that the matrices $L$ and $K$ are generally not orthogonal. A more detailed discussion of the form of the normal modes, particularly with regard to the distribution of potential and kinetic energy in the molecule when each normal mode is excited, has been given by Taylor.\textsuperscript{14}

In the process of determining the best force constants for pentaborane by the procedure to be described it is necessary to try many different values of these constants. With each new set of force constants, or elements of the force constant matrix $f$ for the valence coordinates, it is necessary to recompute the force constant matrix $F^*$. The computer was programmed to compute the matrices $F$ for the symmetry coordinates of each species from the matrix $f$ by means of the relations given in Table 18. As discussed in section $H$, $F^*$, the force constant matrix following the elimination of redundancies is related to $F$ for each species by

$$F^* = Y'FY,$$

where $Y$ is the $(n + r) \times n$ matrix,

$$Y = \begin{pmatrix}
A^{-1} & A
\end{pmatrix}.$$

The matrices $Y$ are obtained by taking the final $n$ columns of the matrices $U^{-1}$ of Table 20. The secular equation may therefore be written in terms of $F$ as

$$| \Gamma^{\frac{3}{2}} (YP)^{\frac{1}{2}} FY - \lambda I | = 0,$$

of

$$| (YP)^{\frac{1}{2}} F (YP)^{\frac{1}{2}} - \lambda I | = 0.$$

The matrix $(YP)^{\frac{1}{2}}$ does not depend on the force constants, as $P \Gamma^{\frac{3}{2}}$

depends only on the $G$ matrix or the atomic masses and geometry of the molecule, while $Y$ depends only on the redundancy conditions or molecular geometry. Thus, the matrices $(YP^{-\frac{1}{2}})$ can be calculated once and for all for each symmetry species, for normal and deuterated pentaborane, prior to the assignment of values to the force constants. Following the assignment of a trial set of force constants the computer is programmed to calculate $(YP^{-\frac{1}{2}})'F(YP^{-\frac{1}{2}})$ by matrix multiplication, and then to diagonalize this matrix by the Jacobi method to obtain $B$, the eigenvector matrix $K = P \Gamma^{-\frac{1}{2}}B$, and the eigenvalues $\lambda$.

### J. Selection of Force Constants to Be Retained

A symmetry species with $n$ degrees of freedom contributes $\frac{1}{2}n(n+1)$ distinct force constants to the general quadratic potential function for the molecule, since the matrix $F^*$ of section $H$ is symmetric. On this basis, there are 98 independent force constants in the general quadratic potential function for pentaborane. These force constants will be linear combinations of valence-type force constants for the original internal coordinates, and only these linear combinations can be determined by studies of the molecule of given symmetry (additional valence force constants are determinable only if the symmetry of the molecule is decreased by unsymmetrical isotopic substitution). It will be recalled that the force constants for valence coordinates are equal in isotopically substituted molecules to a high degree of approximation. If the symmetry, symmetry coordinates, and redundancies are the same for the two molecules, as for $B_5^5H_0$ and $B_5^5D_0$, then the matrices $F$ and $F^*$ are also identical for the two isotopic species, but of course the frequencies and normal modes differ for the two molecules.
Since there are only 25 infrared or Raman active frequencies for pentaborane, it is obvious that even with complete data available for normal and completely deuterated pentaborane the maximum number of force constants which could be determined is 50. Actually the number of frequencies which are observed with sufficient intensity to be useful totals about 40 for both molecules. It is of course desirable to use fewer force constants than the number of observed frequencies so that some internal checks for consistency of the frequency assignments and force constants are available. Hence, it is probably undesirable to try to obtain the values of more than twenty or thirty force constants for pentaborane. The procedure used was the usual one of selecting the force constants assumed to be most important and setting the remaining force constants equal to zero. Unfortunately, even if a set of force constants which gives calculated frequencies in exact agreement with the observed frequencies is obtained, they are not generally unique. In general there exists an infinite number of sets of force constants capable of giving the observed frequencies for a single molecule unless each symmetry species contains only a single mode. The number of additional isotopic molecules required for a complete determination of force constants depends upon their symmetries and the degree of the secular equations for each species. In spite of this element of uncertainty, the calculated force constants are still useful. They aid in confirming the frequency assignment and make possible the estimation of unobserved or inactive frequencies. In addition to their general interest the latter are necessary for the calculation of the vibrational contributions to thermodynamic properties. It may be possible to
transfer some of the force constants obtained for pentaborane to other more complicated boron hydrides, thus simplifying the difficulties in normal coordinate treatments of these molecules.

The choice of which force constants to use is not easy. Certainly it is desirable to use those force constants which have the greatest effect on the potential energy. For this reason all the diagonal valence-type force constants have been retained. There are 12 of these diagonal force constants, but the number was reduced to 11 by the assumption that the force constants for B-H (base) and B₀-H₀ (apex) stretching were equal. Since there was really no logical method of choosing a priori the most important valence-type interaction constants, the program was written in such a way that it was possible to include 29 interaction force constants. Subsequently the 19 of these which appeared to be of least importance were discarded. The 29 interaction constants to be considered initially were chosen largely on the basis of physical intuition. Interaction constants for valence coordinates involving adjacent or common bonds or angles were favored. It was assumed that the r coordinates (B-H stretching) did not interact with any of the other coordinates. This is a good approximation even though not physically correct because of the high frequency of B-H stretching. The 11 diagonal force constants and 29 interaction constants chosen are listed in Table 22. The symbols used for the force constants have been previously defined in connection with the valence force constant matrices given in Table 15.

Before proceeding to a description of the computational methods used in determining the force constants, it is necessary to explain the
| Table 22 | Valence-Type Force Constants Retained for Pentaborane |

**Diagonal Force Constants**

\[
k_{rr} = f_{r_0} r_0
\]

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_{rr})</td>
<td>(f_{r_0} r_0)</td>
</tr>
<tr>
<td>(k_{ll})</td>
<td>(p_{\rho \rho})</td>
</tr>
<tr>
<td>(p_{mm})</td>
<td>(k_{yy})</td>
</tr>
<tr>
<td>(k_{\alpha \alpha})</td>
<td>(k_{dd})</td>
</tr>
</tbody>
</table>

**Interaction Constants**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>(h_{ll})</td>
<td>(a_{\alpha \alpha})</td>
</tr>
<tr>
<td>(n_{ll})</td>
<td>(a_{\Delta \Delta})</td>
</tr>
<tr>
<td>(k_{\alpha \alpha\alpha})</td>
<td>(a_{\beta \beta})</td>
</tr>
<tr>
<td>(k_{\alpha \gamma\alpha})</td>
<td>(a_{\gamma \gamma})</td>
</tr>
<tr>
<td>(k_{\alpha \gamma\gamma})</td>
<td>(a_{\Delta \Delta})</td>
</tr>
<tr>
<td>(h_{\alpha \gamma\alpha})</td>
<td>(a_{\alpha \alpha})</td>
</tr>
<tr>
<td>(n_{\alpha \gamma\gamma})</td>
<td>(a_{\beta \beta})</td>
</tr>
<tr>
<td>(a_{1m})</td>
<td>(v_{mm})</td>
</tr>
</tbody>
</table>
units used in the normal coordinate calculation. Kilpatrick and Pitzer have introduced a set of units which are very convenient for normal coordinate calculations. Bond lengths are expressed in Angstrom units and masses in atomic weight units. Define \( Z = N/40 \pi^2 c^2 = 1.69765 \), where \( N \) is Avogadro's number and \( c \) is the velocity of light in cm. sec\(^{-1}\)

Force constants in c. g. s. units are to be multiplied by the following factors: (1) \( 10^{-5} Z \) for principal stretching constants or stretching-stretching interaction constants; (2) \( 10^{11} Z \) for principal bending constants or bending-bending interaction constants; and (3) \( 10^{3} Z \) for stretching-bending interaction constants. With these conventions the roots \( \lambda \) of the secular equation are related to the frequencies of vibration \( \nu \) in wave numbers by the equation

\[
\lambda = (\nu/1000)^2.
\]

Thus, the roots lie in a convenient numerical range of about 0.1 to 10 for most molecules, whereas with c. g. s. units they are greater by a factor \( 3.6 \times 10^{23} \). Another disadvantage of using c. g. s. units is that the \( F \) and \( G \) matrices will contain elements of widely different orders of magnitude, whereas with the units of Kilpatrick and Pitzer the range of magnitudes is much smaller.

**K. Method of Steepest Descents for Determination of Force Constants**

The procedure for computation of the roots and eigenvectors of the secular equation has been described in section I. This procedure assumes that a set of valence force constants is available. The

conventional procedure is to estimate as many force constants as possible on the basis of analogy with similar molecules (so-called "transference" of force constants), and then to improve these by trial and error procedures so as to improve the agreement between calculated and observed frequencies. However, such unsystematized trial and error procedures become difficult or entirely impracticable if (1) the number of force constants to be determined is relatively large; and (2) little if any aid in estimating the force constants by analogy or transference is available because of the unique structure of the molecule. Both conditions apply in large degree to pentaborane. There is perhaps no series of compounds to which the second of these conditions is more applicable than the boron hydrides with their unusual structures. The only other boron hydride for which normal coordinate analysis has been carried out is diborane,¹⁶,¹⁷ and these provided only very limited aid in selecting force constants for pentaborane (primarily an estimate of the non-bridge B-H stretching constant, because the single bridges connecting pairs of base boron atoms in pentaborane bears little resemblance to the double bridge in diborane). It was therefore considered imperative if any progress was to be made to develop a systematized and largely automated procedure in which an electronic computer would carry out much of the trial and error procedure without any instructions other than those incorporated into the program. It was decided that the most


promising procedure was a method of steepest descents of the same
general type as has been applied to other physical problems in recent
years (a general discussion has been given by Southwell,18 and an
application to molecular orbital theory has been described by McWeeny19).
As used here the method of steepest descents refers to the most effi-
cient minimization in successive steps of a suitably chosen error
function (it has no relation to Debye's method for the asymptotic
evaluation of contour integrals using the path of steepest descent at a
saddlepoint). The error function is usually a sum of squared errors (or
its square root), in which case the method is a variation of the method
of least squares. However, from the present viewpoint the steepest
descent procedure for successive partial minimizations is of more
importance than the particular function minimized.

As previously discussed the valence force constants comprise the
elements of a square symmetric matrix \( f \), with the principal constants
on the diagonal and interaction constants off the diagonal. In a
symmetrical molecule many of the constants of each type may be identical.
Let the number of distinct force constants of both types be \( m \). It is
convenient to regard these \( m \) force constants as the elements of a
column matrix \( \overline{f} \). The ordering of the constants is arbitrary, although
it is natural to place the principal constants before the interaction
constants. Of course in the calculation the force constants are regarded
as variable parameters so that \( \overline{f} \) is a representation of a vector in the

18. R. V. Southwell, Relaxation Methods in Engineering Science,
Oxford University Press, Oxford, 1940.

space of the (distinct) force constants. The only general limitation on $\mathbf{f}$ is that it must be in that region of the space for which the reduced symmetry force constant matrices described in section I, or the matrices $\mathbf{F}^*$, are positive-definite (more accurately, the quadratic potential energy functions derived from these matrices are positive-definite).

This condition is necessarily fulfilled if the roots $\lambda$ of the secular equation are all positive, as the $\mathbf{G}$ matrix is positive-definite.

The measure of the error between the calculated roots $\lambda_i$ and observed roots $\lambda_i^0$ of the secular equation which has been adopted is the root-mean-square percentage error of the calculated roots, or

$$E = 100 \left[ \sum_i \left( \frac{\lambda_i - \lambda_i^0}{\lambda_i^0} \right)^2 \right]^{\frac{1}{2}}$$

In practice the sum must be restricted to those observed frequencies which are sufficiently reliable. In general a weighted sum might be preferable, but the unweighted sum was used for simplicity. As explained in section J the roots are related to the vibration frequencies in cm$^{-1}$ by $\lambda_i = (\nu_i/1000)^2$ and $\lambda_i^0 = (\nu_i^0/1000)^2$. If the errors are small for the final force constants, the percentage error in each $\nu_i$ is approximately half that in $\lambda_i$. Thus, the root-mean-square percentage error in the $N$ frequencies is approximately $E/2N^{\frac{1}{2}}$.

Let the initial set of force constants be $f_{1i}^0$, ..., $f_{1i}^0$, ..., representing the elements of the vector $\mathbf{f}^0$, and denote the corresponding error by $E^0$. If $f_{1i}$ alone is changed to $f_{1i} = f_{1i}^0 + \Delta f_{1i}$, a new value of the error, $E = E^0 + \Delta E_{1i}$, will be obtained. Provided $\Delta f_{1i}$ is sufficiently small ($\partial E/\partial f_{1i})^0$ may be approximated by $\Delta E_{1i}/\Delta f_{1i}$. The gradient of $E$ at $\mathbf{f}^0$, or $(\nabla_{\mathbf{f}} E)^0$, is a vector or column matrix with $(\partial E/\partial f_{1i})^0$, or
(approximately) \( \Delta E/\Delta f_1 \) as its \( i \)th component or element. As is well known, the gradient is directed along (tangent to) the path along which the directional derivative of \( E \) in the space of \( f \) has its maximum value. Conversely, \( E \) decreases most rapidly (per linear "distance" traveled) in the direction of the negative of the gradient. Two anti-parallel vectors have components which are in a constant negative ratio to one another. Thus, the path of steepest initial rate of decrease (or descent) for \( E \) at \( F^0 \) is that for which

\[
\Delta f_1 = -c(\partial E/\partial f_1)^0,
\]

or

\[
\Delta F^0 = -c(\nabla_f E)^0,
\]

with \( c \) a positive constant. If in a given descent certain of the \( f_1 \)'s are held constant, then the first equation still defines the path of steepest descent in the sub-space of the remaining \( f_1 \)'s, which is directed oppositely to the projection of \( (\nabla_f E)^0 \) on this sub-space. In some applications of the method of steepest descents second derivatives of \( E \) are also computed and \( E \) approximated as a quadratic or parabolic function of \( \Delta F \) along the path of steepest descent. A single descent is then made with \( c \) determined so as to minimize this quadratic approximation to \( E \), following which \( \nabla_f E \) is recomputed at the new position and additional descents made in the same manner. In the present application using a computer it was decided that it would be simpler and more reliable to make successive small descents using the same gradient, \( (\nabla_f E)^0 \), and proceed in this manner until \( E \) was observed to increase. The computer was programmed to select the value of \( F \) following the immediately preceding descent, corresponding approximately to a conditional minimum of \( E \) on this straight-line path in the space of \( F \), as the value
of $\Phi^0$ for the next series of descents. Of course $(\nabla f)^0$ was recomputed at the new value of $\Phi^0$ before proceeding. The computer was instructed as to how many such series of descents it should make before stopping. The value of $c$ for each series of descents was taken as

$$c = \frac{b}{\text{Max} |(\partial E/\partial f^0)|}$$

where $b$ was a constant which varied from 0.005 to 0.05 (the value of $b$ or the fineness of the descents was decreased as the calculations progressed), and the denominator on the right-hand side is the maximum absolute value of the partial derivatives at $\Phi^0$.

The initial $\Phi^0$ for the first descent was obtained by choosing reasonable (positive) values for the principal force constants and setting all interaction constants equal to zero. The preceding process was applied to the principal force constants until a minimum in the error was obtained. Because several $B_1$ and $B_2$ frequencies were missing, only the $A_1$ and $E$ frequencies were used in the steepest descent calculation. After the best set of force constants for the $A_1$ and $E$ frequencies were obtained, the $B_1$ and $B_2$ frequencies were calculated, but there was no attempt to improve the error in the $B_1$ and $B_2$ frequencies by application of the steepest descent method. After the best set of principal force constants was obtained, the interaction constants were changed by small amounts. Then those interaction constants which had the greatest effect on the error were treated by the steepest descent method. Finally all the force constants (principal and the chosen interaction constants) were varied until a minimum in the error was obtained. In order to save computer time in the calculation, this method was modified slightly. Once the force constants which had the
greatest effect on the error were determined, not all of the force con-
stants were changed in each descent. Usually four to ten force constants
were varied in a given descent. Then on following descents a different
group of force constants were changed. Eventually all the force
constants were subjected to many descents.

L. Calculated Frequencies and Normal Coordinates

The results of the application of the method of steepest descents
described in the preceding section will now be presented. The observed
values of the frequencies were taken from the assignment discussed in
detail in chapter VIII and summarized in Table 34. This assignment was
based on selection rules, the order and product rules, polarization
data, band contours, and intensities, and comparison of the statistical
and calorimetric entropies. Three different sets of force constants
were found giving (conditional) minimum values for the error. That is,
further changes in each set of force constants gave only extremely small
decreases in the error. The three different sets of force constants
will be denoted by I, II, and III. Sets I and II were obtained prior to
the introduction of the coordinate $\theta$ by starting with different
initial approximations for the other force constants. The chief differ-
ence in the initial approximations for sets I and II was the value
assigned to the force constant $k_{11}$. The final values obtained for this
force constant were 3.901 for I and 2.587 for II. There were only minor
differences in the other force constants, as shown in Table 23. The
existence of two minima at these values of $k_{11}$ was definitely estab-
lished. Sets I and II both gave fairly good values of the frequencies
for the $A_1$ and $E$ vibrational modes of pentaborane as shown in Table 24.
The mean error in the frequencies was slightly smaller for set I (see below). However, when I or II were used to calculate the $B_1$ and $B_2$ frequencies the results were very poor. For the $B_2$ modes of $B_5^1H_9$, calculated frequencies of 109 and 114 cm.\(^{-1}\) were obtained for I and II, respectively. These values are much lower than the observed frequency of 596 cm.\(^{-1}\). This low frequency $B_2$ mode is believed to be a bridge rocking frequency and apparently is not very well described by the coordinates previously used. That is, as a result of the orientation of the plane of the bridges, bridge rocking produces little deformation in certain of the previously selected valence angles, particularly $\beta$, and as a result if a reasonable value is assigned to $p_{\perp \parallel}$ there is insufficient resistance to bridge rocking. For this reason it was considered necessary at this stage of the calculation to add a new force constant $k_{\theta \phi}$, where $\theta$ is the change in the angle between the planes $B_0BB$ and $BB'_H$, or the planes of a bridge and the adjacent side of the boron pyramid (see Fig. 1). An initial approximation for $k_{\theta \phi}$ was chosen such that the lowest calculated $B_2$ frequency was about 500 cm.\(^{-1}\), and the method of steepest descents was applied until a minimum in the error was obtained. By this means the set of force constants III, shown in Table 23, was obtained. These not only give the best fit for the $A_1$ and $E$ frequencies, as shown in Table 24, but also give fairly reasonable values of the $B_1$ and $B_2$ frequencies. The average percentage errors of the $A_1$ and $E$ frequencies for the three sets I, II, and III are 2.78, 2.91, and 2.28, respectively. The maximum percentage errors for I, II, and III are 11.5, 11.0, and 9.0, respectively. In Table 25, the calculated $B_1$, $B_2$, and $A_2$ frequencies for the three sets of force constants
are given. The observed \( B_1 \) and \( B_2 \) frequencies based on the assignment in the next chapter are also given. The \( A_2 \) modes are inactive in both the infrared and Raman spectra.

In Table 26, the eigenvectors of normal and deuterated pentaborane are given for each frequency of each symmetry species. For the \( E \) species only one mode of each degenerate pair is given. These were calculated from the best set of force constants (III of Table 23). The first column in Table 26 lists the symmetry coordinates retained after the removal of redundancies (sections G and H), and the frequencies are given at the top in \( \text{cm}^{-1} \). Under each frequency is given the corresponding column of the matrix \( K = (L^{-1})' \), discussed in section I, or the coefficients in the linear combination of symmetry coordinates at the left which constitutes that normal mode of vibration.
<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
<th>III</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{rr}$</td>
<td>6.215</td>
<td>6.215</td>
<td>6.229</td>
</tr>
<tr>
<td>$k_{ll}$</td>
<td>3.901</td>
<td>2.587</td>
<td>3.487</td>
</tr>
<tr>
<td>$p_{mm}$</td>
<td>1.687</td>
<td>1.829</td>
<td>1.914</td>
</tr>
<tr>
<td>$k_{\alpha\alpha}$</td>
<td>.614</td>
<td>.750</td>
<td>.553</td>
</tr>
<tr>
<td>$p_{BB}$</td>
<td>.429</td>
<td>.486</td>
<td>.484</td>
</tr>
<tr>
<td>$k_{YY}$</td>
<td>.545</td>
<td>.566</td>
<td>1.287</td>
</tr>
<tr>
<td>$p_{\Delta\Delta}$</td>
<td>1.138</td>
<td>1.109</td>
<td>.493</td>
</tr>
<tr>
<td>$k_{\epsilon\epsilon}$</td>
<td>.134</td>
<td>.127</td>
<td>-.063</td>
</tr>
<tr>
<td>$k_{WW}$</td>
<td>.299</td>
<td>.335</td>
<td>.307</td>
</tr>
<tr>
<td>$k_{dd}$</td>
<td>2.711</td>
<td>2.693</td>
<td>2.769</td>
</tr>
<tr>
<td>$n_{ll}$</td>
<td>-.084</td>
<td>-.103</td>
<td>-.185</td>
</tr>
<tr>
<td>$k_{\lambda\gamma}$</td>
<td>-.192</td>
<td>-.190</td>
<td>-.229</td>
</tr>
<tr>
<td>$k_{\alpha\gamma}$</td>
<td>-.170</td>
<td>-.250</td>
<td>-.199</td>
</tr>
<tr>
<td>$a_{1\lambda}$</td>
<td>.233</td>
<td>.142</td>
<td></td>
</tr>
<tr>
<td>$a_{\lambda m}$</td>
<td>.166</td>
<td>.098</td>
<td>-.062</td>
</tr>
<tr>
<td>$a_{\alpha\Delta}$</td>
<td>-.148</td>
<td>-.227</td>
<td>-.204</td>
</tr>
<tr>
<td>$a_{\gamma m}$</td>
<td>.179</td>
<td>.197</td>
<td></td>
</tr>
<tr>
<td>$a_{\gamma\beta}$</td>
<td>-.165</td>
<td>-.148</td>
<td>-.076</td>
</tr>
<tr>
<td>$q_{mm}$</td>
<td>-.243</td>
<td>-.237</td>
<td>-.387</td>
</tr>
<tr>
<td>$q_{\Delta\Delta}$</td>
<td>-.101</td>
<td>-.106</td>
<td>-.414</td>
</tr>
<tr>
<td>$a_{m\epsilon}$</td>
<td>.133</td>
<td>.152</td>
<td>.162</td>
</tr>
<tr>
<td>$k_{\theta\theta}$</td>
<td></td>
<td></td>
<td>.814</td>
</tr>
</tbody>
</table>
TABLE 24
CALCULATED $A_1$ AND $E$ FREQUENCIES

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B_{5}^{D}H_{9}$:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A_1$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2610</td>
<td>2621</td>
<td>.4</td>
<td>2615</td>
<td>.2</td>
<td>2619</td>
<td>.3</td>
</tr>
<tr>
<td>2598</td>
<td>2605</td>
<td>.3</td>
<td>2604</td>
<td>.2</td>
<td>2611</td>
<td>.5</td>
</tr>
<tr>
<td>1842</td>
<td>1791</td>
<td>-2.8</td>
<td>1807</td>
<td>-1.9</td>
<td>1883</td>
<td>2.2</td>
</tr>
<tr>
<td>1123</td>
<td>1186</td>
<td>5.6</td>
<td>1179</td>
<td>5.0</td>
<td>1140</td>
<td>1.5</td>
</tr>
<tr>
<td>986</td>
<td>954</td>
<td>-3.2</td>
<td>987</td>
<td>1.1</td>
<td>1014</td>
<td>2.8</td>
</tr>
<tr>
<td>798</td>
<td>813</td>
<td>1.9</td>
<td>823</td>
<td>3.1</td>
<td>839</td>
<td>5.1</td>
</tr>
<tr>
<td>700</td>
<td>665</td>
<td>-5.0</td>
<td>623</td>
<td>-11.0</td>
<td>637</td>
<td>-9.0</td>
</tr>
<tr>
<td>$E$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2598</td>
<td>2611</td>
<td>.5</td>
<td>2609</td>
<td>.4</td>
<td>2607</td>
<td>.3</td>
</tr>
<tr>
<td>1801</td>
<td>1783</td>
<td>-1.0</td>
<td>1823</td>
<td>1.2</td>
<td>1838</td>
<td>2.0</td>
</tr>
<tr>
<td>1621</td>
<td>1637</td>
<td>1.0</td>
<td>1666</td>
<td>2.8</td>
<td>1498</td>
<td>-7.6</td>
</tr>
<tr>
<td>1413</td>
<td>1250</td>
<td>-11.5</td>
<td>1280</td>
<td>-9.4</td>
<td>1330</td>
<td>-5.9</td>
</tr>
<tr>
<td>1034</td>
<td>1031</td>
<td>-3</td>
<td>1026</td>
<td>-8</td>
<td>988</td>
<td>-4.4</td>
</tr>
<tr>
<td>883</td>
<td>908</td>
<td>2.8</td>
<td>904</td>
<td>2.4</td>
<td>882</td>
<td>-1</td>
</tr>
<tr>
<td>700</td>
<td>701</td>
<td>.1</td>
<td>724</td>
<td>3.4</td>
<td>713</td>
<td>1.9</td>
</tr>
<tr>
<td>616</td>
<td>613</td>
<td>-5</td>
<td>597</td>
<td>-3.1</td>
<td>626</td>
<td>1.6</td>
</tr>
<tr>
<td>567</td>
<td>538</td>
<td>-5.1</td>
<td>539</td>
<td>-4.9</td>
<td>573</td>
<td>1.1</td>
</tr>
<tr>
<td>$B_{5}^{D}D_{9}$:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A_1$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1980</td>
<td>1986</td>
<td>-.3</td>
<td>1966</td>
<td>-.7</td>
<td>1969</td>
<td>-.6</td>
</tr>
<tr>
<td>1967</td>
<td>1936</td>
<td>-1.6</td>
<td>1934</td>
<td>-1.7</td>
<td>1947</td>
<td>-1.0</td>
</tr>
<tr>
<td>1391</td>
<td>1394</td>
<td>-0.2</td>
<td>1387</td>
<td>-3</td>
<td>1386</td>
<td>-4</td>
</tr>
<tr>
<td>959</td>
<td>945</td>
<td>-1.5</td>
<td>913</td>
<td>-4.8</td>
<td>992</td>
<td>3.4</td>
</tr>
<tr>
<td>746</td>
<td>758</td>
<td>1.6</td>
<td>752</td>
<td>3.8</td>
<td>767</td>
<td>2.8</td>
</tr>
<tr>
<td>737</td>
<td>682</td>
<td>-7.5</td>
<td>705</td>
<td>-4.3</td>
<td>717</td>
<td>-2.7</td>
</tr>
<tr>
<td>512</td>
<td>541</td>
<td>5.7</td>
<td>545</td>
<td>6.4</td>
<td>519</td>
<td>1.4</td>
</tr>
<tr>
<td>$E$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1967</td>
<td>1954</td>
<td>-.7</td>
<td>1947</td>
<td>-1.0</td>
<td>1935</td>
<td>-1.6</td>
</tr>
<tr>
<td>1335</td>
<td>1352</td>
<td>1.3</td>
<td>1367</td>
<td>2.4</td>
<td>1319</td>
<td>-1.2</td>
</tr>
<tr>
<td>1178</td>
<td>1169</td>
<td>-.8</td>
<td>1190</td>
<td>1.0</td>
<td>1172</td>
<td>-.5</td>
</tr>
<tr>
<td>1056</td>
<td>1076</td>
<td>1.9</td>
<td>1054</td>
<td>-2</td>
<td>1021</td>
<td>-3.3</td>
</tr>
<tr>
<td>842</td>
<td>869</td>
<td>3.2</td>
<td>863</td>
<td>2.5</td>
<td>840</td>
<td>-.2</td>
</tr>
<tr>
<td>741</td>
<td>689</td>
<td>-7.0</td>
<td>712</td>
<td>-3.9</td>
<td>745</td>
<td>.5</td>
</tr>
<tr>
<td>639</td>
<td>631</td>
<td>-1.3</td>
<td>627</td>
<td>-1.9</td>
<td>609</td>
<td>-4.7</td>
</tr>
<tr>
<td>448</td>
<td>459</td>
<td>2.5</td>
<td>464</td>
<td>3.6</td>
<td>453</td>
<td>1.1</td>
</tr>
<tr>
<td>439</td>
<td>395</td>
<td>-10.0</td>
<td>405</td>
<td>-7.7</td>
<td>444</td>
<td>1.1</td>
</tr>
<tr>
<td>Assigned Frequency</td>
<td>Calc. I</td>
<td>Calc. II</td>
<td>Calc. III</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------------------</td>
<td>--------</td>
<td>----------</td>
<td>-----------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( B_1 )</td>
<td>2598</td>
<td>2605</td>
<td>2603</td>
<td>2604</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1690</td>
<td>1729</td>
<td>1586</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1286</td>
<td>1318</td>
<td>1033</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>785</td>
<td>573</td>
<td>507</td>
<td>551</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>596</td>
<td>300</td>
<td>305</td>
<td>415</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( B_2 )</td>
<td>1750</td>
<td>1771</td>
<td>1651</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1048</td>
<td>1052</td>
<td>1114</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>738</td>
<td>744</td>
<td>740</td>
<td>740</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>470</td>
<td>109</td>
<td>114</td>
<td>545</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( A_2 )</td>
<td>1597</td>
<td>1639</td>
<td>1776</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>962</td>
<td>963</td>
<td>866</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( B_2 )</td>
<td>1944</td>
<td>1936</td>
<td>1931</td>
<td>1928</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( D_2 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( A_2 )</td>
<td>1319</td>
<td>1334</td>
<td>1275</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1205</td>
<td>744</td>
<td>748</td>
<td>790</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>682</td>
<td>699</td>
<td>675</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>77</td>
<td>81</td>
<td>388</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( A_2 )</td>
<td>1140</td>
<td>1173</td>
<td>1288</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>772</td>
<td>771</td>
<td>684</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE 26
NORMAL COORDINATES

\[ A_1 (B_5H_9) \]

<table>
<thead>
<tr>
<th></th>
<th>2619</th>
<th>2611</th>
<th>1883</th>
<th>1140</th>
<th>1014</th>
<th>839</th>
<th>637</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \beta )</td>
<td>.081</td>
<td>.100</td>
<td>.156</td>
<td>1.427</td>
<td>-1.913</td>
<td>.316</td>
<td>2.438</td>
</tr>
<tr>
<td>( \Gamma )</td>
<td>-.045</td>
<td>.012</td>
<td>.683</td>
<td>-.064</td>
<td>.087</td>
<td>-.374</td>
<td>-.986</td>
</tr>
<tr>
<td>( \Delta )</td>
<td>.005</td>
<td>.013</td>
<td>.063</td>
<td>.739</td>
<td>-.103</td>
<td>-.668</td>
<td>-.641</td>
</tr>
<tr>
<td>( E )</td>
<td>.182</td>
<td>.073</td>
<td>-.122</td>
<td>1.682</td>
<td>-2.393</td>
<td>2.857</td>
<td>1.975</td>
</tr>
<tr>
<td>( M )</td>
<td>.118</td>
<td>.010</td>
<td>-.219</td>
<td>.624</td>
<td>-1.749</td>
<td>1.727</td>
<td>-.605</td>
</tr>
<tr>
<td>( R_1 )</td>
<td>-.853</td>
<td>.404</td>
<td>-.113</td>
<td>.096</td>
<td>-.085</td>
<td>.256</td>
<td>-.146</td>
</tr>
<tr>
<td>( R_0 )</td>
<td>-.403</td>
<td>-.360</td>
<td>.025</td>
<td>.136</td>
<td>-.174</td>
<td>.027</td>
<td>.200</td>
</tr>
</tbody>
</table>

\[ A_1 (B_5D_9) \]

<table>
<thead>
<tr>
<th></th>
<th>1969</th>
<th>1947</th>
<th>1386</th>
<th>992</th>
<th>767</th>
<th>717</th>
<th>519</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \beta )</td>
<td>-.228</td>
<td>.263</td>
<td>.379</td>
<td>2.372</td>
<td>1.204</td>
<td>-1.353</td>
<td>1.943</td>
</tr>
<tr>
<td>( \Gamma )</td>
<td>.108</td>
<td>.037</td>
<td>.897</td>
<td>-.315</td>
<td>-.097</td>
<td>.123</td>
<td>-1.319</td>
</tr>
<tr>
<td>( \Delta )</td>
<td>-.016</td>
<td>.037</td>
<td>.144</td>
<td>.597</td>
<td>-.614</td>
<td>-.561</td>
<td>-1.273</td>
</tr>
<tr>
<td>( E )</td>
<td>-.490</td>
<td>.182</td>
<td>-.037</td>
<td>3.320</td>
<td>2.222</td>
<td>1.094</td>
<td>2.559</td>
</tr>
<tr>
<td>( M )</td>
<td>-.312</td>
<td>.018</td>
<td>-.277</td>
<td>1.676</td>
<td>1.917</td>
<td>1.115</td>
<td>-.498</td>
</tr>
<tr>
<td>( R_1 )</td>
<td>1.081</td>
<td>.576</td>
<td>-.283</td>
<td>.377</td>
<td>.176</td>
<td>.491</td>
<td>-.143</td>
</tr>
<tr>
<td>( R_0 )</td>
<td>.564</td>
<td>-1.112</td>
<td>.113</td>
<td>.459</td>
<td>.203</td>
<td>-.223</td>
<td>.297</td>
</tr>
</tbody>
</table>
### Table 26 (contd.)

<table>
<thead>
<tr>
<th></th>
<th>( A_2 (\text{B}_5\text{H}_9) )</th>
<th></th>
<th>( A_2 (\text{B}_5\text{D}_9) )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1776</td>
<td>666</td>
<td>1288</td>
</tr>
<tr>
<td>( B )</td>
<td>( 1.000 )</td>
<td>( 1.000 )</td>
<td>( 1.000 )</td>
</tr>
<tr>
<td>( \Delta )</td>
<td>( -.741 )</td>
<td>( 6.956 )</td>
<td>( -.563 )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>( B_1 (\text{B}_5\text{H}_9) )</th>
<th></th>
<th>( B_1 (\text{B}_5\text{D}_9) )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2604</td>
<td>1586</td>
<td>1033</td>
</tr>
<tr>
<td>( B )</td>
<td>( .027 )</td>
<td>( -.910 )</td>
<td>( 1.194 )</td>
</tr>
<tr>
<td>( \Gamma )</td>
<td>( .007 )</td>
<td>( .346 )</td>
<td>( .535 )</td>
</tr>
<tr>
<td>( L )</td>
<td>( -.009 )</td>
<td>( -1.216 )</td>
<td>( 1.057 )</td>
</tr>
<tr>
<td>( \Delta )</td>
<td>( -.001 )</td>
<td>( .207 )</td>
<td>( .956 )</td>
</tr>
<tr>
<td>( R )</td>
<td>( .956 )</td>
<td>( .047 )</td>
<td>( -.002 )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>( B_2 (\text{B}_5\text{D}_9) )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1928</td>
</tr>
<tr>
<td>( B )</td>
<td>( .066 )</td>
</tr>
<tr>
<td>( \Gamma )</td>
<td>( .018 )</td>
</tr>
<tr>
<td>( L )</td>
<td>( -.026 )</td>
</tr>
<tr>
<td>( \Delta )</td>
<td>( -.002 )</td>
</tr>
<tr>
<td>( R )</td>
<td>( 1.284 )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>( B_2 (\text{B}_5\text{H}_9) )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1651</td>
</tr>
<tr>
<td>( M )</td>
<td>( 1.036 )</td>
</tr>
<tr>
<td>( B )</td>
<td>( .762 )</td>
</tr>
<tr>
<td>( \Delta )</td>
<td>( -.354 )</td>
</tr>
<tr>
<td>( \varepsilon )</td>
<td>( -1.048 )</td>
</tr>
</tbody>
</table>
TABLE 26 (contd.)

\[
\begin{array}{cccccc}
3 (B^9) & 1275 & 790 & 675 & 388 \\
\hline
\times & 1.554 & -0.262 & 1.799 & 3.208 \\
\mathbf{B} & .998 & -2.509 & -0.658 & 7.000 \\
\Delta & -0.429 & 0.470 & 0.527 & 1.511 \\
\mathbf{E} & -1.642 & 3.185 & -1.749 & -7.307 \\
\end{array}
\]

\[
\begin{array}{cccccccc}
E (B^9) & 2607 & 1838 & 1498 & 1330 & 988 & 882 & 713 & 626 & 523 \\
\hline
\mathbf{B} & .046 & -0.262 & -0.040 & -1.083 & .579 & 1.012 & .989 & -1.571 & -2.442 \\
\mathbf{G} & .022 & .509 & -0.666 & -0.378 & .229 & -0.167 & .189 & .847 & .799 \\
\mathbf{B}'' & -0.014 & .370 & .295 & .829 & .124 & .076 & 1.014 & .271 & .249 \\
\mathbf{L}'' & -0.023 & -0.249 & -0.746 & .790 & .371 & -0.742 & .280 & 1.625 & 1.988 \\
\mathbf{L} & .005 & .506 & .219 & -1.037 & .181 & 2.397 & -.015 & -2.536 & -.562 \\
\Delta' & .001 & .114 & .040 & -0.149 & 1.054 & -0.137 & .063 & .208 & -.192 \\
\mathbf{R} & .954 & -.021 & .068 & .075 & .034 & .048 & -0.126 & .028 & .183 \\
\mathbf{W} & .002 & .003 & -.020 & -.022 & .029 & -.322 & .187 & -.643 & .368 \\
\Delta'' & -0.001 & -0.141 & .260 & -.302 & -.088 & -.086 & .666 & .629 & .637 \\
\end{array}
\]
TABLE 26 (contd.)

\[ E (B_{5D9}) \]

<table>
<thead>
<tr>
<th></th>
<th>1935</th>
<th>1319</th>
<th>1172</th>
<th>1021</th>
<th>940</th>
<th>745</th>
<th>609</th>
<th>453</th>
<th>444</th>
</tr>
</thead>
<tbody>
<tr>
<td>B'</td>
<td>.119</td>
<td>-.179</td>
<td>.092</td>
<td>-1.784</td>
<td>.757</td>
<td>-.319</td>
<td>-1.963</td>
<td>1.394</td>
<td>-2.403</td>
</tr>
<tr>
<td>Γ</td>
<td>.056</td>
<td>.651</td>
<td>-.979</td>
<td>-.321</td>
<td>-.023</td>
<td>.174</td>
<td>.212</td>
<td>-1.197</td>
<td>1.020</td>
</tr>
<tr>
<td>B''</td>
<td>-.035</td>
<td>.492</td>
<td>.410</td>
<td>1.011</td>
<td>.252</td>
<td>.165</td>
<td>-1.110</td>
<td>-.611</td>
<td>.869</td>
</tr>
<tr>
<td>X''</td>
<td>-.059</td>
<td>-.546</td>
<td>-1.006</td>
<td>1.136</td>
<td>-.063</td>
<td>.903</td>
<td>.707</td>
<td>-1.844</td>
<td>2.123</td>
</tr>
<tr>
<td>L</td>
<td>.010</td>
<td>-.490</td>
<td>.600</td>
<td>-1.853</td>
<td>2.107</td>
<td>-1.047</td>
<td>-.245</td>
<td>2.762</td>
<td>-.946</td>
</tr>
<tr>
<td>Δ'</td>
<td>.004</td>
<td>.185</td>
<td>-.063</td>
<td>-.302</td>
<td>.238</td>
<td>1.277</td>
<td>-.379</td>
<td>-.403</td>
<td>-.353</td>
</tr>
<tr>
<td>R</td>
<td>1.273</td>
<td>-.062</td>
<td>.169</td>
<td>.171</td>
<td>.173</td>
<td>.147</td>
<td>.339</td>
<td>-.011</td>
<td>.225</td>
</tr>
<tr>
<td>W</td>
<td>.006</td>
<td>.006</td>
<td>-.053</td>
<td>-.027</td>
<td>-.213</td>
<td>.157</td>
<td>-.197</td>
<td>.890</td>
<td>.635</td>
</tr>
<tr>
<td>Δ''</td>
<td>-.002</td>
<td>-.138</td>
<td>.330</td>
<td>-.403</td>
<td>-.287</td>
<td>-.053</td>
<td>-.209</td>
<td>-1.012</td>
<td>1.167</td>
</tr>
</tbody>
</table>


VII. ISOTOPIC EFFECTS IN VIBRATIONAL SPECTRA

A. Introduction

Isotopic substitution is a powerful technique for obtaining additional information on a number of structural features of molecules. The present investigation of deuterated pentaborane is of course an example of this approach. Isotopic substitution provides a means of changing the masses of certain atoms while at the same time producing an essentially negligible change in the geometry and force constants of the molecule. In the Born-Oppenheimer approximation the electronic wave function is obtained by solving the Schrodinger equation for the motion of the electrons while the nuclei are held in fixed positions, and the electronic wave function and energy are therefore independent of the nuclear masses. In a higher approximation in which the center of mass of the molecule is conserved, isotopic substitution alters the total nuclear mass and thus to a small extent the reduced mass for an electron. The resulting change in the electronic wave function and energy is essentially negligible, as stated. The electronic energy or eigenvalue obtained in the Born-Oppenheimer approximation is a function of the nuclear coordinates, and when combined with the internuclear repulsion energy serves as the potential energy in the Schrodinger equation solved subsequently for the nuclear motion. It follows that the classical equilibrium nuclear configuration corresponding to the minimum of this potential, and therefore the corresponding bond lengths and angles, will
be essentially identical for isotopic molecules. The force constants will also be the same, as they represent second and higher derivatives of the potential energy at the minimum. However, the altered nuclear masses resulting from isotopic substitution will produce substantial changes in the eigenvalues and eigenfunctions for the nuclear motion. As a result there will be significant differences in the vibrational frequencies of isotopic molecules, in the zero-point energies, and in the amplitudes of vibration of the atoms (particularly the isotopic atoms). However, there will be no change in mean bond distances or angles in the approximation in which the anharmonicity of the nuclear potential function is neglected.

In this chapter the general theoretical principles and rules useful in the interpretation and correlation of frequency shifts in isotopic molecules will be summarized, with the emphasis on those useful in the assignment to be made in the next chapter. These will include the order and non-crossing rules and their relation to kinetic energy distribution, and the sum and product rules. These are of interest primarily in connection with the large frequency shifts accompanying replacement of hydrogen by deuterium atoms. A discussion will also be given of the so-called "small isotope effect," or the relatively small frequency shifts resulting from the presence of (usually) naturally occurring isotopes of heavier atoms. When two or more such isotopes are present in the same sample they may result in observed splitting or fine-structure in certain vibrational bands. This will be of interest as such splittings are observed in the spectra of both $\text{B}_2\text{H}_6$ and
B_5D_9 as a result of the presence of both B^{10} and B^{11} isotopes, and aid
in the identification of the boron-boron stretching modes. An excellent
review of the theoretical principles needed for the interpretation of
isotopic effects in vibrational spectra, as well as much of the early
data on spectra of deuterated molecules, has been given by Halverson.\(^1\)
Additional references will be given subsequently, particularly for the
sum rules which have been developed since Halverson's review was
prepared.

B. Order Rule

It has been shown by Courant\(^2,\(^3\) that all the frequencies of a
classical harmonic vibrating system decrease (or remain stationary) if a
non-negative quadratic form is added to the kinetic energy, that is, if
one or more masses are increased. Thus, if the normal vibration fre-
quencies of the molecule containing the lighter of two isotopes are
designated as \(\nu_1 < \nu_2 < \ldots < \nu_1 \leq \ldots\), and those of the molecule with
the heavier isotope by \(\nu'_1 < \nu'_2 < \ldots < \nu'_1 \leq \ldots\), both sequences being
ordered according to increasing frequency, it follows from Courant's
result that \(\nu'_1 < \nu_1\), \(\nu'_2 < \nu_2\), \ldots, \(\nu'_1 < \nu_1\). This is commonly called
the "order rule." The order rule makes no assertion concerning the
similarity of the motion (normal mode) for the frequencies \(\nu'_1\) and \(\nu_1\); it
simply states that if a one-to-one correspondence between the frequencies

---

3. R. Courant and D. Hilbert, Methods of Mathematical Physics,
Interscience, New York, 1953.
is established based on their order, then for corresponding frequencies $\nu_1' \leq \nu_1$. Courant's proof is based on the so-called minimax property of a non-negative quadratic form according to which the eigenvalues are the minimum values which the maximum of the quadratic form can assume subject orthogonality of each eigenvector to the eigenvectors for lower eigenvalues. A more elementary proof has been given by Taylor\textsuperscript{4} which provides more insight into the change in form of the normal modes on isotopic substitution. In this proof hypothetical continuous increases in isotopic masses are considered and an expression based on Wilson's s-vectors is derived for the logarithmic derivative of an arbitrary frequency with respect to the mass of an arbitrary atom. It will be shown subsequently that it is virtually impossible for changes of isotopic mass to produce exact degeneracy of two frequencies belonging to the same symmetry species (this excludes, of course, the degeneracy required by symmetry for degenerate symmetry species). It is therefore sufficient to give the result applicable in the absence of accidental degeneracy. Let $\nu_1$ be a normal frequency, and $\lambda_1 = 4\pi^2 \nu_1^2$. Then a slight rearrangement of Taylor's result yields

$$\left( \frac{\partial}{\partial \ln \nu_1} \right) = -(1/m_t) |\mathbf{s}_{it}^0|$$

where $m_t$ is the mass of the $t$th atom and $\mathbf{s}_{it}^0$ is Wilson's vector for the $t$th atom and $i$th normal mode. $\mathbf{s}_{it}^0$ is obtained by applying to the symmetry S-vectors discussed in the preceding chapter the linear transformation leading from symmetry to normal coordinates. It will be

sufficient to consider the case in which the masses of each of a set of m isotopic atoms are varied simultaneously by equal amounts. Then, if $m^\prime$ denotes the common isotopic mass of this set,

$$(\partial \ln \lambda / \partial \ln m^\prime) = - \sum_{i=1}^{m} (1/m^\prime) |\vec{S}_{it}|^2,$$

or

$$(\partial \ln \nu / \partial \ln m^\prime) = -(\frac{1}{2}) \sum_{i=1}^{m} (1/m^\prime) |\vec{S}_{it}|^2.$$

The right-hand side of the equation is negative (or zero), and the logarithmic function is a monotonic increasing function of its argument, from which it follows that each frequency $\nu$ is a monotonic non-increasing function of the isotopic mass $m^\prime$. The order rule, $\nu^\prime \leq \nu$, follows from integration of this relation for a finite change of mass.

An upper bound on the frequency change, or a lower bound on the frequency ratio $\nu^\prime / \nu$, is obtained by combining the preceding relation with the normalization relation for the $\vec{S}$ vectors,

$$G_{i,i}^O = \sum_{i=1}^{m} (1/m_i) |\vec{S}_{it}|^2 = 1.$$

This corresponds to the fact that the transformation to normal coordinates not only diagonalizes the $G$ matrix, but also reduces it to the unit matrix. It follows that

$$-(1/2) \leq (\partial \ln \nu / \partial \ln m^\prime) \leq 0,$$

and integration between two isotopic masses, $m^\prime$ and $m^\prime > m^\prime$, yields

$$-(1/2) \leq \ln(\nu^\prime / \nu) / \ln(m^\prime / m^\prime) \leq 0,$$

or using the monotonic property of the logarithmic function,

$$\left(\frac{m'/m^\prime}{m'/m^\prime}\right)^{1/2} \leq (\nu^\prime / \nu) \leq 1.$$

Here the right-hand inequality is equivalent to the order rule. From the preceding discussion it is clear that $(\partial \ln \nu / \partial \ln m^\prime)$ is equal to half the negative of the fraction of the kinetic energy of the $i$th
normal mode contributed by the set of m isotopic atoms of mass $m_I$ (for a more detailed discussion of the distribution of kinetic and potential energies in a vibrating molecule see Taylor5). The right-hand inequality becomes an equality, or $V_1^' = V_1$, only in the limiting case in which the vectors $S_{1t}^{(\alpha)}$ vanish for each of the m isotopic atoms, so that these atoms are stationary in the $i$th normal mode. On the other hand the left-hand inequality becomes an equality only if the vectors $S_{1t}^{(\alpha)}$ vanish for all atoms other than the set of m isotopic atoms, so that only the isotopic atoms move in the $i$th normal mode. Neither of these limiting cases is likely to occur except in small symmetrical molecules. However, it is clear that if the motion of the isotopic atoms is slight in the $i$th mode ($V_1^'/V_1$) will lie considerably closer to unity than to its lower bound $(m_I^'/m_I)$, while the converse will be true if the $i$th normal mode involves predominantly motion of the isotopic atoms. If the preceding inequality is specialized for the case of substitution of deuterium for hydrogen atoms, $m_I = m_H = 1.0080$, $m_I^' = m_D = 2.0142$, and

$$0.7074 \leq (V_1^'/V_1) \leq 1$$

For substitution of $B^{10}$ by $B^{11}$, $m_I = m(B^{10}) = 10.016$, $m_I^' = m(B^{11}) = 11.013$, and

$$0.9537 \leq (V_1^'/V_1) \leq 1$$

The latter is an example of the small isotope effect, and is more conveniently stated in the equivalent form

$$0 \leq (V_1 - V_1^'/V_1) \leq 0.0486$$

as the heavier isotope $B^{11}$ is more abundant and $V_1'$ is the more intense frequency, with $V_1$ as a weaker satellite.

C. Non-Crossing Rule and a Proposed Reversal Rule

The analysis in the preceding section indicates that the nature and correlation of normal modes in two isotopic species may be clarified by considering, at least qualitatively, the way in which the frequency of the $ith$ mode varies from $V_1$ to $V_1'$ as the isotopic mass is increased continuously from $m_1$ to $m_1'$. Thus, from a preceding equation, the slope of a plot of $\ln V_1$ versus $\ln m_1$ (or $\log V_1$ versus $\log m_1$) is half the negative of the fraction of the kinetic energy of the $ith$ mode contributed by the isotopic atoms. Such plots can be calculated if a set of force constants is available. For example, Figure 9 shows such a plot for each symmetry species of pentaborane for values of the isotopic mass of hydrogen varying from $m_H = 1.008$, through $m_D = 2.014$, to $m_T = 3$. Since the frequencies for different symmetry species are obtained from independent secular equations there is no prohibition against the curves for frequencies of different species crossing, as may be seen by superimposing the plots for different species. However, it will be noted that in no case is there a crossing of two curves within the same species, although in several cases they approach closely. The calculated behavior of the fourth and fifth modes (in order of increasing frequency) in the $E$ species is particularly interesting. As $m_1$ increases from $m_H$ to $m_T$ these at first approach, then recede, reaching their closest distance of approach at a mass intermediate between $m_H$ and $m_D$. It will also be noted that there is a quite definite interchange of the slopes of the
curves following their approach and recession, and therefore an inter-
change of the character of the corresponding normal modes in so far as
this is determined by the distribution of kinetic energy between the
isotopic and non-isotopic atoms. One is thus led to inquire into the
conditions governing the close approach of the two frequencies of the
same species, their interchange of character, and also whether two fre-
quency curves of the same species may ever cross. This section is
concerned with these questions.

In treating this question from first principles it is convenient
to formulate the problem in terms of the roots, \( \lambda_1 = 4\pi^2 \nu^2 \), of the
secular equation, and the reciprocal isotopic mass, \( \mu = m_1^{-1} \). The
expanded form of the secular equation (for a given species) is
\[
f(\mu, \lambda) = \sum_{n=0}^{N} a_n(\mu) \lambda^{N-n} = 0
\]
That is, \( f(\mu, \lambda) \) is a polynomial in \( \lambda \) of degree \( N \) equal to the number of
normal modes of the given species. The roots of this equation are the
\( N \lambda_1 \)'s. Since the secular equation is obtained by expansion of the
characteristic equation of two symmetric (or Hermitian) matrices, \( G \) and
\( F \), the roots must be real. Furthermore, \( G \) and \( F \) are the matrices of
the positive-definite quadratic forms representing the potential and
kinetic energies, so that \( \lambda_1 \geq 0 \) \((i = 1, \ldots, N)\). It may be noted that if
the symmetry species is degenerate the same secular equation is repeated
a number of times equal to the degeneracy. Thus, any degeneracy of the
\( N \lambda_1 \)'s is an accidental degeneracy, in addition to the degeneracies
required by symmetry. The coefficients, \( a_n(\mu) \), in the secular equation
depend on the parameters specifying the equilibrium molecular
configuration, the atomic masses, and the force constants. However, as all these quantities except the isotopic mass \( \mu \) are maintained constant only the dependence on \( \mu \) is indicated explicitly.

The functional dependence of the coefficients on \( \mu \) may be obtained from an expansion of the secular equation,

\[
|GF - \lambda I| = 0
\]
given by Wilson.\(^6\) Equation (10) of Wilson's paper shows that \( a_n(\mu) \) is equal to \((-1)^{N-n}\) times the sum of the products of all pairs of corresponding minors of order \( n \) contained in the \( G \) and \( F \) matrices (that is, minors formed from the same rows and columns of \( G \) and \( F \)). It is easily seen from Wilson's formula for the elements of the \( G \) matrix in section \( H \) of the preceding chapter that each element of \( G \) is either linear in \( \mu \) or independent of \( \mu \). Thus, each \( \text{nth} \) ordered minor of \( G \) is a polynomial in \( \mu \) of degree equal to or less than \( n \). The elements of \( F \), and therefore the minors of \( F \), depend only on the force constants, and possibly the geometrical parameters following the elimination of redundancies, and are independent of \( \mu \). It follows that \( a_n(\mu) \) is a polynomial in \( \mu \) of degree equal to or less than \( n \) (but usually equal to \( n \)),

\[
a_n(\mu) = \sum_{m=0}^{n} c_{mn} \mu^{n-m}
\]

where the coefficients \( c_{mn} \) are independent of \( \mu \). Thus \( f(\mu, \lambda) \) is, in general, a polynomial of degree \( N \) in both \( \lambda \) and \( \mu \),

\[
f(\mu, \lambda) = \sum_{n=0}^{N} \sum_{m=0}^{n} c_{mn} \mu^{n-m} \lambda^{N-m}
\]

---

It is now convenient to consider a three-dimensional orthogonal space in which \( f(\mu, \lambda) \) is represented on an axis \( \xi \) as a function of \( \mu \) and \( \lambda \). As \( \lambda \) is restricted to positive values, and \( \mu \) is inherently positive, only the positive \( \mu, \lambda \) quarter-plane is of interest. It is useful to consider the surface \( \xi = f(\mu, \lambda) \) in this space. \( f(\mu, \lambda) \) may assume either positive or negative values and this surface will intersect the \( \xi = 0 \) plane in \( N \) curves for which the functional relations between \( \lambda \) and \( \mu \) are given by

\[
f(\mu, \lambda_i) = 0; \ i = 1, 2, ..., N.
\]

Thus, each \( \lambda_i \) is determined implicitly as a function of \( \mu \), \( \lambda_i = \lambda_i(\mu) \). The slopes of these curves are determined by a preceding equation, which for the present discussion may be rewritten in the form

\[
(\partial \ln \lambda_i / \partial \ln \mu) = \sum_{i=0}^{m} \mu |S_i|^2.
\]

Thus, each \( \lambda_i \) is a monotonic non-decreasing function of \( \mu \), and

\[
(\partial \ln \lambda_i / \partial \ln \mu) \text{ equals the fraction of the kinetic energy of the } i\text{th mode contributed by the } m \text{ isotopic atoms of mass } m_i = \mu^{-1}.
\]

In the limit \( \mu \to 0 \), or \( m_i \to \infty \), the lowest \( 3m-6 \) roots or \( 3m-5 \) if the isotopic atoms form a linear array will approach zero, while the remaining roots will approach finite positive values. In the limit \( \mu \to \infty \), or \( m_i \to 0 \), the upper \( 3m \) roots will approach \( +\infty \), while the remaining roots will approach finite positive values.

Consider now the conditions under which two frequency curves, \( \lambda_i(\mu) \) and \( \lambda_j(\mu) \), may make a close approach, so that in the neighborhood of a given value of \( \mu \)

\[
\Delta \lambda(\mu) = |\lambda_j(\mu) - \lambda_i(\mu)|
\]

is small (for the present we exclude the degenerate case \( \lambda_i(\mu) = \))
\( \lambda_j(\mu) \) or \( \Delta \lambda(\mu) = 0 \). It follows from the theory of equations that the polynomial equation

\[
f_\lambda(\mu, \lambda) = (\partial f/\partial \lambda) = 0
\]

has at least one real root lying between each real root of the equation \( f(\mu, \lambda) = 0 \). But \( f(\mu, \lambda) \) is of degree \( N \) and has \( N \) real roots, while \( f_\lambda(\mu, \lambda) \) is of degree \( N - 1 \) and must have \( N - 1 \) roots. It follows that one and only one real root of \( f_\lambda(\mu, \lambda) = 0 \) lies between each pair of adjacent roots of \( f(\mu, \lambda) = 0 \), and that this exhausts the roots of \( f_\lambda(\mu, \lambda) = 0 \). Let \( \lambda_0(\mu) \) be the root of \( f_\lambda(\mu, \lambda) = 0 \) lying between \( \lambda_j(\mu) \) and \( \lambda_j(\mu) \); then \( f_\lambda(\mu, \lambda_0) = 0 \). Define \( \xi_0(\mu) = f(\mu, \lambda_0) \). Then in the small interval \( \Delta \lambda, f(\mu, \lambda) \) may be represented by the first two non-vanishing terms of a Taylor series expansion,

\[
f(\mu, \lambda) = \xi_0(\mu) + \frac{1}{2} f_{\lambda\lambda}(\mu, \lambda_0)(\lambda - \lambda_0)^2
\]

where \( f_{\lambda\lambda} = (\partial^2 f/\partial \lambda^2) \). The curves \( \lambda_1(\mu) \) and \( \lambda_j(\mu) \) may therefore be approximately represented in the region of close approach as the two roots of the equation

\[
\xi_0(\mu) + \frac{1}{2} f_{\lambda\lambda}(\mu, \lambda_0)(\lambda - \lambda_0)^2 = 0
\]

or

\[
\lambda = \lambda_0 \pm \left[ 2 \xi_0(\mu)/f_{\lambda\lambda}(\mu, \lambda_0) \right]^{\frac{1}{2}}
\]

It follows that

\[
\xi_0(\mu) = (1/8)f_{\lambda\lambda}(\mu, \lambda_0) \left[ \Delta \lambda(\mu) \right]^2
\]

so that in general \( \xi_0(\mu) = f(\mu, \lambda_0) \) will be small when \( \Delta \lambda(\mu) \) is small. Thus, as the two frequencies approach and recede, the curve in the \( \xi, \mu, \lambda \)-space defined by \( \xi = \xi_0(\mu) \) may be expected to approach and then recede from the surface \( \xi = 0 \). On the other hand this curve may not pass through the surface \( \xi = 0 \), with a resulting change in sign of
\( f_0(\mu), \) as from the preceding equation the two roots \( \lambda_1(\mu) \) and \( \lambda_j(\mu) \) would then become complex and the \( N \) roots of \( f(\mu, \lambda) = 0 \) must all be real. It is therefore clear that, in the neighborhood of closest approach of \( \lambda_1(\mu) \) and \( \lambda_j(\mu) \), \( f_0(\mu) \) must have an extremum which is a maximum if \( f_0'(\mu) \leq 0 \) and a minimum if \( f_0'(\mu) \geq 0 \). Let the value of \( \mu \) for which this extremum occurs be \( \mu_0 \), and the corresponding value of \( \lambda \) be \( \lambda_0 = \lambda_0(\mu_0) \). Then

\[
\left[ \frac{\partial f_0(\mu)}{\partial \mu} \right]_{\mu_0} = \left[ \frac{\partial f(\mu, \lambda_0(\mu))}{\partial \mu} \right]_{\mu_0} = f_\mu(\mu_0, \lambda_0) + f_\lambda(\mu_0, \lambda_0) \left[ \frac{\partial \lambda_0(\mu)}{\partial \mu} \right]_{\mu_0} = 0,
\]

where \( f_\mu(\mu, \lambda) = (\partial f/\partial \mu) \). But by definition,

\[
f_\lambda(\mu_0, \lambda_0) = 0,
\]

and it can be shown from the monotonic property of the function \( \lambda_1(\mu) \) that \( \left[ \frac{\partial \lambda_0(\mu)}{\partial \mu} \right]_{\mu_0} \) is finite. Therefore, also

\[
f_\mu(\mu_0, \lambda_0) = 0,
\]

and the point \((\mu_0, \lambda_0)\) at which \( f_0(\mu) \) has an extremum must be a stationary point of \( f(\mu, \lambda) \). In the neighborhood of this stationary point \( f(\mu, \lambda) \) may be represented by the expansion

\[
f(\mu, \lambda) = f_{00} + \frac{1}{2} f_\mu^0(\mu - \mu_0)^2 + f_\lambda^0(\lambda - \lambda_0)^2 + \frac{1}{2} f_{\mu\lambda}(\lambda - \lambda_0)^2,
\]

where \( f_{00} = f(\mu_0, \lambda_0) \), and \( f_\mu^0 \), \( f_\lambda^0 \), and \( f_{\mu\lambda} \) are the second partial derivatives of \( f(\mu, \lambda) \) with respect to \( \mu \) and \( \lambda \) at \((\mu_0, \lambda_0)\).

Now introduce an orthogonal transformation to variables \( \xi \) and \( \eta \), corresponding to a rotation by angle \(-\phi\) in the \( \mu, \lambda \) plane,

\[
\mu = \xi \cos \phi + \eta \sin \phi,
\]

\[
\lambda = -\xi \sin \phi + \eta \cos \phi.
\]
The partial derivatives of first and second order of \( f(\xi, \eta) = f(\mu, \lambda) \) with respect to \( \xi \) and \( \eta \) evaluated at \( \mu = \mu_0 \) and \( \lambda = \lambda_{oo} \), or \( \xi = \xi_0 \) and \( \eta = \eta_0 \), are readily seen to be

\[
\begin{align*}
\frac{\partial f}{\partial \xi} &= f^0_\xi \cos \phi - f^0_\lambda \sin \phi = 0 , \\
\frac{\partial f}{\partial \eta} &= f^0_\xi \sin \phi - f^0_\lambda \cos \phi = 0 , \\
\frac{\partial^2 f}{\partial \xi^2} &= f^0_{\xi\xi} \cos 2\phi - 2f^0_{\xi\lambda} \sin \phi \cos \phi + f^0_{\lambda\lambda} \sin^2 \phi , \\
\frac{\partial^2 f}{\partial \eta^2} &= f^0_{\eta\eta} \sin^2 \phi + 2f^0_{\eta\lambda} \sin \phi \cos \phi + f^0_{\lambda\lambda} \cos^2 \phi , \\
\frac{\partial^2 f}{\partial \xi \partial \eta} &= \frac{1}{2}(f^0_{\xi\mu} - f^0_{\lambda\mu}) \sin 2\phi + f^0_{\mu\lambda} \cos 2\phi .
\end{align*}
\]

Define \( \phi \) by the condition

\[
\tan 2\phi = 2f^0_{\mu\lambda}/(f^0_{\lambda\lambda} - f^0_{\mu\mu}) ,
\]

so that \( f^0_{\xi \eta} = 0 \). It will be assumed that \( |f^0_{\xi \xi}| \) and \( |f^0_{\eta \eta}| \) are both non-vanishing. Then in the neighborhood of its stationary point \( f(\xi, \eta) \) may be represented as

\[
f(\xi, \eta) = \xi_{oo} + \frac{1}{2} f^0_{\xi \xi} (\xi - \xi_0)^2 + \frac{1}{2} f^0_{\eta \eta} (\eta - \eta_0)^2 .
\]

Clearly the functional relation between \( \xi \) and \( \eta \) implied by the relations \( \lambda = \lambda_1(\mu) \) and \( \lambda = \lambda_j(\mu) \) may be obtained in approximate form in the neighborhood of the stationary point by setting the immediately preceding expression for \( f(\xi, \eta) \) equal to zero. This yields

\[
f^0_{\xi \xi} (\xi - \xi_0)^2 + f^0_{\eta \eta} (\eta - \eta_0)^2 = -2 \xi_{oo} .
\]

If the stationary point were a minimum of \( f(\xi, \eta) = f(\mu, \lambda) \), \( f^0_{\xi \xi} \) and \( f^0_{\eta \eta} \) would both be positive and \( \xi_{oo} \) negative; if a maximum these signs would be reversed. In either case the preceding relation between \( \xi \) and \( \eta \) corresponds to an ellipse. Since \( \mu \) and \( \lambda \) are obtained by an orthogonal transformation, the functional relation between \( \lambda \) and \( \mu \) would be a similar ellipse rotated by angle \( \phi \). It is readily seen that for values of \( \mu \) outside but adjacent to the interval on the \( \mu \)-axis
subtended by this ellipse the two roots $\lambda_1(\mu)$ and $\lambda_j(\mu)$ would become complex conjugate roots. As the roots of the present secular equation must be real, the stationary point of $f(\mu, \lambda)$ may not be a minimum if $F_{oo}$ is negative or a maximum if $F_{oo}$ is positive. This conclusion holds only for stationary points for which $|F_0(\mu)|$ has a minimum, corresponding to a minimum in the separation of two frequency curves, as considered here. Stationary points for which $|F_0(\mu)|$ is a maximum represent minima of $f(\mu, \lambda)$ if $F_0(\mu)$ is negative and maxima if $F_0(\mu)$ is positive, but such stationary points correspond to a maximum separation of two frequency curves and are not of interest in the present connection. Returning to the discussion of stationary points for which $|F_0(\mu)|$ is a minimum, the possibilities of a maximum for $F_{oo}$ negative or a minimum for $F_{oo}$ positive still have to be considered, as the surface $F = f(\mu, \lambda)$ would not then intersect the $F = 0$ plane in the neighborhood of the extremum and the preceding argument is inapplicable. However, in either of these cases it is readily shown that the equation $f_\lambda(\mu_0, \lambda) = 0$ would have at least three real roots $\lambda$ in the interval between $\lambda_1(\mu_0)$ and $\lambda_j(\mu_0)$. But as previously stated only one such root may exist. It follows that extrema of the latter type may never occur, and in view of the preceding discussion stationary points of $f(\mu, \lambda)$ for which $|F_0(\mu)|$ is a minimum may not be extrema (maxima or minima).

The only remaining possibility is that stationary points for which $|F_0(\mu)|$ is a minimum be saddle-points of the $F = f(\mu, \lambda)$ surface. In this case $s_5$ and $s_7$ must be of opposite signs, and the preceding equation defines a hyperbolic relation between $F$ and $\eta$. On carrying out the inverse orthogonal transformation to $\mu$ and $\lambda$ the two branches
of the hyperbola (rotated by \( \phi \)) correspond to the curves \( \lambda = \lambda_1(\mu) \) and \( \lambda = \lambda_j(\mu) \) in the region of their closest approach, or the neighborhood of the vertices of the hyperbola. However, to a coarser degree of approximation the hyperbola may be regarded as a representation of the frequency curves at greater distances from the saddle-point, where the branches of the hyperbola approach its asymptotes. The equations defining these asymptotes are

\[
(x - x_0) = \pm r(y - y_0) ,
\]

where

\[
r = \left( -\frac{f_\gamma^2}{f_{33}^2} \right)^{1/2} .
\]

The two asymptotes lie in the \( \mu,\lambda \)-plane and intersect at the projected position \((\mu_0, \lambda_\infty)\) of the saddle-point in this plane; they do not pass through the saddle-point which is at a distance \(s_\infty = f(\mu_0, \lambda_\infty)\) from this plane except for the degenerate case \(s_\infty = 0\) to be considered subsequently. By carrying out the inverse transformation to \( \mu \) and \( \lambda \), the slopes of the asymptotes are found to be

\[
\left(\frac{d\lambda}{d\mu}\right)_{\text{asymptote}} = \frac{(1 \mp r \tan \phi)}{(\tan \phi \pm r)} .
\]

In the approximation considered these will be the slopes of the frequency curves \( \lambda_1(\mu) \) and \( \lambda_j(\mu) \) for values of \( \mu \) sufficiently far from \( \mu_0 \) so that the hyperbola approaches closely to its asymptotes. Moreover, it is clear that the slopes of the frequency curves will be approximately interchanged as \( \mu \) passes through \( \mu_0 \), and this effect will be more pronounced and occur in a smaller interval of \( \mu \) the closer the approach of the two frequency curves and the greater the difference in the slopes. There will be an essentially comparable interchange in the logarithmic derivatives or slopes, \((d\ln \gamma_1/d\ln \mu)\) and \((d\ln \gamma_j/d\ln \mu)\), or \((d\ln \gamma_1/d\ln m_\perp)\) and \((d\ln \gamma_j/d\ln m_\perp)\), which have been shown previously to be
related to the distribution of kinetic energy between isotopic and non-isotopic atoms. From these considerations it appears that if two frequency curves approach sufficiently closely and with sufficiently different slopes (and then recede without actually touching or intersecting) at an isotopic mass intermediate between the mass $m_1$ and $m_1'$ of two actually occurring isotopes, the kinetic energy or degree of motion of the isotopic atoms will be interchanged for these modes in the two isotopic molecules. That is, if these two modes are correlated by the order rule there will be a reversal in their type, while if they are correlated by type there will be a reversal in their order. It seems appropriate to call this generalization the reversal rule. It supplements but does not violate the order rule.

The preceding discussion makes it clear that when $|\delta_{oo}| > 0$, so that the saddle-point of $f(\mu, \lambda)$ lies above or below the $\mu, \lambda$ plane, the two frequency curves approach and then recede without touching or crossing. The question still remains as to whether the saddle-point may ever lie in the $\mu, \lambda$ plane (i.e., $\delta_{oo} = 0$), and if so what this implies with regard to the crossing or non-crossing of the frequency curves. It has been seen that the saddle-point (as well as other stationary points) occur at values of $\mu$ and $\lambda$ for which the following two equations are satisfied simultaneously,

$$f_{\lambda}(\mu, \lambda) = 0$$
$$f_{\mu}(\mu, \lambda) = 0$$

As previously stated $f(\mu, \lambda)$ is a polynomial in both $\lambda$ and $\mu$, and as a result at least one real root $\lambda$ of the first equation lies between each two roots $\lambda_1(\mu)$ and $\lambda_2(\mu)$ of $f(\mu, \lambda) = 0$, for given $\mu$. However, the
functional relations $\lambda_i(\mu)$ and $\lambda_j(\mu)$ may be inverted to obtain $\mu$ as a function of $\lambda$, or $\mu = \mu_i(\lambda)$ or $\mu_j(\lambda)$. This simply corresponds to looking at the same frequency curves from a different aspect. For given $\lambda$, $\mu_i(\lambda)$ and $\mu_j(\lambda)$ are two real roots of the polynomial $f(\mu, \lambda)$ in $\mu$, and therefore at least one real root of the second equation above must lie between $\mu_i(\lambda)$ and $\mu_j(\lambda)$. It is clear then that the solutions of each of these equations taken separately define at least one curve in the $\mu, \lambda$ plane lying between the two frequency curves, and the stationary points or simultaneous solutions of these two equations simply correspond to intersections of the latter curves. Therefore such stationary points are not likely to be exceptional. On the other hand the occurrence of a stationary point, and in particular a saddle-point of $f(\mu, \lambda)$ in the $\mu, \lambda$ plane requires that $\mu$ and $\lambda$ be simultaneous solutions of the preceding two equations and in addition that the relation

$$f(\mu, \lambda) = 0$$

be satisfied. This implies a particular relation between the remaining parameters of the molecule (bond distances and angles, masses of non-isotopic atoms, and force constants) and can only occur accidentally. It is therefore unlikely that the saddle-point will ever lie precisely in the $\mu, \lambda$ plane for a real molecule. However, if this were to occur then it is clear that a crossing of the two frequency curves in question would occur in the approximation of harmonic forces as previously assumed. For the hyperbolic relation between $\xi$ and $\eta$ obtained previously reduces when $\xi_{oo} = 0$ to the equations of its asymptotes. That is, in this case the asymptotes pass through the saddle-point and represent the two frequency curves in the neighborhood of the
saddle-point. Thus, the two frequency curves cross at the saddle-point without any discontinuities in slope. Even though the frequencies cross, it is clear that the order rule must still be satisfied as it arises from a limitation on the absolute magnitude of the slopes.

Further consideration indicates that although two frequency curves may in rare cases cross in the harmonic approximation, leading to a so-called accidental degeneracy, such a crossing or strict degeneracy of two frequencies of the same species will be prohibited in a higher approximation. This prohibition must in general always occur as a result of Fermi resonance between the two vibrational states involving anharmonic terms in the potential. As is well known such resonance results in "repulsion" of the states in question and prevents their crossing. A more detailed analysis indicates that the lowest order terms in the potential which can produce such resonance between the two vibrational states in question are quartic terms. This conclusion is reached in the following way. In the harmonic approximation the parts of the product-type wave functions for the upper states giving rise to the fundamental frequencies $\nu_1$ and $\nu_j$ will be $H_1(Q_i)H_0(Q_j)$ and $H_0(Q_i)H_1(Q_j)$, respectively, where $H_n(x)$ is the $n$th order Hermite function and $Q_i$ and $Q_j$ the two normal coordinates. The lower state for both transitions will be the ground vibrational state; perturbations of the latter will change both frequencies by the same amount and therefore cannot lead to separation of the frequencies. The question is therefore what are the anharmonic terms of minimum degree in the potential of the
form $k\sum_{j}^{n}Q_{j}^{m+n}$ for which the integral

$$\iint H_{1}(Q_{1})H_{0}(Q_{j})Q_{1}^{m+n}H_{0}(Q_{1})H_{1}(Q_{j})dQ_{1}dQ_{j}$$

is non-vanishing. But the integral

$$\int H_{0}(Q)Q^{n}H_{1}(Q)dQ$$

vanishes for $n = 0, 2, 4, \ldots$, and is non-vanishing for $n = 1, 3, 5, \ldots$. The lowest degree anharmonic terms leading to resonance are therefore the quartic terms $Q_{1}Q_{j}^{3}$ and $Q_{1}^{3}Q_{j}$. The Fermi resonance is therefore of second or higher order (first order Fermi resonance is that arising from cubic terms in the potential).

The discussion of the preceding paragraph shows that when Fermi resonance is taken into account two frequency curves may not cross, even though such a crossing or accidental degeneracy would be predicted in the harmonic approximation. This constitutes the strict non-crossing rule for fundamental vibration frequencies of the same symmetry species. However, it is well known that when a crossing of two states is prevented by Fermi resonance there is a more or less complete interchange of character (wave functions) for the two states at the point of "pseudo-crossing." This is the equivalent of the previously proposed reversal rule in the present case.

D. Product Rule

An important relation relating the products of the normal frequencies of vibration for two isotopic molecules is the product rule of Redlich and Teller.\(^7\)\(^8\) This is derived by considering initially that the


molecule containing n atoms is bound, so that the over-all translations and rotations are converted into vibrations. The secular equation for the 3n-6 true vibration frequencies and the 6 pseudo-vibrations is then written in the usual form

\[ |GF - \lambda I| = 0 \]

As is well known the product of the 3n roots equals \(|GF|\), or \(|G||F|\). On introducing the relation \(\lambda_1 = 4\pi^2 \nu_1^2\), and taking the product of the ratios of the frequencies for two isotopic molecules, one obtains

\[ \prod_{i \neq j} \left( \frac{\nu'_i}{\nu_1} \right) = \left( \frac{|G'||F'|}{|G||F|} \right)^{\frac{1}{2}} = \left( \frac{|G'|}{|G|} \right)^{\frac{1}{2}} \]

since the force constants are equal for the isotopic molecules and \(|F'| = |F|\). If the coordinates are taken to be the Cartesian coordinates of the n atoms, then the mass or kinetic energy matrix is diagonal with the mass of each atom appearing three times on the diagonal (for the x, y, and z components of its motion). Therefore

\[ |G^{-1}| = |G|^{-1} = \prod_{i \neq j} m_i^3 \]

and

\[ \prod_{i \neq j} \left( \frac{\nu'_i}{\nu_1} \right) = \prod_{i \neq j} \left( \frac{m_i}{m_1} \right)^{3/2} \]

A transformation is next made to 3n-6 internal coordinates and 6 external coordinates consisting of the three over-all translations and three rotations about principal axes of inertia. This transformation does not affect the normal frequencies or the ratio given above.

Finally, the force constants restraining the translations and rotations are permitted to approach the limit zero, corresponding to the free molecule. The corresponding frequencies will then approach zero, but it is clear that the ratio of corresponding frequencies of pseudo-translation for the isotopic molecules will approach the limit
\[(\gamma'/\gamma) = \left(\frac{M}{M'}\right)^{\frac{1}{2}}, \text{ where } M \text{ may be regarded as either the total mass of the molecule or the molecular weight, as only the ratio of } M \text{ and } M' \text{ is involved. Similarly the limiting ratio of the frequencies of pseudorotation about the } \alpha \text{th principal axis is } (\gamma'_\alpha/\gamma_\alpha) = \left(\frac{I_\alpha}{I'_\alpha}\right)^{\frac{1}{2}}, \text{ where } I_\alpha \text{ and } I'_\alpha \text{ are the corresponding principal moments of inertia. In the limit therefore the product of the ratios of the } 3n-6 \text{ internal frequencies becomes}
\[
\left(\gamma_1'/\gamma_1\right) = \left(\frac{M'}{M}\right)^{3/2} \prod_{i=1}^{3} \left(\frac{I_i}{I'_i}\right)^{1/2} \prod_{j=1}^{3} \left(\frac{m_j}{m'_j}\right)^{3/2}.
\]
For a symmetrical molecule the product rule holds separately for the frequencies belonging to each symmetry species. In this case it takes the following form \(^9\) which is a slightly more explicit version of the formula given by Herzberg \(^10\). It is assumed that the two isotopic molecules have the same symmetry as in the present investigation although the generalization to other cases is easily made. Let } \Gamma \text{ be an irreducible representation of the molecular point group of dimension } d, \text{ and assume that } \Gamma \text{ appears } f \text{ times in the representation of the internal coordinates of the molecule. Let } t \text{ be the number of times } \Gamma \text{ appears in the representation of the three translations of the molecule (or representation of a vector). Define also a quantity } \delta_{\alpha} \text{ such that } \delta_{\alpha} = 1 \text{ if the } \alpha \text{th rotation belongs to } \Gamma \text{ and } \delta_{\alpha} = 0 \text{ otherwise. The number of times } \Gamma \text{ appears in the representation of the three rotations is then } (\delta_{\alpha} + \delta_{\beta} + \delta_{\gamma})/d. \text{ Finally, let } \gamma \text{ be the number of times } \Gamma \text{ appears in the representation of the } 3m \text{ Cartesian displacements of the}

set of m isotopic atoms for which isotopic substitution is made. Then
\[
\left( \frac{\gamma_1'}{\gamma_1} \right) = \left( \frac{m}{m'} \right)^{\frac{n}{2}} \left( \frac{m'}{m} \right)^{\frac{t}{2}} \left( I_n^l/I_n^t \right)^{\delta_m/2d}
\]
For the point group \( C_{4v} \) of pentaborane the representation of the translations is \( \mathbf{A}_1 + \mathbf{E} \), so that \( t = 1 \) for species \( \mathbf{A}_1 \) and \( \mathbf{E} \) and \( t = 0 \) for other species. The representation of the rotation about the 4-fold or z-axis is \( \mathbf{A}_2 \), while the x- and y-rotations belong to the doubly-degenerate \( \mathbf{E} \) representation. Thus \( \delta = 1 \) for \( \mathbf{A}_2 \), \( \delta_x = \delta_y = 1 \) for \( \mathbf{E} \), and all other \( \delta_x \)'s vanish. In the present investigation all the hydrogen atoms of \( \mathbb{B}_5 \mathbb{H}_9 \) are substituted to obtain \( \mathbb{B}_5 \mathbb{D}_9 \). The representation of the Cartesian displacements of the 9 hydrogen atoms is of dimension 27, and may be reduced by the familiar application of the orthogonality theorem for group characters. However, the results of this reduction have been tabulated in convenient form for the important point groups by Herzberg\(^{11}\) in his Tables 35 and 36. From Table 36 under \( C_{4v} \) one finds that the reduced forms of the representations of the Cartesian displacements are:
- \( \mathbf{A}_1 + \mathbf{E} \) for the apex hydrogen atom, \( H_0 \);
- \( 2\mathbf{A}_1 + \mathbf{A}_2 + 2\mathbf{B}_1 + \mathbf{B}_2 + 3\mathbf{E} \) for the non-bridge base hydrogen atoms, \( H_1 \);
- \( 2\mathbf{A}_1 + \mathbf{A}_2 + \mathbf{B}_1 + 2\mathbf{B}_2 + 3\mathbf{E} \) for the bridge hydrogen atoms, \( H_1' \).
The representation for all the hydrogen atoms is therefore \( 5\mathbf{A}_1 + 2\mathbf{A}_2 + 3\mathbf{B}_1 + 3\mathbf{B}_2 + 7\mathbf{E} \), and the values of \( \gamma \) are simply the numerical coefficients in the latter expression. It has been shown previously (see Table 7) that the reduced representation of the \( 3n-6 = 36 \) internal coordinates of the pentaborane molecule is \( 7\mathbf{A}_1 + 2\mathbf{A}_2 + 5\mathbf{B}_1 + 4\mathbf{B}_2 + 9\mathbf{E} \), and the coefficients in this expression are values of \( f \) as defined.

\(^{11}\) Ibid.
above (the latter representation may be obtained by adding to the representation for the hydrogen atoms as obtained above the representation $3\alpha_1 + \alpha_2 + 2\beta_1 + \beta_2 + 4\varepsilon$ for the boron atoms, obtained in the same manner from Herzberg's table, and subtracting the representations for translation and rotation as given above).

The form the product rule takes for each species of $B_\text{5H}_9$ and $B_\text{5D}_9$ is given below. The numerical values have been calculated from the molecular weights $M = 63.182$ and $M' = 72.238$ for $B_\text{5H}_9$ and $B_\text{5D}_9$, respectively, atomic weights $m = 1.0080$ and $m' = 2.0142$ for H and D, respectively, and the moments of inertia as computed in Table 9 for boron atoms of average or chemical atomic weight 10.822.

- $A_1$: $\sum (\gamma_1^\prime / \gamma_1) = (m/m')^{5/2}(M/M)^{1/2} = 0.1894$;
- $A_2$: $\sum (\gamma_1^\prime / \gamma_1) = (m/m')^{1/2}(I_z/I_x)^{1/2} = 0.5731$;
- $B_1$: $\sum (\gamma_1^\prime / \gamma_1) = (m/m')^{3/2} = 0.3540$;
- $B_2$: $\sum (\gamma_1^\prime / \gamma_1) = (m/m')^{3/2} = 0.3540$;
- $E$: $\sum (\gamma_1^\prime / \gamma_1) = (m/m')^{7/2}(M'/M)^{1/2}(I_x/I_x)^{1/4}(I_y/I_y)^{1/4} = 0.1104$.

These calculated values for the ratios are strictly correct only for harmonic vibrations. The effect of anharmonic terms in the potential has been discussed briefly by Herzberg.\(^\text{12,13}\) For the purposes of the present discussion let $\nu_1^e$ and $\nu_1^e'$ be the (hypothetical) harmonic frequencies of vibration for the $i$th mode of the isotopic molecules.

\(^{12,13}\) Ibid.

calculated at the minimum of the potential function or by setting all anharmonicity constants equal to zero, and let $\nu_1$ and $\nu_1'$ be the frequencies for the fundamental or $0 \rightarrow 1$ transition as observed spectroscopically. Then

$$\nu_1 = \nu_e(1 - 2x_e),$$
$$\nu_1' = \nu_e'(1 - 2x_e'),$$

where $x_e$ and $x'_e$ are the usual anharmonic constants for the two molecules. The preceding formulas and numerical values refer in each case to $(\nu_e'/\nu_e)$. Therefore the correction factor by which they must be multiplied to obtain the observed product rule ratio,

$$\frac{\nu_1'}{\nu_1},$$

is

$$\frac{\int_{-\infty}^{\infty} (1 - 2x_e')/(1 - 2x_e)}{\int_{-\infty}^{\infty}} [1 + 2(x_e' - x_e^e)],$$

since $x_e$ and $x_e'$ are small compared to unity. It has been shown by Morse that if the anharmonic potential for a diatomic molecule is represented by his well-known exponential-type function, $x^e$ is inversely proportional to the square root of the effective or reduced mass for the vibration. The frequency of vibration $\nu_1^e$ is also inversely proportional to the square root of the mass, so that for a given potential function $x^e$ is proportional to $\nu_1^e$. Thus, for two isotopic molecules

$$\frac{x_1^{e'}}{x_1^e} = \frac{\nu_1^{e'}}{\nu_1^e} = \frac{\nu_1'}{\nu_1}.$$

This relation is not strictly applicable to a polyatomic molecule, as the change in the masses will affect to some extent the form of the normal modes and therefore the potential functions will not be identical.
for the modes in the two molecules. However, it does indicate that the
anharmonicity constant $x'_1$ for the heavier isotope will be smaller in
magnitude than that for the lighter isotope, $x_1$. These constants are
usually positive, and therefore $(x'_1 - x_1)$ will usually be positive. It
follows that the observed product rule ratio will normally be somewhat
greater than that calculated above. According to Halverson, Redlich
has found

$$\frac{\gamma_1}{\gamma_1} / \frac{\gamma_1}{\gamma_1} = 1 + 2(x'_1 - x'_1)$$

to be approximately 1.013 and 1.011 for aliphatic and aromatic C-H
stretching modes, respectively. For bending vibrations this ratio or
correction factor was variable and in fact sometimes less than unity.
However, this ratio almost invariably fell within the limits 0.98 to
1.02.

E. Sum Rules

In section C it has been pointed out that when the secular equa-
tion is written in expanded form, the coefficient $a_n(\mu)$ of $\lambda^{N-n}$ is a
polynomial of degree $n$ (or less) in the isotopic masses $\mu$. On the
other hand the secular equation can always be written in the form

$$\prod_{\lambda_1} (\lambda_1 - \lambda) = 0$$

leading to the well-known result that

$$a_n(\mu) = \sum_{\lambda_1} \cdots \sum_{\lambda_n} \lambda_{\lambda_1} \lambda_{\lambda_2} \cdots \lambda_{\lambda_n}$$

where the sum is over all products of $n$ roots for which no index is
repeated (a root may be repeated if it is degenerate). It follows that

the symmetric nth degree form in the $\lambda$'s on the right-hand side of the last equation is a polynomial of degree $n$ (or less) in $\mu$. In particular, 
\[
a_1(\mu) = \sum_{i,j} \lambda_{ij} = 4n^2 \sum_{i,j} \nu_{ij}^2 = \text{Trace}[GF] = \sum_{i,j} G_{ij}F_{ij}.
\]
But 
\[
G_{ij} = \sum_{x} \mu_x \overline{s_{it}} \cdot \overline{s_{jt}},
\]
so that 
\[
\sum_{i,j} \nu_{ij}^2 = \left(4n\right)^{-1} \sum_{x} \mu_x \sum_{i,j} \left(\overline{s_{it}} \cdot \overline{s_{jt}}\right) F_{ij}.
\]
Now assume that $M_1, M_2, \ldots, M_N$ are different isotopic species to which numerical weights $c_1, c_2, \ldots, c_N$ can be assigned such that at each atomic position
\[
\sum_{\alpha} c_{\alpha} (\mu_t)_{\alpha} = 0,
\]
where $(\mu_{t})_{\alpha}$ is the reciprocal mass at the $t$th position in the $\alpha$th species. If, as will generally be the case, non-isotopic atoms are present, then the last equation must apply also for such atoms. If the atom at $t'$ is a non-isotopic atom of fixed reciprocal mass $\mu_{t'}$ (independent of $\alpha$) then 
\[
\mu_{t'}, \sum_{\alpha} c_{\alpha} = 0.
\]
The force constants $F_{ij}$ will be identical for the isotopic species. Assume also that the same internal coordinates are chosen for the different species. This is always possible for geometrical coordinates not depending on the masses, as the isotopic species have identical equilibrium geometrical configurations (neglecting small zero-point vibrational effects). If the isotopic species have the same symmetry the internal coordinates can be chosen to simultaneously reduce the secular equation of each to factors for each symmetry species. If the isotopic species do not have the same symmetry, but have certain
symmetry elements, and thus a certain point group, in common, the coor-
dinates can be chosen to reduce the secular equation to the extent of a
factor for each symmetry species of this common point group. The
s-vectors depend only on the form of the internal coordinates, and will
therefore be the same for the s isotopic species. It therefore follows
on combining the preceding equations and making an interchange of the
order of summation, that for each symmetry species \( \Gamma \) of the common
point group, containing \( n_r \) frequencies, say,
\[
\sum_{\alpha i} c_{\alpha i} \sum_{\kappa i}^{\eta} (\nu_{\alpha i})^2 = (4\pi)^{-1} \sum_{\kappa l} \sum_{\nu j} \langle \overline{3} \rangle_{it} \cdot \overline{3} \rangle_{jt} F_{ij} \sum_{\kappa i} c_{\alpha i} (\nu \cdot \alpha) = 0.
\]
This is the sum rule of Decius and Wilson.  

Higher order sum rules can clearly be obtained related to the
dependence of higher order coefficients, \( a_2(\mu) \), \( a_3(\mu) \), etc., on the
atomic masses. These extended sum rules can be used to relate all the
frequencies of a sufficiently large group of isotopic molecules, so
that in principle the study of additional isotopic species yields no
new information regarding force constants. It can be seen that the
product rule falls naturally into this scheme, since
\[
a_N(\mu) = \prod_{\alpha i} \lambda_{\alpha i} = (2\pi)^2 N(\prod_{\alpha i} \nu_{\alpha i}) = |G||F|.
\]
However, the product rule which is discussed in detail in the preceding
section, is applicable to two isotopic species, while the sum rules

17. S. Broderson and A. Langseth, Math. fys. Skrifter Danske
18. J. Heicklen, Abstracts of Symposium on Molecular Structure
and Spectroscopy, Columbus, Ohio, June 1961, page 40.
yield useful information only when applied to three or more species. Since only the two species $\text{B}_2\text{H}_9$ and $\text{B}_2\text{D}_9$ are considered in the present investigation, the sum rules are not applicable.

F. Small Isotope Effect

In general the effects of isotopic mass changes on vibrational spectra are much smaller than those due to replacement of hydrogen by deuterium because of the smaller percentage mass differences for other isotopes. The preceding general product and sum rules are applicable to such small isotopic shifts, but in general it is more useful to use relations which relate directly to the isotopic shifts in frequency. Teller$^{19}$ and Wilson$^{20}$ first discussed small isotope effects, and a summary of their treatment has been given by Halverson.$^{21}$ Further discussions have been given by Edgell,$^{22}$ Taylor,$^{23}$ and Wilson, Decius, and Cross.$^{24}$ Consider first the non-isotopically substituted or "normal" molecule, and let the secular equation be written in the form

$$|F - \lambda G^{-1}| = 0.$$  

Then, as discussed in detail in chapter VI the transformation to normal coordinates reduces $G^{-1}$ to the unit matrix, and $F$ to a diagonal matrix,

$^{21}$ Halverson, op. cit.  
$^{24}$ Wilson, Decius, and Cross, op. cit., Chapter 8.
with the roots \( \lambda_i^0 \) appearing on the diagonal, so that the secular equation assumes the form

\[
| ( \lambda_i^0 - \lambda ) \delta_{ij} | = 0
\]

The secular equation for the isotopically substituted molecule may be formulated using as coordinates the normal coordinates for the normal molecule (which will not in general be precisely the normal coordinates for the substituted molecule but will be an approximation to the latter for small mass changes), and will then take the form given by Wilson.

\[
| \lambda_i^0 \delta_{ij} - \lambda \left[ \delta_{ij} + \sum_t \Delta m_t \mathbf{r}_{it}^0 \cdot \mathbf{r}_{jt}^0 \right] | = 0
\]

Here \( \Delta m_t \) is the mass increment (positive, negative, or zero) for the \( t \)th atom, and the sum extends over all atoms. The vector \( \mathbf{r}_{it}^0 \) represents the displacement of the \( t \)th atom in the \( i \)th normal mode of the "normal" molecule. These vectors are to be normalized by the relation

\[
\sum_t m_t | \mathbf{r}_{it}^0 |^2 = 1
\]

and also satisfy the orthogonality relations

\[
\sum_t m_t \mathbf{r}_{it}^0 \cdot \mathbf{r}_{jt}^0 = 0, \quad i \neq j
\]

In particular, the vectors for the normal modes must be orthogonal to translation and rotation of the molecule, so that

\[
\sum_t m_t \mathbf{r}_{it}^0 = 0
\]

and

\[
\sum_t m_t \mathbf{R}_t \times \mathbf{r}_{it}^0 = 0
\]

where \( \mathbf{R}_t \) is the vector from the center of mass to the \( t \)th atom. Additional relations satisfied by the vectors \( \mathbf{r}_{it}^0 \) have been given by Teller.

In the preceding secular equation \( \lambda_i^0 \) is the \( i \)th root for the normal molecule, and the roots \( \lambda_i \) of this equation are those for the
substituted molecule. Of course the corresponding frequencies are
related to the roots by \( \lambda^0_1 = 4\pi^2 \nu_1^0 \) and \( \lambda_1 = 4\pi^2 \nu_1 ^2 \), so that the
isotopic frequency shifts, \( \Delta \nu_1 = \nu_1 - \nu_1^0 \) are readily evaluated. For
small frequency shifts the approximation
\[
\left( \Delta \nu_1 / \nu_1^0 \right) = \left( \Delta \lambda_1 / 2 \lambda_1^0 \right)
\]
where \( \Delta \lambda_1 = \lambda_1 - \lambda_1^0 \), is adequate. The preceding secular equation
for the substituted molecule is exact (in the harmonic approximation),
and if solved exactly it yields not only the frequencies for the substitu-
ted molecule, but also through its eigenvectors the transformation to
the exact normal modes for the isotopic molecule. However, for small
mass differences an approximate solution is usually sufficient. A
perturbation treatment through terms of second order has been given by
Edgell. The solution correct to terms of first order in the mass
differences may be obtained by simply discarding all off-diagonal terms
in the preceding secular equation. This yields
\[
\left( \lambda_1 - \lambda_1^0 \right) / \lambda_1 = \sum \Delta m_t | \tilde{r}_it |^2
\]
or approximately, since \( \Delta \lambda_1 \) is assumed small,
\[
\Delta \lambda_1 / \lambda_1^0 = \sum \Delta m_t | \tilde{r}_it |^2
\]
An alternative treatment in terms of Wilson's s-vectors has been
given by Taylor in which the secular equation for the substituted
molecule takes the form
\[
| \lambda_1^0 \left[ S_{ij} + \sum \Delta \left( m_t^{-1} \right) \tilde{S}_{it} \cdot \tilde{S}_{jt} \right] - \lambda | = 0
\]
where \( \tilde{S}_{it} \) is the s-vector for the \( t \)th atom and \( i \)th normal mode of the
normal molecule. The orthonormality conditions for these vectors are
\[
\sum \Delta \left( m_t^{-1} \right) \tilde{S}_{it} \cdot \tilde{S}_{jt} = \delta_{ij}
\]
The vectors $\bar{S}_{i}^{\circ}$ for the normal modes are derived from the vectors $\bar{S}_{i}$ for the internal coordinates or internal symmetry coordinates by the transformation

$$
\bar{S}_{i}^{\circ} = \sum_{j} (L^{-1})_{ij} \bar{S}_{j}
$$

where $L$ is the matrix of eigenvectors discussed in chapter VI. The preceding secular equation expressed in terms of $s$-vectors is also exact, and yields the same roots and normal modes for the substituted molecule as that of Wilson. For small mass differences it may also be treated approximately by neglecting off-diagonal terms, and then yields the following equation correct to the first order in $\Delta(m_i^{-1})$,

$$
\Delta \lambda_i / \lambda_i^{\circ} = \sum_{k} \Delta(m_i^{-1}) |\bar{S}_{i}^{\circ}|^2 .
$$

On substitution of the preceding equation for $\bar{S}_{i}^{\circ}$ this yields

$$
\Delta \lambda_i / \lambda_i^{\circ} = \sum_{k} \Delta(m_i^{-1}) \sum_{j,j'} (L^{-1})_{ij} (L^{-1})_{ij'} \bar{S}_{j} \cdot \bar{S}_{j'}
$$

which is equivalent to Eq. (40) of Wilson, Decius, and Cross. However, the earlier equation of Taylor expressing $\Delta \lambda_i / \lambda_i^{\circ}$ in terms of $\bar{S}_{i}^{\circ}$ seems more convenient and has been used in the calculations which follow.

The small isotope effect in pentaborane is due to the substitution of $B^{10}$ for the more abundant isotope $B^{11}$, and has been calculated because of its usefulness in identifying the boron-boron stretching modes. Based on abundances of 81.17 and 18.83 for $B^{11}$ and $B^{10}$, respectively, Hrostowski and Pimentel have calculated the abundances

---

for several isotopic species based on a random distribution of the isotopes. The results of their calculations are given in Table 27.

**TABLE 27**

**ABUNDANCE OF BORON ISOTOPIC SPECIES OF PENTABORANE**

<table>
<thead>
<tr>
<th>Species</th>
<th>Symmetry</th>
<th>Description</th>
<th>Abundance</th>
<th>Relative Abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B^{11}_5H_9$</td>
<td>$C_4v$</td>
<td></td>
<td>0.344</td>
<td>(1.00)</td>
</tr>
<tr>
<td>$B^{11}_4B^{10}_9$</td>
<td>$C_s$</td>
<td>$B^{10}$ in base</td>
<td>0.336</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>$C_{4v}$</td>
<td>$B^{10}$ at apex</td>
<td>0.084</td>
<td>0.24</td>
</tr>
<tr>
<td>$B^{11}_3B^{10}_2H_9$</td>
<td>$C_s$</td>
<td>$B^{10}$ in base, apex</td>
<td>0.077</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>$C_s$</td>
<td>$B^{10}$ in base, adjacent</td>
<td>0.077</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>$C_{2v}$</td>
<td>$B^{10}$ in base, opposite</td>
<td>0.038</td>
<td>0.11</td>
</tr>
<tr>
<td>$B^{11}_2B^{10}_3H_9$</td>
<td>$C_s$</td>
<td>$B^{11}$ in base, apex</td>
<td>0.016</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>$C_s$</td>
<td>$B^{11}$ in base, adjacent</td>
<td>0.016</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>$C_{2v}$</td>
<td>$B^{11}$ in base, opposite</td>
<td>0.008</td>
<td>0.02</td>
</tr>
</tbody>
</table>

The isotope shifts resulting from the substitution of one $B^{10}$ in $B^{11}_5H_9$ and $B^{11}_5D_9$ to yield $B^{11}_4B^{10}_9$ and $B^{11}_4B^{10}_9$, have been calculated from the preceding equations. The vectors $\overline{S}_{it}$ were calculated from the symmetry vectors $\overline{S}_{it}$ given in Table 14 and the transposed eigenvector matrices, $K = (L^{-1})^t$, given in Table 26. For the substitution of one $B^{10}$ for $B^{11}$,

$$\Delta(\text{amu}^{-1}) = (10.016)^{-1} - (11.013)^{-1} = 0.00904,$$

in atomic weight units. The calculations have been carried out only for the $A_1$ symmetry species, as the small $B^{10} - B^{11}$ isotope splitting...
is observed only for certain bands which are polarized in the Raman spectrum. Values are given for the substitution of $B^{10}$ at the apex position, and one $B^{10}$ in the base position. To the first order in $\Delta (m^{-1})$ values for substitution of two or more $B^{10}$'s may be obtained by appropriately weighted addition of these values. Values of $\Delta V_i/V^o_i$ were calculated first, and $\Delta V_i$ was then estimated from the values of $V^o_i$ calculated in the normal coordinate analysis. This seems more self-consistent than the use of observed frequencies, although the use of the latter would produce essentially negligible changes (10 percent or less) in the $\Delta V_i$'s. The calculated isotope shifts are given in Table 28. Further discussion of these isotopic effects will be deferred to the next chapter.

**Table 28**

<table>
<thead>
<tr>
<th>Normal Isotopic Species</th>
<th>Frequency</th>
<th>Isotopic Frequency Shift</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\nu$(obs.)</td>
<td>$\nu$(calc.)</td>
</tr>
<tr>
<td></td>
<td>(cm$^{-1}$)</td>
<td>(cm$^{-1}$)</td>
</tr>
<tr>
<td>$B^{11}D_9^{5}$</td>
<td>2610</td>
<td>2619</td>
</tr>
<tr>
<td></td>
<td>2598</td>
<td>2611</td>
</tr>
<tr>
<td></td>
<td>1842</td>
<td>1883</td>
</tr>
<tr>
<td></td>
<td>1123</td>
<td>1140</td>
</tr>
<tr>
<td></td>
<td>986</td>
<td>1014</td>
</tr>
<tr>
<td></td>
<td>798</td>
<td>839</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>637</td>
</tr>
<tr>
<td>$B^{11}H_9^{5}$</td>
<td>1980</td>
<td>1969</td>
</tr>
<tr>
<td></td>
<td>1967</td>
<td>1947</td>
</tr>
<tr>
<td></td>
<td>1391</td>
<td>1386</td>
</tr>
<tr>
<td></td>
<td>959</td>
<td>992</td>
</tr>
<tr>
<td></td>
<td>746</td>
<td>767</td>
</tr>
<tr>
<td></td>
<td>737</td>
<td>717</td>
</tr>
<tr>
<td></td>
<td>512</td>
<td>519</td>
</tr>
</tbody>
</table>
VIII. ASSIGNMENT OF VIBRATIONAL FREQUENCIES

A. Introduction

In theory the assignment of the observed vibrational frequencies of normal and deuterated pentaborane to their respective symmetry species should be relatively unambiguous based on the following principles discussed in detail in preceding chapters. Of primary importance are the selection rules and polarization characteristics, as shown in Table 29. The type of infrared band is also indicated in the table, but as discussed in chapter V the moments of inertia of pentaborane are such that parallel and perpendicular bands have similar envelopes so that this classification is not likely to be very useful.

TABLE 29
ACTIVITY OF VIBRATIONAL MODES OF PENTABORANE

<table>
<thead>
<tr>
<th>Symmetry Species</th>
<th>Number of Modes</th>
<th>Infrared Activity</th>
<th>Band Type</th>
<th>Raman Activity</th>
<th>Polarization in Raman</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₁</td>
<td>7</td>
<td>Active</td>
<td>Parallel</td>
<td>Active</td>
<td>Polarized</td>
</tr>
<tr>
<td>A₂</td>
<td>2</td>
<td>Inactive</td>
<td>--</td>
<td>Inactive</td>
<td>--</td>
</tr>
<tr>
<td>B₁</td>
<td>5</td>
<td>Inactive</td>
<td>--</td>
<td>Active</td>
<td>Depolarized</td>
</tr>
<tr>
<td>B₂</td>
<td>4</td>
<td>Inactive</td>
<td>--</td>
<td>Active</td>
<td>Depolarized</td>
</tr>
<tr>
<td>E</td>
<td>9</td>
<td>Active</td>
<td>Perpendicular</td>
<td>Active</td>
<td>Depolarized</td>
</tr>
</tbody>
</table>
From Table 29 the $A_1$ fundamentals may be assigned as those frequencies active in both the infrared and Raman, and polarized in the Raman. The $E$ frequencies are those also active in both spectra but depolarized in the Raman. The assignment of the $A_1$ and $E$ frequencies should exhaust the infrared active fundamentals. The remaining Raman active fundamentals, all of which should be depolarized, must be assigned to species $B_1$ or $B_2$ but cannot be further classified on the basis of selection rules and polarization data alone. As the $A_2$ frequencies are inactive in both spectra the only hope of obtaining experimental values for them is through a thorough study of overtone or combination bands. The activities of the latter have been given in Table 8. Fortunately there are only two $A_2$ modes in pentaborane.

In practice, the assignment of vibrational frequencies is more difficult than the preceding discussion would indicate. Certain fundamentals, although allowed by selection rules, may be weak and either not observed in the infrared or Raman spectra or not clearly assignable as fundamentals. Some Raman lines may be so weak that their polarization or depolarization cannot be determined accurately. Finally two or more fundamentals may approximately coincide, giving the appearance of one band whereas there are in reality several bands.

Additional aid is available from the order and product rules when assignments are made simultaneously for the deuterated and non-deuterated molecules as in the present case for $B_5H_9$ and $B_5D_9$ (the sum rules are useful only when comparisons are made between at least three isotopic species). These rules are discussed in chapter VII. The order rule places upper and lower bounds on each frequency of one isotopic species
once those of the other species have been assigned. The product rule is extremely useful since it provides a definite value, accurate except for small anharmonic effects, for the ratio of the products of frequencies for the two isotopic species within each symmetry species. It may be used to calculate a missing frequency but is more satisfactory when applied as a check on the assignment of observed fundamentals.

Additional progress in the assignment is possible only on the basis of a more detailed classification of the vibrational modes of each symmetry type with regard to the type of motion predominantly involved. For covalent molecules with directional bonds the usual classification is into bond stretching and bond angle bending modes, with further subdivision according to the type of bond or bonds involved. In pentaborane the types of bonds to be considered are boron-boron and boron-hydrogen (or deuterium) bonds. The boron-boron bonds may be subdivided into base-apex (B-B₀) and base-base (B-B) bonds. This classification does not necessarily imply that base-base bonds of significant strength exist, but refers simply to vibrational change of the B-B distance (see the discussion of bonding in pentaborane in chapter II). The boron-hydrogen bonds may be classified into ordinary terminal bonds of two types (base, or B-H, and apex, or B₀-H₀ bonds) and boron-hydrogen bridge bonds (B-H').

Bonds of each type give rise to stretching and bending motions. In most cases these stretching or bending coordinates occur in equivalent sets of 4 or 8 coordinates. Linear combinations of each equivalent set which transform according to the irreducible representations or symmetry
species of the point group $C_{4v}$ can be formed in the familiar way. Thus, the 4 B-B stretchings yield $A_1$, $B_2$, and E, and the 4 B-B$_0$ and 4 B-H stretchings each yield $A_1$, $B_1$, and E combinations. The single B$_0$-H$_0$ stretching is $A_1$. The 8 B-H' bridge stretchings yield $A_1$, $A_2$, $B_1$, $B_2$, and two E combinations. However, it is convenient to classify these further by first forming symmetrical and unsymmetrical combinations corresponding to the sum and difference of the two B-H' stretchings in each bridge. The 4 symmetrical bridge stretchings then classify as $A_1$, $B_2$, and E, and the unsymmetrical bridge stretchings as $A_2$, $B_1$, and E.

It will be convenient to regard the 4-fold symmetry axis of the molecule as "vertical," and to describe certain motions as "vertical" if the motion of the atoms is restricted to planes containing the symmetry axis (the motions are not necessarily parallel to the axis). Similarly, atomic motions restricted to planes perpendicular to the symmetry axis will be called "horizontal." Each terminal B-H bond gives rise to one vertical and one horizontal bending. The 4 vertical B-H bendings classify as $A_1$, $B_1$, and E, and the 4 horizontal B-H bendings as $A_2$, $B_2$, and E. The single apex B$_0$-H$_0$ bond yields a doubly-degenerate (horizontal) E bending. Each B-H'-B boron-hydrogen bridge might be regarded as giving rise to two symmetrical bending modes. In one of these the H' atom moves perpendicularly to the equilibrium plane of the bridge. This will be referred to as vertical bridge rocking, and the 4 bridge rockings of this type yield $A_1$, $B_2$, and E combinations. The other or in-plane bridge bending is that of the central B-H'-B angle, and may be described as symmetrical bridge bending. However, it is
readily seen that only three coordinates are required to fix the configuration of each bridge within its own plane. These may be taken to be the B-B and two B-H\textsuperscript{1} bond lengths. As the stretchings corresponding to these bonds have already been introduced (in the case of the two B-H\textsuperscript{1} bonds through the symmetrical and unsymmetrical combinations), the addition of the symmetrical bridge bendings would be equivalent to the introduction of 4 redundant coordinates. Although no hesitancy was shown in introducing redundant coordinates in the normal coordinate analysis of chapter VI, in order to admit additional valence force constants, the use of redundant coordinates is undesirable in the present qualitative classification. However, as an alternative to the preceding description the in-plane configuration of the bridges could also be described in terms of the symmetrical and unsymmetrical bridge stretchings and the symmetrical bridge bendings. In this case the 4 symmetrical bridge bendings would simply replace the 4 base B-B stretchings, and would also yield A\textsubscript{1}, B\textsubscript{2}, and E combinations. This classification may even be more realistic in terms of the bonding in pentaborane, since as discussed in chapter II, it is doubtful if base B-B bonds of very significant strength actually exist. However, because these motions involve in any case considerable motion of the boron atoms, and this results in some cases in observable B\textsuperscript{10}-B\textsuperscript{11} isotopic splitting, the description in terms of B-B base stretching has been chosen in preference to that of symmetrical bridge bending.

The problem of avoiding redundant coordinates also enters into the description of the deformation of the B\textsubscript{5} boron pyramid or "skeleton" of the molecule. A non-linear structure of 5 atoms has 9 independent
internal degrees of freedom. The choice of the $4\, B-B$ and $4\, B-B_0$ bond stretchings has already fixed 8 of these, so that only one deformation mode independent of the stretchings can exist. This deformation will be referred to as skeletal bending and is of symmetry $B_1$. Its qualitative form may be seen by considering a tetragonal pyramid of freely jointed links of fixed length. Such a structure has only a single deformation mode in which opposite corners of the square base of the pyramid (opposite base boron atoms) alternatively approach and recede. Since this mode involves motion of the heavy boron atoms and (as an idealization at least) only bond bending as opposed to stretching, it is expected to be the lowest vibrational frequency of the molecule.

The preceding qualitative classification of the vibrational modes of pentaborane is summarized in Table 30, which is arranged for convenience by symmetry species. However, it should be realized that the true normal modes are in general mixtures of the bond stretchings and bendings within each symmetry species, which can be determined only by a complete normal coordinate analysis such as that in chapter VI. The qualitative classification will be useful in making rough estimates of the frequencies of certain modes based on the frequencies of similar modes in normal and deuterated diborane. This is the only other boron hydride for which a complete assignment and normal coordinate analysis is available. The spectral data and assignments for $B_2H_6$ and $B_2D_6$ are summarized in Table 31. The values calculated by Bell and Longuet-Higgins from a normal coordinate analysis are also given. All the other authors contributed new spectroscopic data in addition to making assignments. The several assignments are relatively concordant except for that of Anderson and
TABLE 30

CLASSIFICATION OF VIBRATIONAL MODES OF PENTABORANE

$A_1$ Symmetry Species

- B-H stretching
- B$^0$-H$^0$ stretching
- B$^0$H' symmetrical bridge stretching
- B-H vertical bending
- Vertical bridge rocking
- B-B base stretching
- B-B$^0$ pyramidal stretching

$A_2$ Symmetry Species

- B-H' unsymmetrical bridge stretching
- B-H horizontal bending

$B_1$ Symmetry Species

- B-H stretching
- B-H' unsymmetrical bridge stretching
- B-H vertical bending
- B-B$^0$ pyramidal stretching
- Boron skeletal bending

$B_2$ Symmetry Species

- B-H' symmetrical bridge stretching
- B-H horizontal bending
- Vertical bridge rocking
- B-B base stretching

$E$ Symmetry Species

- B-H stretching
- B-H' symmetrical bridge stretching
- B-H' unsymmetrical bridge stretching
- B-H vertical bending
- B-H horizontal bending
- B$^0$-H$^0$ apex bending
- Vertical bridge rocking
- B-B base stretching
- B-B$^0$ pyramidal stretching
<table>
<thead>
<tr>
<th>Description</th>
<th>Number</th>
<th>Symmetry</th>
<th>$\tilde{3}_{2}H_6$ (cm$^{-1}$)</th>
<th>$I^a$</th>
<th>$II^b$</th>
<th>$III^c$</th>
<th>$IV^d$</th>
<th>$ve^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-H stretching</td>
<td>1</td>
<td>$A_1$</td>
<td>2495, 2523, 2523, 2523, 2524</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>$B_3$</td>
<td>2475, 2558, 2522, 2522, 2525</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>$B_3^u$</td>
<td>2585, 2625, 2514, 2609, 2612</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>$B_3^u$</td>
<td>2530, 2489, 2591, 2591, 2591</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bridge stretching</td>
<td>2</td>
<td>$A_2$</td>
<td>1985, 2102, 2102, 2102, 2104</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>$A_2$</td>
<td>1861, 1861, 1861, 1988, 1914</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>$A_2$</td>
<td>1540, 1745, 1321, 1758, 1768</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>17</td>
<td>$A_2$</td>
<td>1608, 1608, 1604, 1604, 1602</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BH$_2$ bending</td>
<td>3</td>
<td>$A_3$</td>
<td>1190, 1180, 1180, 1180, 1180</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>$B_3$</td>
<td>1178, 1178, 1175, 1174, 1177</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BH$_2$ rocking (in plane)</td>
<td>9</td>
<td>$B_3$</td>
<td>1450, 1405, 1283, 369, 950</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>$B_3$</td>
<td>800, 821, 764, 505, 920</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BH$_2$ wagging (out of plane)</td>
<td>14</td>
<td>$B_3^u$</td>
<td>920, 981, 974, 973, 973</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BH$_2$ vs. bridge torsion</td>
<td>7</td>
<td>$B_3$</td>
<td>1059, 1008, 1013, 764, 1035</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bridge flexing</td>
<td>5</td>
<td>$A_1$</td>
<td>890, 613, 1013, 829</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B-B stretching</td>
<td>15</td>
<td>$B_3^u$</td>
<td>1505, 1321, 1745, 1012</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>$B_3^u$</td>
<td>350, 412, 369, 1857, 358</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>$A_1$</td>
<td>792, 792, 792, 793, 794</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

b. Ibid., assigned values.
g. Used in deriving the force constants.
h. Observed value of 412 is high frequency branch of 369 cm$^{-1}$ band.
i. Corrected for Fermi resonance.
j. Derived from overtones or combinations.
k. Observed but not assigned.
l. Calculated.
<table>
<thead>
<tr>
<th>VI&lt;sup&gt;f&lt;/sup&gt;</th>
<th>VII&lt;sup&gt;e&lt;/sup&gt;</th>
<th>VIII&lt;sup&gt;e&lt;/sup&gt;</th>
<th>IX&lt;sup&gt;f&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>2532</td>
<td>1960&lt;sup&gt;i&lt;/sup&gt;</td>
<td>1967</td>
<td></td>
</tr>
<tr>
<td>1950</td>
<td>1845&lt;sup&gt;i&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1994</td>
<td>1999&lt;sup&gt;i&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2600</td>
<td>1980&lt;sup&gt;i&lt;/sup&gt;</td>
<td>1968&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>2109</td>
<td>1511</td>
<td>1515</td>
<td></td>
</tr>
<tr>
<td>1461</td>
<td>1465&lt;sup&gt;i&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1273</td>
<td></td>
<td>1287</td>
<td></td>
</tr>
<tr>
<td>1184</td>
<td>929</td>
<td>912</td>
<td></td>
</tr>
<tr>
<td>876&lt;sup&gt;j&lt;/sup&gt;</td>
<td>874&lt;sup&gt;j&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>914&lt;sup&gt;j&lt;/sup&gt;</td>
<td>705&lt;sup&gt;j&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>722&lt;sup&gt;i&lt;/sup&gt;</td>
<td>719&lt;sup&gt;i&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>722&lt;sup&gt;j&lt;/sup&gt;</td>
<td>870&lt;sup&gt;j&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1026&lt;sup&gt;k&lt;/sup&gt;</td>
<td>522</td>
<td>600&lt;sup&gt;i&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>1310&lt;sup&gt;k&lt;/sup&gt;</td>
<td>730</td>
<td></td>
<td></td>
</tr>
<tr>
<td>788&lt;sup&gt;a&lt;/sup&gt;</td>
<td>726</td>
<td>712</td>
<td></td>
</tr>
</tbody>
</table>

Calculated values.

<sup>1</sup>H<sub>6</sub> and <sup>3</sup>Li<sub>6</sub>.

Frequencies for <sup>1</sup>H<sub>2</sub> and <sup>1</sup>Li<sub>2</sub>.
Barker for $B_2H_6$; in a private communication Barker has indicated he believes several changes should be made in this assignment, the general effect of which is to bring it into better agreement with the others. For this reason the assignment of Anderson and Barker will be discounted where it conflicts with the other assignments. The frequencies corrected for Fermi resonance will also be ignored as the accuracy of the corrections has not been evaluated.

As a final overall check on the frequency assignment for $B_5H_9$ there is available the calorimetric or third law entropy of the latter. After subtraction of the calculated translational and rotational entropies this yields a value for the vibrational entropy at a single temperature ($296^0K$). This is primarily useful as a check on the lowest frequencies, as these make the largest contributions to the entropy.

Following the completion of the assignment of the $A_1$ and $E$ modes, a normal coordinate analysis for $B_5H_9$ and $B_5D_9$ was undertaken as described in chapter VI. To some degree this may be regarded as a confirmation of the assignment for these two species. For example, the $B^{10}-B^{11}$ isotope splittings computed in Table 28 support the assignment of the B-B and B-B$_0$ stretching modes. However, the principal aid obtained from the normal coordinate analysis lay in the calculated frequencies for the $B_1$ and $B_2$ modes, and especially the two $A_2$ modes which are not active as fundamentals in either the infrared or Raman spectrum. These calculated frequencies were used in the calculation of the vibrational entropy where observed frequencies were not available.

This is far preferable to merely estimating such frequencies, which would give one enough disposable parameters to fit the entropy exactly and render any agreement between calculated and experimental entropies more or less meaningless.

Before discussing the assignment, it will be helpful to recall that the spectral data for $B_5^H$ and $B_5^D$ have been given in chapter III. The infrared frequencies for $B_5^D$ and $B_5^H$ are listed in Tables 2 and 3, respectively. The infrared spectra in the NaCl and KBr regions for these two molecules are given in Figures 3, 4, 5, and 6. The Raman data for $B_5^D$ and $B_5^H$ are listed in Tables 4 and 5, respectively, and the densitometer tracings of the Raman films are shown in Figure 7.

B. Terminal Hydrogen and Deuterium

**Stretching Frequencies**

Prior to the assignment of the remaining vibration frequencies for each symmetry species it seems simplest to assign as a group the terminal hydrogen and deuterium stretching modes. Table 31 shows that the terminal B-H and B-D stretching frequencies are 2522, 2523, 2591, and 2614 for $B_2^H_6$ (column III) and 1845, 1860, 1980, and 1999 cm$^{-1}$ for $B_2^D_6$ (column VIII). In each case the two lowest frequencies represent symmetric or in-phase stretching of the two B-H (or B-D) bonds in the terminal BH$_2$ (or BD$_2$) groups, while the two higher frequencies represent the unsymmetric or out-of-phase stretchings. Two frequencies of each type appear as there are two such groups. These terminal B-H stretching frequencies are without doubt the most characteristic and accurately transferable frequencies of the boron hydrides. The structures of all
the boron hydrides are discussed and illustrated by Lipscomb et al.\textsuperscript{2,3} The only spectra available for $\text{B}_4\text{H}_{10}$ and $\text{B}_5\text{H}_{11}$ are tracings of infrared spectra of the vapors given by McCarty et al.\textsuperscript{4} Gibbins and Shapiro\textsuperscript{5} give a similar tracing of the infrared spectrum of $\text{B}_6\text{H}_{10}$. Frequencies given here and elsewhere have been interpolated from the scales on their figures, except in a few cases in which the authors give numerical values. For $\text{B}_{10}\text{H}_{14}$, Keller and Johnston\textsuperscript{6} have reported both infrared and Raman spectra, the first for the crystal and a 13 percent by weight solution in $\text{CS}_2$, and the second for the solution only. $\text{B}_4\text{H}_{10}$ shows strong absorption maxima centered at about 2470 and 2570 cm$^{-1}$, with some evidence of resolution of each into two or more bands. $\text{B}_5\text{H}_{11}$ has strong absorptions at 2470 and 2565 cm$^{-1}$. Both of these molecules possess $\text{BH}_2$ groups, two equivalent groups occurring in $\text{B}_4\text{H}_{10}$, and three such groups in $\text{B}_5\text{H}_{11}$ of which two are equivalent. From the molecular symmetries it is easily shown that all symmetric and unsymmetric $\text{BH}_2$ stretching modes in these two molecules would be infrared active. Comparison with $\text{B}_2\text{H}_6$ leaves little doubt that the lower and higher frequency absorption bands include the symmetric and unsymmetric $\text{BH}_2$ stretchings in each case. The hydrides $\text{B}_6\text{H}_{10}$ and $\text{B}_{10}\text{H}_{14}$ are similar to $\text{B}_5\text{H}_{9}$ in that they contain no

\begin{itemize}
\end{itemize}
\( \text{BH}_2 \) groups, but only single terminal B-H groups. \( \text{B}_6\text{H}_{10} \) shows a single strong and very sharp infrared absorption at 2600 cm\(^{-1} \), and no appreciable absorption is observed between this frequency and the bridge stretching absorption at 1950 cm\(^{-1} \). The infrared spectrum of \( \text{B}_5\text{H}_9 \) in this region is essentially identical, with a strong absorption at 2600 cm\(^{-1} \), and only weak absorption between this and the bridge frequencies (see Table 3). The Raman spectrum of \( \text{B}_5\text{H}_9 \) also shows only a strong rather broad line at 2600 cm\(^{-1} \), with no other lines above 2280 cm\(^{-1} \).

These facts are strong evidence that all the terminal B-H stretching modes of \( \text{B}_5\text{H}_9 \) and \( \text{B}_6\text{H}_{10} \) have frequencies close to 2600 cm\(^{-1} \). This is significant because in each of these molecules there occurs one terminal B-H bond at the apex of the boron pyramid (which has previously been designated as \( \text{B}_0\text{-H}_0 \)), while the remaining B-H bonds (4 in \( \text{B}_5\text{H}_9 \) and 5 in \( \text{B}_6\text{H}_{10} \)) are associated with boron atoms at the base of the pyramid.

There is no a priori reason to expect such close agreement of the stretching frequencies for apex and base BH bonds in view of the considerable difference in the stereochemical configuration about the apex and base boron atoms. In \( \text{B}_{10}\text{H}_{14} \) there occur 10 terminal B-H bonds, of which 4 are essentially of apex type, and 6 of base type. The Raman spectrum shows a single broad band at 2550-2600, and the infrared spectrum of the crystal strong or very strong absorptions at 2532, 2544, 2566, 2578, 2613, and 2624 cm\(^{-1} \). These observations have little relevance to \( \text{B}_5\text{H}_9 \) because of the greater complexity of the \( \text{B}_{10}\text{H}_{14} \) molecule and the fact that the frequencies may be shifted or split by intermolecular interactions in the crystal.
In view of the preceding discussion, there is no doubt that the strong Raman activity at 2600 cm\(^{-1}\) in \(B_5^2H_9\) and 1944 and 1979 cm\(^{-1}\) in \(B_5^2D_9\) represent terminal B-H and B-D stretching, respectively. The ratios of the latter two frequencies to the former are .748 and .761, respectively, which are within the theoretical limits of .707 to 1.000 discussed in the preceding chapter, and relatively close to the lower limit as expected for hydrogen modes. These bands, which are quite broad, almost certainly represent superpositions of the \(A_1\), \(B_1\), and \(E\) B-H and B-D stretchings and the \(A_1\) \(B_0\) and \(B_0\) \(D_0\) stretchings. The 2600 cm\(^{-1}\) band of \(B_5^2H_9\) coincides with the strong 4915 A. mercury line, which occurs at a position equivalent to a Raman displacement of 2602 cm\(^{-1}\). Probably as a result of this no resolution of detail is observed in the 2600 cm\(^{-1}\) Raman band, and even the precise position of the maximum is obscured. However, there is a fairly definite indication that the high frequency side of the band is partially polarized as shown in Figure 7, indicating that at least one of the \(A_1\) components lies on the high-frequency side. In the present investigation using a NaCl prism no resolution of detail is observed in the strong infrared band at 2610 cm\(^{-1}\), although Hrostowski and Pimentel\(^7\) who studied this region with a LiF prism report a maximum at 2598 and a shoulder at 2610 cm\(^{-1}\).

The situation is somewhat similar in \(B_5^2D_9\), where two partially resolved Raman lines are observed at 1944 and 1979 cm\(^{-1}\), the first slightly and the second more strongly polarized. In the infrared a

strong absorption maximum is observed at 1967, with a shoulder at 1980 cm\(^{-1}\) Hrostowski and Pimentel report for this infrared band a very strong maximum at 1962 cm\(^{-1}\), and a shoulder of nearly equal strength at 1972 cm\(^{-1}\), in good agreement with the frequencies 1967 and 1980 cm\(^{-1}\) obtained in the present investigation. However, the authors also report two additional features of this band of about 1/6 the peak intensity at 1989 and 2005 cm\(^{-1}\) Approximately they studied this band with a NaCl prism as in the present investigation, as they state the LiF prism was used only above 2100 cm\(^{-1}\) An examination of their published spectrum, as well as the original of our spectrum which is reproduced on a small scale in Figure 3, shows that these additional frequencies correspond to inconspicuous shoulders on the high frequency side of the band. These slight features of the infrared band do not seem to be sufficiently definite for serious consideration as fundamentals and are ignored in the present assignment.

The frequencies calculated for terminal hydrogen and deuterium stretching in the normal coordinate analysis of chapter VII are shown in Table 32. The same force constant was assumed for the \(B_0-H_0\) and \(B-H\) bonds in these calculations, and therefore no significance can be attached to the relative values for the apex and base stretching modes. However, some weight must be given to the relative values of the base stretching modes for each molecule, which indicate that the \(B_1\) and \(E\) frequencies lie below the \(A_1\) frequency. It will also be noted that considerably greater frequency separations of these modes are predicted for \(B_5D_9\) than \(B_5H_9\), which is consistent with the resolution of two Raman bands for \(B_5D_9\) and only one for \(B_5H_9\).
### TABLE 32

CALCULATED TERMINAL HYDROGEN AND DEUTERIUM STRETCHING FREQUENCIES

<table>
<thead>
<tr>
<th>Bond Type</th>
<th>Mode</th>
<th>Frequency (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$B_{5}H_{9}$</td>
</tr>
<tr>
<td>Apex</td>
<td>$A_1$</td>
<td>2611</td>
</tr>
<tr>
<td>Base</td>
<td>$A_1$</td>
<td>2619</td>
</tr>
<tr>
<td></td>
<td>$B_1$</td>
<td>2604</td>
</tr>
<tr>
<td></td>
<td>$E$</td>
<td>2607</td>
</tr>
</tbody>
</table>

One of the $A_1$ stretchings in $B_{5}D_{9}$ must certainly be assigned to the 1979 cm$^{-1}$ Raman and 1980 cm$^{-1}$ infrared bands. Presumably the $B_1$ B-D stretch is responsible for the Raman line at 1944 cm$^{-1}$. The assignment of the remaining $A_1$ and $E$ stretchings is somewhat arbitrary. Both are assigned to the 1967 cm$^{-1}$ infrared band as they should be infrared active, and will not interact because they belong to different species. The slight polarization of the 1944 cm$^{-1}$ Raman band may be a result of overlap with a polarized but unresolved $A_1$ Raman band at about 1967 cm$^{-1}$. Another possibility is the assignment of the second $A_1$ and the $B_1$ mode to the 1944 cm$^{-1}$ band in the Raman, but the assignment of the second $A_1$ to 1967 cm$^{-1}$ has been preferred because it should be infrared active.

With this assignment for $B_{5}D_{9}$, it is consistent to assign one $A_1$ terminal hydrogen stretching of $B_{5}H_{9}$ to the 2610 cm$^{-1}$, and the other $A_1$ and $E$ stretchings to the 2598 cm$^{-1}$ infrared bands. The $B_1$ stretching evidently contributes to the broad Raman band at 2600 cm$^{-1}$ but is
unresolved. As is clear from Figures 3, 5, and 7, these Raman and infrared bands are all sufficiently broad to include the scattering or absorption arising from the four modes under consideration. The uncertainties in the assignments of the individual modes have a negligible effect on the thermodynamic functions to be computed subsequently because of the high values of these frequencies.

C. Assignment of \(A_1\) Frequencies

1. Polarized Raman Lines

As shown by Table 5 the following Raman lines of \(3\frac{1}{2}H_9\) are definitely polarized: 793, 803, 986, 1001, 1120, 1830, 2077, and 2152 cm\(^{-1}\). The depolarization ratio of 0.81 for the 700 cm\(^{-1}\) line indicates that it is probably polarized, especially since the ratios for all definitely depolarized lines are greater than the theoretical 0.86, apparently as a result of a systematic error in the polarization measurements. The polarization characteristics of the 2600 cm\(^{-1}\) band are obscured by an overlying mercury line, as discussed in the preceding section, but it appears to be partly polarized. There is also some indication from the densitometer tracings that the weak lines at 1170 and 1193 cm\(^{-1}\) are polarized, but no quantitative depolarization ratios were obtainable. For \(3\frac{3}{2}D_9\), Table 4 shows that the 737, 959, 975, and 1979 cm\(^{-1}\) lines are strongly polarized. The depolarization ratios for the 639, 682, and 1393 cm\(^{-1}\) lines are in the neighborhood of the theoretical 0.86 for depolarized lines, but in view of the difficulties discussed there relative to quantitative photographic photometry at these low intensities, not much weight can be assigned to the
depolarization ratios. However, as will be developed on the basis of other arguments, the 639 and 682 cm\(^{-1}\) lines are believed to correspond to non-totally symmetric vibrations and therefore to be depolarized.

2. Bridge Stretching Frequencies

The terminal hydrogen and deuterium stretchings have been dealt with in the preceding section, and assigned to the 2600 cm\(^{-1}\) band of \(\text{B}_5\text{H}_9\) and the 1944 and 1979 cm\(^{-1}\) bands of \(\text{B}_5\text{D}_2\). The \(A_1\) bridge stretchings will be considered next. These are symmetric bridge stretchings in which the two bonds of each \(\text{B-H'-B}\) or \(\text{B-D'-B}\) bridge stretch in phase (unsymmetric bridge stretchings with the two bonds out of phase also occur but not as \(A_1\) modes). The diborane molecule has two symmetric bridge stretching modes, having symmetries of \(A_{1g}\) and \(B_{2u}\) under the molecular point group \(D_{2h}\). Table 31 shows that the observed frequencies of these two modes are 2101 and 1861 cm\(^{-1}\), respectively, for \(\text{B}_2\text{H}_6\). It would perhaps be expected \textit{a priori} that the \(A_1\) bridge stretching in pentaborane in which the four bridges are in phase would have a frequency closer to the higher \(A_{1g}\) mode of diborane in which both bridges are also in phase. However, accurate transference of frequencies from the double bridges of diborane to the single bridges of pentaborane is not to be expected. Intensity considerations should probably be given more weight. The \(A_{1g}\) bridge stretchings of \(\text{B}_2\text{H}_6\) and \(\text{B}_2\text{D}_6\) give rise to very strong Raman lines, and it is reasonable to expect that the \(A_1\) bridge stretching in pentaborane will have considerable strength also. The three polarized Raman lines of \(\text{B}_5\text{H}_9\) in this frequency range with their relative intensities are 1830 (.15), 2077 (.05), and 2152.
cm\(^{-1}\) (0.95), respectively. On the basis of its much greater intensity the 1830 cm\(^{-1}\) line is assigned to the A\(_1\) bridge stretching. The disposition of 2077 and 2152 cm\(^{-1}\) lines, which are almost certainly overtones or combinations, will be discussed subsequently.

The infrared spectrum of B\(_5\)H\(_9\) shows a strong absorption maximum at 1812 cm\(^{-1}\), with shoulders at 1792, 1821, and 1848 cm\(^{-1}\), while weak absorptions occur at 2055, 2110, and 2155 cm\(^{-1}\). This tends to support the preceding assignment as the A\(_1\) bridge stretching is infrared active and would be expected to show considerable intensity as it involves the displacement in phase of four protons with a large component of the resulting dipole along the symmetry axis. However, there are also two infrared active bridge stretchings of symmetry E, and it is most likely that one of the E modes is to be assigned to the absorption maximum at 1812 cm\(^{-1}\), while one of the shoulders at 1821 or 1848 (or both) are to be correlated with the 1830 cm\(^{-1}\) polarized or A\(_1\) Raman band. The latter value for the frequency at the maximum of this quite diffuse Raman band was obtained by interpolation on the densitometer tracing of film No. 64. Earlier visual comparator readings on several Raman films gave an average value of 1843 cm\(^{-1}\). The reason for the discrepancy is not known, but in view of the diffuseness and unsymmetrical nature of the band the densitometer tracing has been given more weight. In addition, it should be noted that the infrared and Raman spectra were observed with gaseous and liquid pentaborane, respectively, so exact coincidence of frequencies is not to be expected.
The frequencies of the $A_{1g}$ and $B_{2u}$ symmetrical bridge stretching modes in $B_2D_6$ are 1513 and 1461 cm$^{-1}$, respectively. The ratios of these two frequencies to the corresponding frequencies of $B_2H_6$ are .720 and .785, respectively, or fairly close to the theoretical lower limit of .707 as anticipated for modes involving primarily hydrogen motion. The Raman spectrum of $B_5D_9$ shows the following bands in this region (relative intensities in parentheses): 1274 (.15), 1333 (.17), 1393 (.22), and 1492 cm$^{-1}$ (.17). The ratios of these frequencies to the $A_1$ bridge stretching frequency, 1830 cm$^{-1}$, of $B_5H_9$ are .696, .728, .761, and .815, respectively. The first is lower than the theoretical lower limit, the second and third lie in the range calculated for the two diborane modes, while the fourth is somewhat higher than expected for a hydrogen mode.

The 1393 cm$^{-1}$ Raman line of $B_5D_9$ is assigned to the $A_1$ bridge stretching on the basis of its greater strength and the fact that there is a slight indication that it is polarized (see Table 4). The infrared spectrum shows an infrared band at 1393 cm$^{-1}$ which is assigned to the same mode.

There are four other Raman active and two other infrared active symmetric and unsymmetric bridge stretchings which can account for at least a large part of the additional Raman and infrared activity in this frequency range, as discussed subsequently.

The preceding identification of the bridge stretching frequencies in pentaborane is based primarily on the values of these frequencies in diborane. However, it is of some interest to note the more intense bands of other boron hydrides in this frequency range which are also generally considered to be bridge stretching frequencies. The sources of data have been presented previously. The hydrides $B_4H_{10}$, $B_5H_{11}$,
$B_6H_{10}$, and $B_{10}H_{14}$ all have several single $B-H'-B$ bridges similar to the single bridges in $B_5H_9$. The resemblance is most striking in the cases of $B_5H_{11}$ and $B_6H_{10}$. $B_4H_{10}$ shows a very strong absorption at 2140 cm$^{-1}$ and weaker absorptions at 1740, 1875, and 2295 cm$^{-1}$. $B_5H_{11}$ shows a moderately strong absorption at 2050 cm$^{-1}$ and weak absorptions at 1805, 1880, and 2295 cm$^{-1}$. $B_6H_{10}$ shows a medium strength absorption at 1950 cm$^{-1}$ and very weak absorption at 1640 and 1710 cm$^{-1}$. Gibbins and Shapiro tentatively assign the 1950 cm$^{-1}$ band as bridge stretching, but also a band at 1490 which seems too low and more likely to be terminal BH bending. Eighteen infrared bands are observed for $B_{10}H_{14}$ in the bridge stretching range, 1600-2300 cm$^{-1}$. Of these ten are very weak and are probably overtones or combinations. The remaining infrared bands are a strong band at 1875 cm$^{-1}$, medium strength bands at 1625, 1665, 1795, 1900, and 1925 cm$^{-1}$, and weak bands at 1820 and 1950 cm$^{-1}$. In the Raman spectrum of the solution only two bands at 1880 and 1946, both reported as weak, are observed. Decaborane has symmetry $C_{2v}$, and four equivalent bridges. The four symmetric bridge stretchings and the four unsymmetric bridge stretchings each yield vibrations of species $A_1$, $A_2$, $B_1$, and $B_2$. All species are Raman active and all but $A_2$ are infrared active. There should therefore be eight Raman active bridge stretching modes and six infrared active modes. The two $A_1$ or totally-symmetric Raman modes probably have the greatest intensity and correspond to the two observed bands at 1820 and 1950 cm$^{-1}$. Although these are reported as weak, the Raman spectrum was observed for a relatively dilute solution of decaborane in $CS_2$ under unfavorable conditions (decomposition, solid sediment, etc.).
The preceding data indicate that all the boron hydrides have frequencies falling in the range expected for bridge stretching. However, the frequencies must be expected to vary somewhat as a result of differences in molecular structure and bonding in the various hydrides. It should also be noted that only in diborane and pentaborane are the bridges required to be symmetrical by symmetry. In the other hydrides, and especially $^{5}$H$_{10}$ and $^{10}$H$_{14}$, the bridges are unsymmetrical (except that one symmetrical bridge occurs in $^{5}$H$_{11}$).

3. Boron-Boron Stretching Frequencies and the Small Isotope Effect

In pentaborane, as in all the boron hydrides for which the structure is known, two types of boron-boron bonds occur which may be classified as bridge and non-bridge bonds. Bridge bonds may involve one or two protons (single or double bridges) at positions intermediate to the two boron atoms, with an electron pair associated with each proton (or bridge). The only known case of a double bridge is that in $^{2}$H$_{6}$. In the remaining boron hydrides single bridges occur as follows: $^{4}$H$_{10}$ (4); $^{5}$H$_{9}$ (4); $^{5}$H$_{11}$ (3); $^{5}$H$_{10}$ (4); and $^{10}$H$_{14}$ (4). In pentaborane the four base boron-boron bonds are single bridge bonds, which might be written B-H'-B in the notation of Figure 1, but will more commonly be represented as B-B with the understanding that these are bridge bonds. It is clearly somewhat arbitrary to refer to changes in the distance between the two boron atoms in this case as B-B stretching, as it is at least as realistic to regard this motion as bending of the B-H'-B bridge. This is primarily a question of whether the electron-pair bonding is entirely through the bridge, or exists in part directly between the
boron atom. It seems likely that the latter is the case, so that the bridge bond is a three-center or $A$ bond. Otherwise it is difficult to see how a characteristic B-B distance, or bridge angle ($< B-H'-B$) would be maintained, since the 1s orbital of the proton has no directional properties. This conclusion is supported by the necessity in the normal coordinate calculation of chapter VI for inserting a force constant for B-B stretching in addition to constants for $B-H'$ stretching and $B-H'-B$ bending. In any case, the base boron-boron stretching will be referred to as B-B stretching for simplicity. Further justification for this is provided by the fact that in both diborane and pentaborane boron isotope shifts are observed for this mode. The four base-apex or $B-B_0$ bonds in pentaborane (see Fig. 1) are non-bridge bonds. Such bonds in the boron hydrides are in general electron deficient and are explainable only by the concepts of molecular orbital theory. A discussion of the bonding in pentaborane has been given in chapter II.

The most important aid in identifying the $A_1$ boron-boron stretching modes in pentaborane has proved to be the small isotope effect resulting from the presence of isotopes $B^{10}$ and $B^{11}$, with concentrations of 19 and 81 percent, respectively, in natural boron. It is therefore of some interest to review the similar identification through the boron isotope shifts of the boron-boron stretching frequency in diborane, as this will indicate the order of magnitude to be expected for the isotopic shifts.

In $B_2H_6$ containing the normal ratio of the isotopes $B^{10}$ and $B^{11}$ the B-B stretching mode gives rise to a triplet of lines in the Raman
spectrum. The frequencies of these as measured with a liquid sample have been reported as 793, 806, and 821 cm\(^{-1}\) by Anderson and Burg\(^8\), as 794, 811, and 820 cm\(^{-1}\) by Webb, Neu, and Pitzer\(^9\) (at another point in their paper these authors give 792, 808, and 821 cm\(^{-1}\)), and as 794, 807, and 820 cm\(^{-1}\) by Lord and Nielsen\(^10\). The average of these values is 794, 808, and 821 cm\(^{-1}\). Taylor and Emery\(^11\) report the values 788, 802, and 818 cm\(^{-1}\) for the vapor at 4 atm. pressure. All these authors attribute this triplet to the small isotope effect, the three frequencies arising from the molecules \(\text{B}_2\text{H}_6\), \(\text{B}^{10}\text{B}^{11}\text{H}_6\), and \(\text{B}^{10}\text{H}_6\), respectively. This is confirmed beyond doubt by Taylor and Emery's observation that for vapor containing 96 percent \(\text{B}^{10}\text{H}_6\) only a single Raman line at 816 cm\(^{-1}\) occurs. Both sets of data give 14 cm\(^{-1}\) as the isotopic shift resulting from the substitution of one \(\text{B}^{10}\) in \(\text{B}^{11}\text{H}_6\).

The boron small isotope effect in \(\text{B}_2\text{D}_6\) is apparently smaller than that in \(\text{B}_2\text{H}_6\), as a result of the increased mass of the molecule, so that resolution of the effect is more difficult. Rice\(^12\) and Taylor and Emery report a single unresolved band for \(\text{B}_2\text{D}_6\) containing the natural isotopic mixture, at 710 and 712 cm\(^{-1}\), respectively. As the three molecules \(\text{B}_2\text{D}_6\), \(\text{B}^{10}\text{D}_6\), and \(\text{B}^{10}\text{D}\) have relative abundances of 66, 31, and 3.6

\(^12\) Lord and Nielsen, op. cit., Table 4.
percent, respectively, the observed frequency will be presumed to be a mean with these weights of the frequencies for the three isotopic species. Lord and Nielsen and Taylor and Emery have also reported the frequency as 726 and 721 cm\(^{-1}\), respectively, for pure \(B_2^{10}D_6\). If the quite accurate assumption is made that the frequency for \(B_2^{10}B_2^{11}D_6\) is the mean of the frequencies for \(B_2^{10}D_6\) and \(B_2^{11}D_6\), then it can be calculated from the data of Taylor and Emery that the isotopic frequency shift in going from \(B_2^{11}D_6\) to \(B_2^{10}B_2^{11}D_6\) is 3 cm\(^{-1}\), as compared with the corresponding shift of 14 cm\(^{-1}\) for \(B_2^2H_6\).

The spectra available for the other boron hydrides (exclusive of pentaborane) are not of sufficient resolution to show isotopic shifts arising from the boron isotopes. In addition there is little regularity in the observed frequencies for \(B_4^{10}H_6\), \(B_5^{11}H_6\), \(B_5^{10}H_6\), and \(B_10^{10}H_4\) in the range where boron-boron stretching frequencies are expected to occur. As other deformation and bending frequencies can occur in the same range it is not possible to obtain any significant aid from the infrared spectra of these molecules, at least. For \(B_10^{10}H_4\) the Raman spectrum has been reported and shows lines at 350, 709, and 858 cm\(^{-1}\) which are much stronger than any other lines in the spectrum (except the broad band at 2550-2600 cm\(^{-1}\) arising from the superposition of 10 B-H stretching modes). These three strongest lines are very probably associated with totally-symmetric vibrational modes of the boron skeleton of \(B_10^{10}H_4\), with the 350 cm\(^{-1}\) line representing a low-frequency deformation or bending mode, and the 709 and 858 cm\(^{-1}\) lines modes which are primarily boron-boron stretching. It is quite possible that the occurrence of these two frequencies is connected with the presence of two
types of boron-boron bonds, corresponding to bridge-bonded and non-
bridge bonded boron pairs.

The polarized Raman lines of $B_5H_9$ remaining after the assignment
of the $A_1$ terminal and bridge hydrogen stretching modes are the very
strong doublets at (793,803) and (986,1001) cm$^{-1}$, a strong line at 1120
cm$^{-1}$, a medium strength line at 700 cm$^{-1}$, weak lines at 2077 and 2152
cm$^{-1}$, and possibly the very weak lines at 1170 and 1193 cm$^{-1}$ The bands
at 2077 and 2152 cm$^{-1}$ are not only weak but have frequencies much too
high to be considered for any of the remaining $A_1$ fundamentals, and must
therefore be overtone or combination bands. The polarization of the
lines at 1170 and 1193 cm$^{-1}$ is doubtful. If they are depolarized they
may possibly represent $B_1$, $B_2$, or $E$ fundamentals. If they are polarized
then in view of their very low intensity they must be assigned as over-
tones or combinations, since as will be seen from the discussion to
follow the number of strong polarized lines remaining is just equal to
the number of as yet unassigned $A_1$ modes after allowance is made for the
boron isotope effect. These remaining frequencies are the doublets at
(793,803) and (986,1001) cm$^{-1}$, and 700 and 1120 cm$^{-1}$ The only two
definitely polarized Raman lines of $B_5D_9$ which remain following the
assignment of the $A_1$ terminal and bridge deuterium stretching modes are
the very strong line at 737 cm$^{-1}$ and doublet at (959,975) cm$^{-1}$.

The $A_1 B-B$ and $B-B_0$ stretching modes in pentaborane, which repre-
sent symmetrical "breathing" modes of the boron skeleton, are expected
to be the two strongest lines in the Raman spectrum, with the possible
exception of the 2600 cm$^{-1}$ band of $B_5H_9$ and 1944 and 1979 cm$^{-1}$ bands of
$B_5^7D_9$ which represent the superposition of four terminal hydrogen or deuterium stretching modes. Of the 24 bonding electrons, 14 are associated with the bonding of the boron skeleton, of which 8 and 6 are to be assigned to the bridge and non-bridge boron-boron bonds. In general molecular polarizabilities increase as the number of electrons increase.

On this basis alone the two $A_1$ boron stretching modes would most probably be assigned to the Raman doublets at (793, 803) and (986, 1001) cm$^{-1}$ for $B_5^7H_9$, and the line at 737 cm$^{-1}$ and doublet at (959, 975) cm$^{-1}$ for $B_5^7D_9$.

This assignment is greatly strengthened by the resolution of three of these Raman lines into doublets as indicated. This doubling is reasonably interpreted as an example of the small isotope effect, for which the theory has been presented in chapter VII, and due in the present case to the occurrence of two boron isotopes, $B^{10}$ and $B^{11}$, with abundances 19 and 81 percent, respectively. As shown by Table 27, the two most abundant molecular species in $B_5^7H_9$ prepared from natural boron are $B_5^{11}H_9$ and $B_4^{11}B^{10}H_9$, representing 34.4 and 42.0 percent, respectively, of the total isotopic species present. On a statistical basis 1/5 of the $B_4^{11}B^{10}H_9$ will have the $B^{10}$ atom at the apex position and 4/5 at a base position of the boron pyramid. Therefore the abundances of $B_4^{11}B_0^{10}H_9$ and $B_3^{11}B_0^{10}B_0^{11}H_9$ are 8.4 and 33.6 percent, respectively, where $B_0$ denotes the apex atom. It would be expected from qualitative considerations that the substitution of $B^{10}$ at the apex would produce a considerably larger frequency shift for $B_{-3}B_0$ than for $B_{-3}B$ stretching, and conversely for substitution of a $B^{10}$ in a base position. From the abundances given, the satellite produced by substitution at the apex should have about 1/4 the
intensity, and by substitution in the base about the same intensity, as the principal line arising from \( ^{11} \text{H}_2 \). Examination of Figure 7 and the intensities in Tables 4 and 5 indicates that in the doublets (986,1001) for \( ^3 \text{H}_2 \) and (959,975) cm\(^{-1}\) for \( ^3 \text{D}_2 \) the higher frequency component has an intensity about 1/3 that of the lower frequency component, while in the doublet at (793,803) cm\(^{-1}\) for \( ^3 \text{H}_2 \) this ratio is about 3/4. When allowance is made for the uncertainty in the intensities and the neglect of the other isotopic species in Table ?? these observed intensities indicate that the (986,1001) and (959,975) cm\(^{-1}\) doublets are to be assigned to \( ^3 \text{H}_2 \) stretching, and the (793,803) cm\(^{-1}\) doublet to \( ^3 \text{D}_2 \) stretching. The 800 cm\(^{-1}\) band of \( ^3 \text{H}_2 \) occurs with moderate strength in the infrared spectrum, where as seen in Figure 5, it shows remarkably well resolved isotopic shifts. Two extremely sharp peaks of nearly equal intensity are observed at 800 and 808 cm\(^{-1}\), with less intense peaks at 812, 817, 820, and 325 cm\(^{-1}\). This is consistent with the conclusions above. An accurate value of 7.7 cm\(^{-1}\) for the difference in frequency of the peaks at 800 and 808 cm\(^{-1}\) was obtained by observation of the difference in the wavelength counter readings as the peaks were scanned slowly. The peaks at 812-825 cm\(^{-1}\) may plausibly be assigned to isotopic species containing two or more \( ^{10} \text{H} \) atoms. These conclusions are summarized by the assignment in Table 32.

The calculated values in the final column of Table 32 are taken from Table 28 and are only as accurate as the form of the normal modes obtained in the normal coordinate analysis of chapter VI. As is well known the stationary property of the eigenvalues of a vibrating system
has the consequence that the normal modes obtained in such a calculation may be in error by considerably more than the calculated frequencies. Thus, the qualitative agreement between observed and calculated isotopic shifts is satisfactory. It will also be noted that the calculated shifts

<table>
<thead>
<tr>
<th>Isotopic Assignment and Frequency Shifts</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>For Boron-Boron Stretching Frequencies</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Mode</th>
<th>Isotopic Species</th>
<th>Observed Frequency (cm(^{-1}))</th>
<th>Raman Infrared</th>
<th>Infrared</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>B(_5)H(_9)</td>
<td>3-3 stretch</td>
<td>B(_{115})H(_9)</td>
<td>793</td>
<td>800</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>B(<em>{113})B(</em>{10})H(_9)</td>
<td>803</td>
<td>808</td>
<td>10</td>
<td>7.7</td>
</tr>
<tr>
<td>B(_5)H(_9)</td>
<td>B-B(_0) stretch</td>
<td>B(_{115})H(_9)</td>
<td>986</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>B(<em>{114})B(</em>{0})H(_9)</td>
<td>1001</td>
<td>-</td>
<td>15</td>
<td>-</td>
</tr>
<tr>
<td>B(_5)D(_9)</td>
<td>3-B(_0) stretch</td>
<td>B(_{115})D(_9)</td>
<td>959</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>B(<em>{114})B(</em>{10})D(_9)</td>
<td>975</td>
<td>-</td>
<td>16</td>
<td>-</td>
</tr>
</tbody>
</table>

in Table 28 are in qualitative agreement with the conclusion that the B-B\(_0\) and B-B stretching frequencies are affected primarily by substitution of B\(_{10}\) in the apex and base positions, respectively. An exception to this is the 737 cm\(^{-1}\) B-B stretching frequency for B\(_5\)D\(_9\), for which the calculated shifts are relatively small and are not resolved in the spectrum. The normal coordinate analysis and the discussion in the next section indicate that two A\(_1\) modes of B\(_5\)D\(_9\)
having frequencies lying quite close to one another both contribute to
the Raman band centered at 737 cm\(^{-1}\), and in addition that there is con-
siderable mixing of the \(A_1\) boron-boron stretching and B-D bending modes
of \(B_2D_2\). It is also believed that an \(E\) mode contributes to the activity
in this region because of the intense infrared absorption at 746 cm\(^{-1}\).

4. 

**Hydrogen Bending and Bridge Rocking Frequencies**

Following the preceding assignments there remain only two polar-
ized Raman lines of \(B_5H_9\) which are sufficiently intense to be funda-
mentals. These are the lines at 700 and 1120 cm\(^{-1}\). The \(A_1\) modes remaining
to be assigned are the vertical base hydrogen bending and the bridge
rocking. Table 31 shows that the \(A_{1g}\) and \(B_{2u}\) \(B_2H_2\) bending modes of \(B_2H_6\)
have frequencies of 1180 and 1175 cm\(^{-1}\), respectively. These modes would
appear to represent the closest analogy in \(B_2H_6\) to the \(A_1\) hydrogen
bending in \(B_5H_9\), although the analogy is admittedly not very close
because \(3-H\) rather than \(3H_2\) bending is involved in the latter molecule.

Certainly, however, the relation is close enough to indicate that the
1120 cm\(^{-1}\) frequency in \(B_5H_9\) represents primarily hydrogen bending. The
single remaining polarized line at 700 cm\(^{-1}\) must therefore be assigned
to the bridge rocking mode. There is no analogy for the pentaborane
bridge rockings in diborane because in the latter molecule there exists
no high inertia boron framework against which such rocking can occur.

Very similar single bridges on a similar boron framework do occur in
\(B_5H_{11}\) and \(B_5H_{10}\), and it is perhaps worth noting that the infrared
spectra of these molecules show bands at 705 and 685 cm\(^{-1}\), respectively.
The infrared spectrum of $B_5^1H_9$ shows a weak band at 701 cm$^{-1}$ and medium to weak bands at 1127 and 1143 cm$^{-1}$. The 701 cm$^{-1}$ band may be assignable to the $A_1$ bridge rocking mode. However, as will be seen subsequently the product rule and also the relatively small degree of polarization of the 700 cm$^{-1}$ Raman band support the assignment of an E mode at about this same frequency. The 1127 cm$^{-1}$ infrared band is extremely sharp, comparable in this respect to the 800 and 808 cm$^{-1}$ infrared bands. The 1143 cm$^{-1}$ is much less sharp and of about half the intensity of that at 1127 cm$^{-1}$. Hrostowski and Pimentel regarded the 1143 cm$^{-1}$ as representing a satellite or satellites of the 1127 cm$^{-1}$ band resulting from boron isotopic shifts. However, there is little resemblance between the structure of the 1127 and 1143 cm$^{-1}$ bands and the isotopic structure of the 900, 808, 812, 817, etc., boron isotope bands. In addition the 1120 cm$^{-1}$ Raman band is the sharpest line in the Raman spectrum, with no trace of isotopic satellites of intensity remotely comparable to the principal line. Hrostowski and Pimentel took note of the isotopic structure of the 900 cm$^{-1}$ infrared band also, but had available only a brief report of the Raman spectrum. They therefore did not attach sufficient importance to the isotopic doublets at (793, 803) and (986, 1001) cm$^{-1}$ in the Raman spectrum which have been assigned as the boron-boron stretching modes in the preceding section. It is therefore felt that the sharp infrared band at 1127 cm$^{-1}$ is to be correlated with the 1120 cm$^{-1}$ Raman band as $A_1$ hydrogen bending, but that another explanation must probably be found for the 1143 cm$^{-1}$ band (it might, for example, be an overtone of an infrared band at 568 cm$^{-1}$).
The $A_1$ modes of $B_2^1H_9$ have now been completely assigned with what would appear to be very little uncertainty, in view of the polarization data utilized. The assigned frequencies (for $B_2^{11}H_9$) are 700, 793, 986, 1120, 1830, 2598, and 2610 cm$^{-1}$. The $A_1$ frequencies of $B_2^{12}H_9$ which have been assigned with comparable certainty are 737, 959, 1393, 1967, and 1980 cm$^{-1}$. From the product rule ratio 0.1894 for the $A_1$ frequencies as given in chapter VII, it is easily calculated that the two remaining $A_1$ frequencies of $B_2^{12}H_9$ must have a product of $3.76 \times 10^5$ cm$^{-2}$, and a geometric mean of 613 cm$^{-1}$, within deviations of a few percent permitted as a result of anharmonicities.

From the discussion of upper and lower bounds on the frequencies of isotopic molecules given in connection with the order rule in chapter VII, it can be concluded that the lowest $A_1$ frequency of $B_2^{12}H_9$, which in the present discussion will be denoted by $\nu'_a$, must be in the interval

$$0.7074 \nu_a \leq \nu'_a \leq \nu_a,$$

where $\nu_a$ is the lowest $A_1$ frequency of $B_2^1H_9$. Insertion of the value $\nu_a = 700$ cm$^{-1}$ yields

$$495 \text{ cm}^{-1} \leq \nu'_a \leq 700 \text{ cm}^{-1}.$$

Similarly, at least one $A_1$ frequency of $B_2^{12}H_9$ must lie in each of the intervals 561-793, 697-986, and 792-1120 cm$^{-1}$, whereas only two frequencies, 737 and 959 cm$^{-1}$, have been assigned which fall in one or another of these intervals. Since 737 cm$^{-1}$ lies in the first two intervals, and 959 cm$^{-1}$ in the last two, the only conclusion which can
be drawn from the order rule alone is that the other unassigned $A_1$ frequency of $B_5D_9$, say $\nu_b'$, must lie in the interval

$$561 \text{ cm}^{-1} \leq \nu_b' \leq 1120 \text{ cm}^{-1}$$

However, as noted above, the product rule requires that

$$(\nu_a', \nu_b')^{\frac{3}{2}} = 613 \text{ cm}^{-1}$$

or, since by definition $\nu_a' \leq \nu_b'$,

$$\nu_a' \leq 613 \text{ cm}^{-1}, \quad \nu_b' \geq 613 \text{ cm}^{-1}$$

Combination of the preceding inequalities yields

$$495 \text{ cm}^{-1} \leq \nu_a' \leq 613 \text{ cm}^{-1},$$

$$613 \text{ cm}^{-1} \leq \nu_b' \leq 1120 \text{ cm}^{-1}$$

Application of the relation for the geometric mean further restricts the allowed interval for $\nu_b'$ as follows,

$$613 \text{ cm}^{-1} \leq \nu_b' \leq 760 \text{ cm}^{-1}$$

The $A_1$ modes of pentaborane are infrared and Raman active. The only infrared band of $B_5D_9$ observed in the interval permitted for $\nu_a'$ is one having a relatively sharp central maximum at 512 cm$^{-1}$, with subsidiary maxima at 499 and 522 cm$^{-1}$. These values agree well with the calculated separation of the P and Q (or Q and R) rotational branches for a symmetric rotor with the moments of inertia of $B_5D_9$, which is 12.4 cm$^{-1}$ for vibrational bands of species $A_1$. As previously remarked, however, the superficial resemblance of this and other band contours in the infrared spectra of $B_5H_9$ and $B_5D_9$ to parallel bands does not conclusively differentiate between $A_1$ and E modes, because the moments of inertia are such that E bands may have much the same contour. Thus, Hrostowski and Pimentel calculate the preceding separation of rotational branches as 10 cm$^{-1}$ for bands of species E. It is worth recalling that
the well defined band at 512 cm\(^{-1}\) was first obtained in the present investigation. It appears as an extremely weak and poorly defined peak in the spectra of Hrostowski and Pimentel, and was ignored by them in their assignment for \(\mathrm{B}_5\mathrm{D}_9\). The only Raman bands of \(\mathrm{B}_5\mathrm{D}_9\) observed in the present investigation in the permitted interval for \(\nu_1\) are two diffuse lines at 507 and 537 cm\(^{-1}\), and a broad plateau at 580-615 cm\(^{-1}\). These features of the Raman spectrum were so weak under the relatively unfavorable conditions prevailing in the present investigation that they are not visible on the polarization films so that no information regarding their polarization is available. However, it appears reasonable to correlate the Raman line of the liquid at 507 cm\(^{-1}\) with the infrared band of the vapor at 512 cm\(^{-1}\). As there is no significant infrared absorption in the interval 535-615 cm\(^{-1}\) the Raman activity at 537 cm\(^{-1}\) and 580-615 cm\(^{-1}\) is unlikely to represent \(A_1\) or \(E\) modes and may be excluded from the present discussion. Furthermore, \(\nu_1'\) of \(\mathrm{B}_5\mathrm{D}_9\), which is correlated with the 700 cm\(^{-1}\) frequency of \(\mathrm{B}_5\mathrm{H}_9\), must represent primarily the \(A_1\) rocking of the deuterium bridges and should certainly show infrared activity of strength comparable to that observed for the \(\mathrm{B}_5\mathrm{H}_9\) band at 701 cm\(^{-1}\). In view of the preceding discussion the only reasonable assignment for \(\nu_1'\) is 512 cm\(^{-1}\) (taking the value from the infrared). This yields a reasonable frequency ratio for bridge rocking,

\[
\left( \frac{\nu_1'}{\nu_1} \right) = \left( \frac{512}{701} \right) = 0.730 .
\]

From the value \(\nu_1' = 512\) cm\(^{-1}\), and the value 613 cm\(^{-1}\) for the geometric mean of \(\nu_1'\) and \(\nu_2'\) obtained from the product rule, the remaining \(A_1\) frequency of \(\mathrm{B}_5\mathrm{D}_9\) is now calculated as \(\nu_2' = 734\) cm\(^{-1}\). A reasonable
allowance for the error in the predicted value of \( \nu_b' \) is perhaps 3 percent or ± 22 cm\(^{-1}\).

The preceding assignment of \( \nu_a' \) has been justified at such length because it leads to an assignment for \( \nu_b' \) which appears at first to be unreasonable on the basis of the usually accepted rule that approximate accidental degeneracy of frequencies of the same symmetry species is not to be expected. Thus, the only observed Raman band of \( \text{B}_2\text{D}_9 \) within the specified range for \( \nu_b' \) is the strong polarized band centered at 737 cm\(^{-1}\), which has already been assigned as an \( A_1 \) fundamental prior to and in part as a basis for the deduction of \( \nu_a' \) and \( \nu_b' \). The conclusion is thus reached that two \( A_1 \) frequencies of \( \text{B}_2\text{D}_9 \) are approximately accidentally degenerate. However, it is clear that the preceding argument based in part on the product rule only establishes the geometric mean of these two frequencies as approximately 737 cm\(^{-1}\), and not their precise separation. The 737 cm\(^{-1}\) Raman line is quite broad, extending over the range 712-762 cm\(^{-1}\), with a perceptible shoulder on the high-frequency side, so that it can well represent a superposition of two unresolved \( A_1 \) fundamentals. This view is strengthened by the infrared spectrum, which shows a very strong absorption extending over the range 700-815 cm\(^{-1}\).

The contour of this band is also unusual, with peaks at 741, 746, and 751 cm\(^{-1}\) (of which the second is somewhat the stronger), and shoulders at 744, 762, and 770 cm\(^{-1}\). This infrared band is exceeded in intensity only by those at 1057 and 1967 cm\(^{-1}\). Somewhat arbitrarily the two \( A_1 \) frequencies of \( \text{B}_2\text{D}_9 \) in this region have been assigned as 737 and 746 cm\(^{-1}\).
5. Application of Order, Product, and Reversal Rules

This completes the assignment of the $A_1$ modes of $B_5^7H_9$ and $B_5^7D_9$. However, because of the rather unusual assignment of approximately coincident frequencies to two $A_1$ modes of $B_5^7D_9$, some further discussion of the correlation of the $A_1$ modes in $B_5^7H_9$ and $B_5^7D_9$ is desirable. A detailed discussion has been given in chapter VII of the theoretical basis for this correlation, including the order rule. The relation between the slopes of the logarithmic plots of frequency versus isotopic mass and the character of the vibrational modes (distribution of kinetic energy between isotopic and non-isotopic atoms) has been considered, and plots of this type for each symmetry species based on the present assignment and normal coordinate calculation are given in Figure 9. The conditions under which two frequencies of the same species may be approximately accidentally degenerate have been examined, and it has been demonstrated that approximate degeneracy is entirely compatible with the dynamics of the vibration problem. This should, in fact, have been clear from the fact that approximate degeneracies of certain classes of frequencies of the same species are commonly observed and occasion no comment. This is the case with so called group or characteristic frequencies, such as the terminal $B-H$ and $B_0^0-H_0^0$ stretching frequencies, for example. An analysis of the form of the normal modes for such vibrations, such as is given in Table 26, will show that such modes usually involve a considerable admixture of coordinates, and yet have very nearly equal frequencies. The analysis has shown that for frequencies which are less characteristic approximate accidental degeneracies must still occur occasionally at particular values of the isotopic
masses. Thus, if at one isotopic mass the higher of two neighboring frequencies corresponds to a mode involving a greater degree of motion of the isotopic atoms than for the lower frequency mode, an increase in the isotopic mass will cause these two frequencies to approach. However, the non-crossing rule prohibits intersection of the frequency curves or exact degeneracy, and usually the frequencies will separate again at still higher masses. It has also been concluded that following a close approach and separation of this type the character of the two modes will be interchanged to a considerable degree, producing in a sense a pseudo-crossing of the modes. This constitutes the proposed reversal rule.

The reason that approximate accidental degeneracies of this type are seldom observed within a symmetry species other than for certain group or characteristic frequencies, is simply that they are predicted only for particular isotopic masses which do not in general correspond sufficiently closely with actually occurring isotopes. Only for the case of substitution of hydrogen by deuterium (or tritium) is the change in isotopic mass ratio great enough to make the occurrence of such approximate degeneracies or reversals of character reasonably likely in the isotopic molecule.

The application of the order rule to the assigned $A_1$ frequencies for $B_5^{H_9}$ and $B_5^{D_9}$ yields the correlations and frequency ratios given in Table 33. The frequency ratios all lie within the permitted range, 0.7074 to unity. The observed and theoretical product rule ratios are also given. The observed value is 1.7 percent higher than the theoretical value. As discussed in chapter VII, the normal effect of anharmonicities is to increase the ratio slightly, so that the observed value is entirely reasonable.
### TABLE 33
CORRELATION OF $A_1$ FREQUENCIES BY THE ORDER AND PRODUCT RULES

<table>
<thead>
<tr>
<th>Description in $B_2H_9$</th>
<th>$\gamma (B_2H_9)$ cm$^{-1}$</th>
<th>$\gamma' (B_2D_9)$ cm$^{-1}$</th>
<th>$(\gamma'/\gamma)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_0-H_0$ stretching</td>
<td>2610</td>
<td>1980</td>
<td>.759</td>
</tr>
<tr>
<td>B-H stretching</td>
<td>2598</td>
<td>1967</td>
<td>.757</td>
</tr>
<tr>
<td>Bridge stretching</td>
<td>1830</td>
<td>1393</td>
<td>.761</td>
</tr>
<tr>
<td>B-H bending</td>
<td>1120</td>
<td>959</td>
<td>.856</td>
</tr>
<tr>
<td>B-$B_0$ stretching</td>
<td>986</td>
<td>746</td>
<td>.757</td>
</tr>
<tr>
<td>B-B stretching</td>
<td>793</td>
<td>737</td>
<td>.929</td>
</tr>
<tr>
<td>Bridge rocking</td>
<td>700</td>
<td>512</td>
<td>.731</td>
</tr>
</tbody>
</table>

Observed product rule ratio, $\Pi (\gamma'/\gamma)$ = .1926
Theoretical product rule ratio, $\Pi (\gamma'/\gamma)$ = .1894

It is informative to consider the frequency ratios in Table 33 in conjunction with the theoretically calculated variation of the $A_1$ frequencies with isotopic mass as illustrated in Figure 9. Quantitative agreement between the theoretical and observed ratios is scarcely to be expected because of the approximate nature of the assumed potential function, but there is good qualitative agreement. The first column of Table 33 gives the description of the normal modes approximately applicable for $B_2H_9$. The observed frequency ratios for $B_0-H_0$, B-H, and bridge stretching and bridge rocking of .73 to .75 clearly identify these as predominantly hydrogen modes in $B_2H_9$ and deuterium modes in $B_2D_9$. That is, these modes behave normally and undergo no marked change.
of character on isotopic substitution. This is easily understandable as Figure 9 shows that each of these frequencies is well separated from other frequencies (except for the first two which are an example of the "characteristic" frequencies previously mentioned).

The variation of the B-H bending and B-B\(_0\) and B-B stretching frequencies is anomalous and more interesting. The B-H bending frequency of 1120 cm\(^{-1}\) in \(\text{B}_5\text{H}_9\) correlates through the order rule with the 959 cm\(^{-1}\) of \(\text{B}_5\text{D}_9\), which the observed boron small isotope effect indicates is largely the B-B\(_0\) stretching mode in \(\text{B}_5\text{D}_9\). This change in character is consistent with the observed frequency ratio of 0.856 which is intermediate between the expected values for hydrogen and boron modes. On the other hand, the 786 cm\(^{-1}\) frequency in \(\text{B}_5\text{H}_9\), which is clearly B-B\(_0\) stretching on the basis of the observed boron isotope effect, correlates with the 746 cm\(^{-1}\) frequency of \(\text{B}_5\text{D}_9\). The low value of the frequency ratio, 0.757, and the fact that no boron isotope effect is observed for this mode in \(\text{B}_5\text{D}_9\), clearly show that this mode has changed its character from B-B\(_0\) stretching in \(\text{B}_5\text{H}_9\) to B-D bending in \(\text{B}_5\text{D}_9\). That is, the two immediately preceding modes have effectively interchanged their character as a result of isotopic substitution. This may be regarded as an example of the proposed reversal rule in which on the basis of the approximate calculations illustrated in Figure 9 the closest approach of the two frequency curves occurs at about the isotopic mass \(m = 1\) occurring in \(\text{B}_5\text{H}_9\).

The remaining mode in Table 33 is the B-B stretching mode in \(\text{B}_5\text{H}_9\), unambiguously identified as such by the boron isotope effect, and
having a frequency of 793 cm\textsuperscript{-1} in B\textsubscript{5}H\textsubscript{9}. This frequency correlates with the frequency 737 cm\textsuperscript{-1} of B\textsubscript{5}D\textsubscript{9}. The frequency ratio of .929 is characteristic of a boron mode indicating that this mode remains largely B-B stretching in B\textsubscript{5}D\textsubscript{9}. This is entirely reasonable, as elimination of the previously assigned modes shows that the remaining mode in B\textsubscript{5}D\textsubscript{9} must be B-B stretching. The fact that no boron isotope effect is observed for the 737 cm\textsuperscript{-1} Raman band of B\textsubscript{5}D\textsubscript{9} may be accounted for by the overlap of this mode with that at 746 cm\textsuperscript{-1}, combined with the fact that the theoretical boron isotope shift for substitution of B\textsuperscript{10} for B\textsuperscript{11} at a base position is considerably smaller for the B-B stretching mode in B\textsubscript{5}D\textsubscript{9} than in B\textsubscript{5}H\textsubscript{9} (see Table 28). Finally, it is clear that the approximate degeneracy of the 746 and 737 cm\textsuperscript{-1} frequencies in B\textsubscript{5}D\textsubscript{9} is easily understandable on the basis of the preceding analysis and Figure 9. The 746 cm\textsuperscript{-1} frequency arises from the 986 cm\textsuperscript{-1} frequency of B\textsubscript{5}H\textsubscript{9}, which decreases rapidly with increasing isotopic mass because of its change from boron to deuterium motion. The 737 cm\textsuperscript{-1} frequency correlates with the 793 cm\textsuperscript{-1} frequency of B\textsubscript{5}H\textsubscript{9}, which is relatively insensitive to increasing isotopic mass because it remains largely a boron motion. Under these conditions a close approach of the two frequencies is essentially inevitable.

D. Assignment of E Frequencies

1. Introduction

Vibrations of species E are active in both the infrared and Raman, and depolarized in the latter spectrum. As the depolarization ratios of some Raman lines are uncertain all Raman lines will be considered in
the present section which are (1) not definitely polarized, (2) have not been assigned as $A_1$ modes in the preceding section, and (3) can be correlated with infrared bands of sufficient strength to be considered $E$ fundamentals. All of the stronger infrared bands not yet assigned will be considered, as $E$ modes do not necessarily have high Raman intensity. Reference should be made to Tables 2 to 5 and Figures 3 to 7 for the spectral data. The nine $E$ modes to be assigned are listed in Table 30. The assignment of the terminal hydrogen and deuterium stretching modes of species $E$ has been given in section 3.

2. Bridge Stretching Frequencies

The symmetrical and unsymmetrical bridge stretching modes of species $E$ will be considered first. The $A_1$ symmetrical bridge stretching frequencies have been assigned to the polarized Raman bands of $B_5^H$ at 1830 and $B_5^D$ at 1393 cm$^{-1}$. The strongest infrared bands in the bridge stretching region occur at 1812 cm$^{-1}$ for $B_5^H$ and 1333 cm$^{-1}$ for $B_5^D$, and have much the same appearance. Their frequency ratio of .736 is slightly smaller than that for the $A_1$ frequencies but appropriate for a hydrogen mode. The Raman spectrum of $B_5^H$ shows evidence of a depolarized band of lower frequency (1800-1910 cm$^{-1}$) underlying the polarized band at 1830 cm$^{-1}$. The Raman spectrum of $B_5^D$ shows a band at 1333 cm$^{-1}$ which was too weak for a determination of its depolarization ratio, but is presumably depolarized as there can be only one $A_1$ mode in this frequency range. It is clear from the foregoing facts that the 1812 and 1333 cm$^{-1}$ infrared bands must represent bridge stretchings of species $E$ in $B_5^H$ and $B_5^D$, respectively, and they are so assigned. The $A_1$ and $E$
symmetrical bridge stretching frequencies were calculated in the normal coordinate analysis of chapter VI as 1883 and 1838 cm$^{-1}$, respectively, for $B_9^5$ and 1386 and 1319 cm$^{-1}$ for $B_9^5$. This supports the assignment of somewhat lower values to the $E$ than to the $A_1$ modes.

The assignment of the unsymmetrical bridge stretching mode of species $E$ is somewhat more difficult. Table 31 shows that the unsymmetrical bridge stretchings of $B_6^2$ lie at about 1604 and 1750 cm$^{-1}$, and those of $B_6^2$ at 1204 and 1280 cm$^{-1}$. The most prominent additional bands in this region in the infrared spectrum lie at 1626, 1733, and 1916 cm$^{-1}$ for $B_9^5$ and 1182, 1289, and 1506 cm$^{-1}$ for $B_9^5$ (the band at 1393 cm$^{-1}$ may be correlated with the Raman band at the same frequency which has been assigned to $A_1$ bridge stretching in $B_9^5$). These three pairs of frequencies have ratios .727, .744, and .786, respectively. The last value is somewhat higher than expected for a hydrogen mode. The most significant features of the Raman spectra not yet assigned are a weak diffuse band at about 1600 cm$^{-1}$ for $B_9^5$, and weak bands at 1274 and 1492 cm$^{-1}$ for $B_9^5$. Thus, one of each pair of infrared bands can be correlated approximately with a Raman band. The highest frequency pair, 1916 and 1506 cm$^{-1}$ is disregarded because the assignments for diborane indicate that the unsymmetrical bridge stretching should be significantly lower in frequency than the symmetrical stretchings, which have been assigned at 1812 and 1393 cm$^{-1}$ for $B_9^5$ and $B_9^5$, respectively. The choice between the two lowest pairs of frequencies has been made on the basis of the following factors: (1) the 1733 and 1289 cm$^{-1}$ infrared bands are superimposed on the strong bands at 1812 and 1333 cm$^{-1}$,
respectively, so that their true strength is probably considerably less
than indicated in Tables 2 and 3; and (2) the assignments of the unsym-
metrical bridge stretchings at 1504 and 1204 cm\(^{-1}\) in \(\text{B}_2\text{H}_6\) and \(\text{B}_2\text{D}_6\),
respectively, seem to be somewhat more certain than the assignments at
1750 and 1280 cm\(^{-1}\). The unsymmetrical E bridge stretchings are therefore
assigned the frequencies 1626 cm\(^{-1}\) for \(3\text{\textsubscript{5}}\text{H}_9\) and 1182 cm\(^{-1}\) for \(3\text{\textsubscript{5}}\text{D}_9\).

The form of the normal modes for the two E bridge stretchings as
given in Table 26 supports on the whole the preceding classification of
the E bridge stretchings as symmetrical and unsymmetrical, corresponding
to relatively large coefficients for the symmetry coordinates \(L\) and \(M''\),
respectively. However, it is also clear that there is considerable
mixing, so that neither E bridge stretching mode is strictly symmetrical
or unsymmetrical.

This completes the assignment of all infrared active terminal and
bridge hydrogen stretchings. The remaining unassigned infrared bands
above the 1526 cm\(^{-1}\) \(\text{B}_5\text{H}_9\) and 1182 cm\(^{-1}\) \(\text{B}_5\text{D}_9\) bands must be regarded as
overtones or combinations (or possibly in the case of \(\text{B}_5\text{D}_9\) as arising
from isotopic species such as \(\text{B}_5\text{D}_8\text{H}\)). From the discussion of the
remaining modes which follows it is extremely unlikely that any addi-
tional infrared active fundamentals could occur above these frequencies.
The only remaining Raman active fundamentals which occur at or above
the frequencies stated are the \(3\text{\textsubscript{1}}\) and \(B_2\) bridge stretching modes which
are assigned in section E.

3. Vertical B-H Bending Frequencies

As discussed in section A the four base hydrogens in pentaborane
give rise to four vertical B-H bending modes classified as \(A_1\), \(B_1\), and
E, and four horizontal B-H bending modes classified as $A_2$, $B_2$, and $E$.

The $E$ vertical B-H bendings are discussed in this section and the horizontal B-H bendings in the next section. In section C the $A_1$ vertical B-H bending frequency is unambiguously assigned to the 1120 cm$^{-1}$ polarized Raman band of $B_5^9$. In $B_5^9$ the identification of this mode is less definite, but it appears from the discussion in section C.5 that it is principally the 746 cm$^{-1}$ mode and to a smaller extent the 959 cm$^{-1}$ mode that represent vertical B-D bending. In the infrared spectrum of $B_5^9$ the significant bands occurring in this region are medium strength bands at 1127 and 1044 cm$^{-1}$ (with a shoulder at 1032 cm$^{-1}$ probably representing a rotational branch), and weak bands at 1081 and 1143 cm$^{-1}$. The 1127 cm$^{-1}$ band is correlated with the 1120 cm$^{-1}$ Raman band as $A_1$ vertical B-H bending. There is no reasonable alternative to the assignment of the 1044 cm$^{-1}$ band as the $E$ vertical B-H bending in $B_5^9$, as it has 2.5 times the peak intensity of the two weak bands and far greater integrated strength. The significant absorptions in this region of the infrared spectrum of $B_5^D$ are a series of three closely spaced peaks of medium strength at 844, 850, and 856 cm$^{-1}$, and two weak but sharp peaks at 961 and 964 cm$^{-1}$ followed by a broader maximum at 981 cm$^{-1}$. This weak band of rather complicated structure can be correlated with the 959 cm$^{-1}$ polarized Raman band, and its boron isotope satellite at 975 cm$^{-1}$, which have been assigned to $A_1$ B-B$^0$ stretching in $B_5^D$ (two similar but extremely weak peaks at 984 and 988 cm$^{-1}$ are resolved in the infrared spectrum of $B_5^9$ and can be correlated with the polarized Raman band at 986 cm$^{-1}$ also representing B-B$^0$ stretching).

The spacing of the bands at 844, 850, and 856 cm$^{-1}$ is about half that
calculated for rotational branches, and they probably represent an example of the boron isotope effect, with the lowest frequency at 844 cm\(^{-1}\) to be assigned to the isotopic species \(B_5^{11}\)\(D_9\). Assuming this interpretation, and the preceding disposition of the other bands in this region, 844 cm\(^{-1}\) is the only reasonable assignment for the infrared active mode in \(B_5^D\) which is correlated by the order rule with the 1044 cm\(^{-1}\) mode of \(B_5^H\). However, the discussion in section 6 will indicate that although the 1044 cm\(^{-1}\) band of \(B_5^H\) represents primarily vertical B-H bending, the 844 cm\(^{-1}\) band of \(B_5^D\) represents B-B\(_0\) stretching rather than vertical B-D bending, as a result of the reversal of character of two modes. Thus, the title of the present section is not entirely accurate.

4. **Horizontal B-H Bending Frequencies**

The assignments as completed to this point account for all the prominent infrared absorption bands of \(B_5^H\) and \(B_5^D\) above, and inclusive of, the bands at 1044 and 844 cm\(^{-1}\), respectively, with the outstanding exception of the very strong \(B_5^H\) band at 1408 cm\(^{-1}\) and \(B_5^D\) band at 1057 cm\(^{-1}\). These bands are exceeded in intensity only by the 896 and 2598 cm\(^{-1}\) bands of \(B_5^H\) and the 1967 cm\(^{-1}\) band of \(B_5^D\). The \(B_5^H\) band exhibits a sharp maximum at 1408 cm\(^{-1}\), with peaks of decreasing strength at 1422, 1445, and 1460 cm\(^{-1}\), and a shoulder on the low frequency side at about 1397 cm\(^{-1}\). The \(B_5^D\) band has an equally sharp maximum at 1057 cm\(^{-1}\), and a similar shoulder at about 1047 cm\(^{-1}\) but only one additional peak at 1070 cm\(^{-1}\). Except for the latter difference the overall band contours of the two bands are similar. The contour of the
1057 cm\(^{-1}\) \(B_7D_9\) band may reasonably be assigned to rotational branches, while that of the 1408 cm\(^{-1}\) \(B_5H_9\) is perhaps due to a superposition of rotational structure and boron isotope effects. There is little Raman activity at the frequencies of these strong infrared bands. The Raman spectrum of \(B_5H_9\) shows extremely weak and diffuse bands at about 1390 and 1435 cm\(^{-1}\). No activity is visible above the relatively strong background on the Raman films for \(B_5D_9\) in this region, although the densitometer tracing suggests the possibility of similar extremely weak and diffuse activity at about 1035 cm\(^{-1}\). It is clear that in view of their intensity in the infrared spectrum the 1408 cm\(^{-1}\) band of \(B_5H_9\) and 1057 cm\(^{-1}\) band of \(B_5D_9\) must be assigned as fundamental vibration frequencies. The lack of significant strength or definite polarization in the Raman spectrum is a strong indication that they represent fundamentals of species E, aside from the fact that all \(A_1\) fundamentals have now been assigned (in most cases to polarized Raman bands of considerable strength).

It is clear from the previous E assignments that the 1408 and 1057 cm\(^{-1}\) frequencies are correlated by the order rule (each is the fourth largest E frequency of the molecule concerned), and their ratio of 0.751 clearly identifies them as primarily hydrogen or deuterium motions. The only remaining motions of this type of symmetry E are horizontal B-H bending, \(B_0-H_0\) bending, and bridge rocking. The \(A_1\) bridge rockings have been quite definitely assigned at 700 and 512 cm\(^{-1}\) for \(B_5H_9\) and \(B_5D_9\), respectively, and it is clearly impossible for the E bridge rockings to have frequencies as high as the bands under
consideration. The choice therefore reduces to horizontal $B$-$H$ bending or $B_0$-$H_0$ bending. Rather strong reasons will be given in the following section for believing that $B_0$-$H_0$ bending lies at a much lower frequency comparable to bridge rocking. The $1408 \text{ cm}^{-1}$ band of $B_5^9$ and the $1057 \text{ cm}^{-1}$ band of $B_5^9$ are therefore assigned to horizontal $B$-$H$ and $B$-$D$ bending, respectively. The assignment of the horizontal and vertical $B$-$H$ bending modes in this and the preceding sections is further strengthened by the form of the $E$ normal modes in Table 26 corresponding (approximately) to the frequencies under discussion. Here large and small coefficients of the symmetry coordinate $\Delta^1$ distinguish vertical and horizontal $B$-$H$ bending, respectively. Of course, all modes of a given species can mix, so that the classification of the modes adopted here are only approximate. Thus, neither $B$-$H$ bending mode is strictly vertical or horizontal.

5. Bridge Rocking and Apex $B_0$-$H_0$ Bending Frequencies

There is a minimum of information on which to base an estimate of the bridge rocking frequencies in pentaborane, because no complete assignment is available for any other boron hydrides containing single bridges attached to a heavy boron skeleton as in pentaborane. The configuration of the double bridge in diborane is too different to be of much aid. The mode most resembling bridge rocking in diborane is the $B_{1u}$ mode $\nu_{10}$ of Bell and Longuet-Higgins,\(^{13}\) which played an important

\(^{13}\) Bell and Longuet-Higgins, op. cit.
role in the verification of the bridge structure, and is reliably
assigned at 368 cm\(^{-1}\) in \(\text{B}_2\text{H}_6\) and 262 cm\(^{-1}\) in \(\text{B}_2\text{D}_6\). However, the analogy
to the rocking of the single bridges in pentaborane is not close, and
these values merely suggest that the bridge rocking frequencies will be
among the lowest frequencies of pentaborane. The only really solid
information on which to proceed is the assignment of the \(A_1\) bridge
rocking frequency in pentaborane discussed in section C. Because of the
good polarization data available for \(\text{B}_2\text{H}_2\) this frequency can be quite
unambiguously assigned as 700 cm\(^{-1}\), and the order rule then establishes
the frequency in \(\text{B}_2\text{D}_2\) as 512 cm\(^{-1}\). It seems likely that the \(A_1\) mode will
be the highest of the bridge rocking frequencies because the configura-
tion of the bridges is such that all four bridge protons approach in
this mode. This may be contrasted with the mode \(\gamma_{10}\) of diborane
referred to above in which the equilibrium configuration of the bridge system

\[
\begin{align*}
\text{B} & \text{H} \quad \text{B} \\
\text{H} & \quad \text{B}
\end{align*}
\]

is planar, so that the out-of-plane motion of the protons produces no
changes in the interatomic distances to the first order. It is to this
fact that the exceptionally low frequency of the bridge frequency \(\gamma_{10}\)
is attributed by Bell and Longuet-Higgins. The situation with regard to
the \(E\) (and also the \(B_2\)) bridge rocking mode in pentaborane appears to
be intermediate between these extreme cases, and a plausible estimate of
their frequencies is therefore 500-600 cm\(^{-1}\).

Another \(E\) mode of pentaborane which is expected to fall in about
the same frequency range is the apex hydrogen or \(B_0\text{-H}_0\) bending. The
discussion of bonding in pentaborane in chapter 2 indicates that the apex boron atom \( B_0 \) is bonded to the four base boron atoms by three occupied molecular orbitals involving \( 2\sigma, 2p\pi, \) and \( 2p\pi' \) orbitals of \( B_0 \). That is, there is essentially a triple bond between \( B_0 \) and the \( 3_4 \) base taken as a unit, rather than four directed covalent \( B_0-B \) bonds. This suggests that the bending of the \( B_0-H_0 \) bond perpendicular to the symmetry axis of the molecule is probably not resisted by strong forces associated with the preservation of the normal \( B-B_0-H_0 \) bond angles. It seems more reasonable to assume that the restoring forces are more similar to those for the bending mode of an acetylenic hydrogen atom in the system \(-\equiv\equiv\equiv\equiv H \) perpendicular to the molecular axis. This is particularly clear if the part of the pentaborane molecule involved is represented as \((3_4)\equiv B_0-H_0\). The two perpendicular \( \Pi_2 \) and \( \Pi_u \) hydrogen bending modes in \( \text{HCCH} \) are 612 and 729 cm\(^{-1}\), in \( \text{DCCD} \) 505 and 537 cm\(^{-1}\), and in \( \text{HCCD} \) 519 and 633 cm\(^{-1}\), respectively.\(^{14}\) The frequency for a single acetylenic hydrogen may be estimated as the mean value, 670 cm\(^{-1}\), for \( \text{HCCH} \), or the higher frequency, 683 cm\(^{-1}\), of \( \text{HCCD} \). Correspondingly, for a single acetylenic deuterium the mean for \( \text{DCCD} \) is 522 cm\(^{-1}\), and the lower frequency of \( \text{HCCD} \) is 519 cm\(^{-1}\). The \( B_0-H_0 \) and \( B_0-D_0 \) bendings in pentaborane might be expected to lie somewhat below these values because of the increased mass of the \( 3_4 \) base.

Both the E bridge rocking and \( B_0-H_0 \) bending modes are infrared and Raman active. The lowest frequency lines in the Raman spectrum of \( B_0H_9 \) are a very weak line at 470 cm\(^{-1}\), a weak line at 566 cm\(^{-1}\); and a

medium strength line at 596 cm\(^{-1}\) with a prominent shoulder at about 616 cm\(^{-1}\). The first line was too weak for a polarization determination, while the remainder appear to be depolarized. The infrared spectrum extends to 400 cm\(^{-1}\), and shows no absorption below 700 cm\(^{-1}\) other than a strong band of symmetrical contour having a central maximum at 614 cm\(^{-1}\), and a medium strength band at 568 cm\(^{-1}\). These are quite clearly the two lowest frequency E fundamentals, and in view of their inactivity in the infrared the 470 and 596 cm\(^{-1}\) Raman bands must represent 3 fundamentals. The lowest frequency lines in the Raman spectrum of \(\text{B}_5\text{D}_9\) are extremely weak lines at about 425, 507, and 537 cm\(^{-1}\), all too weak for polarization measurements. The only infrared absorption of \(\text{B}_5\text{D}_9\) in the range 400-600 cm\(^{-1}\) is the 512 cm\(^{-1}\) band already assigned as \(A_1\) bridge rocking, and broad absorption of unusual contour with maxima at 415, 429, 433, 439, 445, 448, 454, and 459 cm\(^{-1}\). The most intense maxima occur at 439, 445, and 448 cm\(^{-1}\). Even with allowance for rotational branches and boron isotope effects, the number of resolved maxima shows that this band is a superposition of (at least) two fundamentals. These must be E fundamentals as all \(A_1\) fundamentals have been assigned. The 425 and 507 cm\(^{-1}\) Raman bands may be correlated with one or the other of these E modes and the 512 cm\(^{-1}\) \(A_1\) mode, or could represent B modes, while the 537 cm\(^{-1}\) Raman band is rather definitely a B mode.

The E bridge rocking and \(\text{B}_0\text{-H}_0\) bending modes of \(\text{B}_5\text{H}_9\) may be assigned with considerable certainty to the two lowest E fundamentals at 568 and 614 cm\(^{-1}\), although not necessarily in that order. The ratio of the \(A_1\) bridge rocking frequencies in \(\text{B}_5\text{D}_9\) and \(\text{B}_5\text{H}_9\) is 0.731, and the mean
acetylenic deuterium and hydrogen bending frequencies which are roughly analogous to $B_0^-H_0$ bending have a ratio of $0.75$ in mean isotopic ratio of 0.75 to the two $E$ frequencies for $B_5^D$ yields 425 and 460 as rough estimates of the corresponding $E$ frequencies for $B_5^D$. This confirms the previous conclusion that the $415-459$ cm$^{-1}$ infrared band of $B_5^D$ must represent a superposition of two $E$ fundamentals. Because of the unusual envelope of this absorption it is difficult to make a reliable assignment for the centers of these bands. Rather arbitrarily, therefore, the $E$ bridge rocking and $B_0^-D_0$ bending modes in $B_5^D$ are assigned to the prominent infrared absorption maxima at 439 and 448 cm$^{-1}$. The near coincidence of these two frequencies of the same species is not unreasonable because the bridges and apex deuterium are at opposite ends of the boron framework and there should be negligible direct potential or kinetic interaction between these two motions.

A clue as to the form of these two normal modes may be obtained from Table 26, where the coefficients of the symmetry coordinates $\Gamma$ and $W$ may be regarded as measures of degree of $E$ bridge rocking and $B_0^-H_0$ bending, respectively. It is clear that both modes involve about equal mixtures of bridge rocking and $B_0^-H_0$ bending, but with the relative phases of these two types of motion reversed in the two modes. This is the expected behavior for two weakly coupled oscillators of approximately equal frequencies. The absence of repulsion of the frequency-mass curves for these two modes in Figure 9 also indicates the absence of any large kinetic interaction between bridge rocking and $B_0^-H_0$ bending (compare the similar behavior of the two $A_1$ terminal hydrogen stretching modes).
6. **Boron-Boron Stretching Frequencies**

The only remaining E frequencies to be assigned are the B-B and E-B\(_2\) stretching frequencies. In section C.3 the corresponding A\(_1\) frequencies have been assigned. In B\(_5\)\(_H\) the B-B\(_0\) stretching mode is unambiguously identified with the strong polarized Raman line at 986 cm\(^{-1}\), but the assignment of this frequency in B\(_5\)\(_D\) is complicated by a reversal effect, as discussed in section C.5. The 986 cm\(^{-1}\) B\(_5\)\(_H\) frequency is correlated by the order rule with the 746 cm\(^{-1}\) mode of B\(_5\)\(_D\), but the boron isotope effect identifies the next higher frequency of B\(_5\)\(_D\), 959 cm\(^{-1}\), as that representing primarily B-B\(_0\) stretching. It will be seen that a similar reversal affects the E E-B\(_0\) stretching frequency.

The only strong infrared band of B\(_5\)\(_H\) not yet assigned has absorption maxima at 883, 990, and 896 cm\(^{-1}\), and several considerably weaker maxima or shoulders at 916 and 929 cm\(^{-1}\). This is the second most intense band in the absorption spectrum of B\(_5\)\(_H\). The spacing of the three prominent maxima is about half that calculated for rotational branches and is probably an example of the boron isotope effect, with 883 cm\(^{-1}\) as the frequency to be assigned to the species B\(_{1\, 1}\)\(_H\). This band is undoubtedly correlated with the depolarized Raman line of medium strength at 884 cm\(^{-1}\). The only reasonable assignment of the 883 cm\(^{-1}\) band is as a boron-boron stretching mode, although as a result of the interaction discussed below it undoubtedly contains a good deal of vertical B-H bending which contributes to its infrared intensity.

The third strongest band in the infrared spectrum of B\(_5\)\(_D\) has maxima at 741, 746, and 751 cm\(^{-1}\), and shoulders at 734, 762, and
770 cm\(^{-1}\). A strong polarized Raman band occurs at 737 cm\(^{-1}\), and the \(A_1\) B-B stretching was assigned to this Raman band. In \(\text{B}_5\text{H}_9\) the B-3 stretching mode was similarly assigned to a strong polarized Raman band at 793 cm\(^{-1}\), but the corresponding infrared band at 800 cm\(^{-1}\) is only of medium intensity. As the absorption coefficient of the 741 cm\(^{-1}\) infrared band in \(\text{B}_5\text{D}_9\) exceeds that of the 800 cm\(^{-1}\) band of \(\text{B}_5\text{H}_9\) by a factor of 16, it seems unlikely that more than a relatively small part of the intensity of the former is contributed by the 737 cm\(^{-1}\) \(A_1\) mode. Probably the shoulder on the infrared band at 734 cm\(^{-1}\) is to be assigned to this mode. The product rule also forced the assignment of a second \(A_1\) mode of \(\text{B}_5\text{H}_9\) at a frequency in the neighborhood of the 737 cm\(^{-1}\) \(A_1\) mode. This second \(A_1\) mode is correlated by the order rule with the B-B\(_0\) stretching mode of \(\text{B}_5\text{H}_9\) which gives rise to a very strong polarized Raman band at 986 cm\(^{-1}\), but has an infrared absorption coefficient which is so small as to be scarcely measurable. In fairness it should also be stated that the discussion in section C.5 indicates that this second \(A_1\) mode in \(\text{B}_5\text{D}_9\) also contains a large component of vertical B-D bending. However, the absorption coefficient of the 741 cm\(^{-1}\) infrared band of \(\text{B}_5\text{D}_9\) is 16 times as great as that of the 1127 cm\(^{-1}\) infrared band of \(\text{B}_5\text{H}_9\) and 12 times as great as that of the 1044 cm\(^{-1}\) band, which have been assigned to \(A_1\) and E vertical B-H bending, respectively. Thus, it is also unlikely that this second \(A_1\) mode of \(\text{B}_5\text{D}_9\) can account for the major part of the intensity of the 741 cm\(^{-1}\) infrared band. The conclusion is thus reached that the greater part of the intensity of this band must
be assigned to an E mode, and the frequency of the latter is taken somewhat arbitrarily as that of the peak at 741 cm$^{-1}$.

The E modes of $^3_5\text{H}_9$ and $^3_5\text{D}_9$ which have now been assigned to the very strong infrared bands at 883 and 741 cm$^{-1}$, respectively, must be correlated by the order rule, and yield a ratio of .839 which is intermediate between that expected for boron and hydrogen modes. In section D.3 the medium strength infrared band of $^3_5\text{H}_9$ at 1044 cm$^{-1}$ was assigned to vertical B-H bending, and was correlated by the order rule with the 844 cm$^{-1}$ band of $^3_5\text{D}_9$, yielding also an intermediate ratio .808. The frequency-mass curves in Figure 9 clearly indicate an interaction between these modes at an isotopic mass intermediate between hydrogen and deuterium with an interchange of the character of the modes. This is quantitatively confirmed by Table 26, where the coefficients of the symmetry coordinates $\Delta^1$ and $L$ are measures of degree of vertical B-H bending and B-$\text{H}_0$ stretching. It is clear that in $^3_5\text{H}_9$ the 1044 and 883 cm$^{-1}$ frequencies (corresponding to the calculated values 988 and 982 cm$^{-1}$ in the table) represent primarily vertical B-H bending and B-$\text{H}_0$ stretching, respectively. On the other hand, in $^3_5\text{D}_9$ the frequencies 844 and 741 cm$^{-1}$ (corresponding to the values 840 and 745 cm$^{-1}$ in the table) represent primarily B-$\text{D}_0$ stretching and vertical B-D bending, respectively. This is another example of the reversal rule proposed in chapter VII.

The one E frequency still to be assigned is that for B-B stretching. In $^3_5\text{H}_9$ the $A_1$ B-B stretching is definitely identified through the boron isotope effect with the strong polarized Raman line at 793 cm$^{-1}$ and the medium strength 800 cm$^{-1}$ infrared band. The order rule
then identifies this frequency in $B_5D_9$ with the strong polarized 737 cm$^{-1}$ Raman line, yielding a frequency ratio 0.929 characteristic of a boron motion. It will also be recalled that the frequencies of the $A_1$ and $E$ modes representing primarily $3-B_0$ stretching are 986 and 883 cm$^{-1}$, respectively, in $B_5H_9$, and 959 and 844 cm$^{-1}$ in $B_5D_9$ (account being taken of the reversal of character of the $B-3q$ and $B-H$ bending modes in the latter case). Thus, in the case of $B-B_0$ stretching the $E$ mode lies 103 cm$^{-1}$ lower than the $A_1$ mode in $B_5H_9$, and 115 cm$^{-1}$ lower in $B_5D_9$. There is no clear reason the $B-B$ stretching frequencies should show the same shifts, but these values at least suggest that the $E$, $B-B$ stretching frequencies may be about 100 cm$^{-1}$ below the $A_1$ frequencies referred to above, or in the neighborhood of 700 and 630 cm$^{-1}$ for $B_5H_9$ and $B_5D_9$, respectively. The infrared spectrum of $B_5D_9$ shows a medium strength band with maxima of nearly equal strength at 638 and 647 cm$^{-1}$. The Raman spectrum shows a strong line at 639 cm$^{-1}$ for which the polarization data are inconclusive. However, it must be assumed to be depolarized because the carefully considered assignment of $A_1$ frequencies and particularly the application of the product rule indicate that no $A_1$ band can occur at this position. On the other hand the considerable strength of the 639 cm$^{-1}$ Raman line suggests that it represents a boron skeletal motion. The $E$ $B-B$ stretching frequency in $B_5D_9$ may therefore be quite conclusively assigned the value 639 cm$^{-1}$ (from the Raman spectrum). The two maxima of the infrared band may represent either rotational bands or boron isotope splitting.
By the order rule the $3$-$B$ stretching frequency in $B_5^H$ may now be calculated to be in the range 639-900 cm$^{-1}$. There are no unassigned infrared absorption bands in this range. The only unassigned Raman band in this frequency range is the strong depolarized line at 738 cm$^{-1}$, although there are definite indications of depolarized bands at about 700 and 793 cm$^{-1}$ (underlying the polarized $A_1$, 700, and 793 cm$^{-1}$ bands). In this situation it seems best to rely on the product rule to calculate the one remaining $E$ frequency of $B_5^H$. This is possible as all the $E$ frequencies of $B_5^D$ have been assigned. From the frequency ratios tabulated in Table 34 for all modes other than $3$-$B$

**TABLE 34**

**CORRELATION OF $E$ FREQUENCIES BY THE ORDER AND PRODUCT RULES**

<table>
<thead>
<tr>
<th>Description in $B_5^H$</th>
<th>$(B_5^H)$ cm$^{-1}$</th>
<th>$(B_5^D)$ cm$^{-1}$</th>
<th>$(\nu'/\nu)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B$-$H$ stretching</td>
<td>2598</td>
<td>1967</td>
<td>.757</td>
</tr>
<tr>
<td>Symmetrical bridge stretching</td>
<td>1312</td>
<td>1333</td>
<td>.736</td>
</tr>
<tr>
<td>Unsymmetrical bridge stretching</td>
<td>1626</td>
<td>1182</td>
<td>.727</td>
</tr>
<tr>
<td>$B$-$H$ horizontal bending</td>
<td>1408</td>
<td>1057</td>
<td>.751</td>
</tr>
<tr>
<td>$B$-$H$ vertical bending</td>
<td>1044</td>
<td>844</td>
<td>.808</td>
</tr>
<tr>
<td>$B$-$B_0$ stretching</td>
<td>883</td>
<td>741</td>
<td>.839</td>
</tr>
<tr>
<td>$B$-$B$ stretching</td>
<td>700</td>
<td>639</td>
<td>.913</td>
</tr>
<tr>
<td>$B_0$-$H_0$ bending</td>
<td>614</td>
<td>448</td>
<td>.730</td>
</tr>
<tr>
<td>Bridge rocking</td>
<td>568</td>
<td>439</td>
<td>.773</td>
</tr>
</tbody>
</table>

Observed product rule ratio, $\prod(\nu'/\nu) = 0.1061$

Theoretical product rule ratio, $\prod(\nu'/\nu) = 0.1104$
stretching, and the theoretical product rule ratio 0.1104, the calculated frequency ratio for B-B stretching is 0.949. The E B-B stretching frequency in $B_5^2H_9$ is therefore calculated as 673 cm$^{-1}$ from the product rule. In view of the uncertainty in the precise value of certain frequencies (for example, the frequencies for bridge rocking, B-D$^0$ bending, and B-D stretching in $B_5^2D_9$), and the error due to anharmonicities, the permissible range for the frequency in question is at the most 640-715 cm$^{-1}$ (the order rule fixes the lower limit). The only bands of $B_5^2H_9$ observed in this range are the weak 701 cm$^{-1}$ infrared band (with what appear to be three rotational branches) and the slightly polarized 700 cm$^{-1}$ Raman band, which have been assigned as A$_1$ bridge rocking. The use of the strong 738 cm$^{-1}$ Raman band would lead to a virtually impossible error of 9.6 percent in the product rule. However, as previously suggested, the slight degree of polarization of the 700 cm$^{-1}$ Raman band, as well as its asymmetric contour and considerable strength, are consistent with the presence of an underlying depolarized E band at about the same frequency. As there is no reasonable alternative, the remaining E B-B bending mode of $B_5^2H_9$ is assigned the somewhat nominal frequency 700 cm$^{-1}$. This assignment leads to a frequency ratio of 0.913 for the E B-B stretching frequency and an observed product rule ratio of 0.1061, as shown in Table 34. The apparent error in the product rule as applied to the 18 frequencies of species E is 4.0 percent. Assuming a random distribution of errors this corresponds to a mean error of 0.94 percent per frequency, including errors in the assignment and errors due to anharmonicity. Since the anharmonic errors may be as
high as ±2 percent for bending modes the overall error is not unreasonable.

E. Assignment of $A_2$, $B_1$, and $B_2$ Frequencies

1. $A_2$ Frequencies

$A_2$ modes are inactive in both the infrared and Raman spectra, and therefore the only hope of obtaining direct experimental information is through the study of overtones or combinations (except for the slight possibility of perturbation induced transitions in condensed states). Thus, the values of the $A_2$ frequencies required for the calculation of thermodynamic functions must either be estimated or calculated by a normal coordinate analysis such as that in chapter VI. The latter procedure is certainly preferable, as the calculated values are derived from a potential function based on other observed fundamentals. In the present investigation the two $A_2$ modes have been assigned the calculated values as given in Table 35. That is, the unsymmetrical bridge stretching frequencies are assigned the values 1776 and 1288 cm$^{-1}$, and the horizontal S-H bending the values 866 and 684 cm$^{-1}$ in $^{3}_5H_9$ and $^{3}_5D_9$, respectively. Of course the accuracy of the calculated values is uncertain, but the advantage of using the theoretical as opposed to rounded values is that they are consistent with the theoretical $A_2$ product rule ratio of .5731. The calculated values in Table 35 are taken from the final column of Table 25.
### TABLE 35

**CALCULATED VALUES OF A₂, B₁, AND B₂ FREQUENCIES FOR B₅H₉ AND B₅D₉**

<table>
<thead>
<tr>
<th>Species</th>
<th>Description of Mode</th>
<th>Frequencies (cm⁻¹)</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>γ(B₅H₉)</td>
<td>γ'(B₅D₉)</td>
</tr>
<tr>
<td>A₂</td>
<td>Unsymmetrical bridge stretching</td>
<td>1776</td>
<td>1288</td>
</tr>
<tr>
<td></td>
<td>B-H horizontal bending</td>
<td>866</td>
<td>684</td>
</tr>
<tr>
<td></td>
<td><strong>Theoretical product rule ratio</strong></td>
<td>.5731</td>
<td></td>
</tr>
<tr>
<td>B₁</td>
<td>B-H stretching</td>
<td>2604</td>
<td>1928</td>
</tr>
<tr>
<td></td>
<td>Unsymmetrical bridge stretching</td>
<td>1586</td>
<td>1129</td>
</tr>
<tr>
<td></td>
<td>B-H vertical bending</td>
<td>1033</td>
<td>976</td>
</tr>
<tr>
<td></td>
<td>B-B₀ stretching</td>
<td>551</td>
<td>498</td>
</tr>
<tr>
<td></td>
<td>Boron skeletal bending</td>
<td>415</td>
<td>364</td>
</tr>
<tr>
<td></td>
<td><strong>Theoretical product rule ratio</strong></td>
<td>.3540</td>
<td></td>
</tr>
<tr>
<td>B₂</td>
<td>Symmetrical bridge stretching</td>
<td>1651</td>
<td>1275</td>
</tr>
<tr>
<td></td>
<td>B-H horizontal bending</td>
<td>1114</td>
<td>790</td>
</tr>
<tr>
<td></td>
<td>B-B stretching</td>
<td>740</td>
<td>675</td>
</tr>
<tr>
<td></td>
<td>Bridge rocking</td>
<td>545</td>
<td>388</td>
</tr>
<tr>
<td></td>
<td><strong>Theoretical product rule ratio</strong></td>
<td>.3540</td>
<td></td>
</tr>
</tbody>
</table>

---

2. **Selection Rules and Calculated Values**
   for **B₁ and B₂ Frequencies**

B₁ and B₂ modes are active and depolarized in the Raman spectrum but inactive in the infrared. Therefore the Raman bands which may be considered as B (i.e., B₁ or B₂) fundamentals are those (1) not yet assigned as A₁ or E fundamentals, (2) not definitely polarized, and (3) not showing infrared activity at the same position. It is, of course, quite possible for vibrations frequencies of different species to have the same or nearly the same value. If an A₁ and B mode
approximately coincide they can in some cases be distinguished by the distribution of polarized and depolarized radiation in the Raman spectrum, as in the case of the ~785 cm⁻¹ Raman band of $^{3}B_{5}H_{9}$ discussed below. On the other hand it would be essentially impossible to distinguish a $B$ mode sufficiently coincident with an $E$ mode as both are depolarized in the Raman spectrum. Conceivably the $3$ frequency could be identified through a study of overtones or combinations.

The calculated values of $B_{1}$ and $B_{2}$ frequencies have also been included in Table 35, as they will be useful to some extent as a guide in the assignment of observed $B_{1}$ and $B_{2}$ frequencies, and in addition will be used in the calculation of thermodynamic properties in those cases where $B_{1}$ and $B_{2}$ frequencies are not observed. The ratios of the calculated frequencies for $B_{5}D_{9}$ and $B_{5}H_{9}$ are also given as they are useful in distinguishing boron and hydrogen modes. Of course, Table 26 provides more detailed information concerning the form of the modes. The theoretical product rule ratios for each species are also given in Table 35, as those for the $B_{1}$ and $B_{2}$ species are required subsequently. The calculated frequencies in Table 35 are of course consistent with the theoretical ratios.

3. **High Frequency $B_{1}$ and $B_{2}$ Modes**

It is convenient to consider separately the higher $B_{1}$ and $B_{2}$ frequencies, including terminal and bridge hydrogen stretching and $B$-$H$ bending. The remaining lower frequencies for which more spectral information is available will be considered in the next section.
Terminal hydrogen and deuterium stretching frequencies of all species have been discussed in section B. The $B_1$ B-H stretching mode of $B_5D_9$ was assigned to the largely depolarized Raman band at 1944 cm$^{-1}$, and the corresponding mode of $B_5^H9$ to the broad Raman band at 2600 cm$^{-1}$.

It is difficult to make a definite assignment of the $B_1$ unsymmetrical and $B_2$ symmetrical bridge stretching frequencies on the basis of the available spectral data. The strong polarized Raman band of $B_5^H9$ at 1830 cm$^{-1}$ has been assigned to $A_1$ bridge stretching, and the depolarized shoulder at 1800-1810 cm$^{-1}$ and weak 1600 cm$^{-1}$ band to $E$ bridge stretchings on the basis of coincident infrared bands at 1812 and 1626 cm$^{-1}$. The remaining features of the Raman spectrum of $B_5^H9$ above ~1500 cm$^{-1}$, which are either depolarized or too weak for the measurement of polarization, are a broad shoulder at ~1730 cm$^{-1}$ and weak or very weak lines at 1950, 1970, 2010, 2040, 2105, 2120, 2196, 2240, and 2280 cm$^{-1}$. The infrared absorption at 1733 cm$^{-1}$ precludes the assignment of the 1730 cm$^{-1}$ Raman band as a $B$ mode. There is also considerable infrared absorption over the range covered by the weak lines, as shown by Table 3. In addition, the lowest of these lines lies about 300 cm$^{-1}$ above the calculated $B_1$ and $B_2$ stretching frequencies, and it seems unlikely that the error in the calculated values can be this great. The $B_1$ and $B_2$ modes are therefore assumed to be unobserved, and are assigned the calculated values 1586 and 1651 cm$^{-1}$, respectively, given in Table 35. They could, of course, contribute to the depolarized radiation in the range 1600-1800 cm$^{-1}$ in spite of the infrared activity in this region.
The polarized Raman band of $B_5^9$ at 1393 cm$^{-1}$ and apparently depolarized band at 1333 cm$^{-1}$ have been assigned to $A_1$ and $E$ bridge stretchings on the basis of the infrared bands at the same frequencies. There is no significant Raman activity at the frequency of the remaining $E$ bridge stretching, which has been assigned to the 1182 cm$^{-1}$ infrared band. The remaining significant features of the Raman spectrum in this region are a very weak and probably depolarized band at 1274 cm$^{-1}$, and a weak band at 1492 cm$^{-1}$ for which there is some evidence of polarization. The calculated values for the $B_1$ and $B_2$ modes from Table 35 are 1129 and 1275 cm$^{-1}$, respectively. The 1492 cm$^{-1}$ Raman band is excluded because of its possible polarization, the fact that it lies 200 cm$^{-1}$ above the highest calculated value, and the occurrence of a weak infrared band at 1506 cm$^{-1}$. The agreement of the calculated $B_2$ frequency with the 1274 cm$^{-1}$ Raman band may be a coincidence, because a medium to strong infrared band occurs at 1289 cm$^{-1}$. There is no significant Raman activity in the neighborhood of the calculated $B_1$ frequency. In view of these uncertainties the $B_1$ and $B_2$ bridge stretching frequencies in $B_5^9$ are tentatively assigned the calculated values above.

The remaining two modes to be considered in the present section are the $B_1$ vertical and $B_2$ horizontal $B-H$ bending. The calculated values of these frequencies from Table 35 are 1033 and 1114 cm$^{-1}$, respectively, for $B_5^9$. The previously assigned values for $B-H$ bending modes are $A_1$ vertical, 1120 cm$^{-1}$; $E$ vertical, 1044 cm$^{-1}$; and $E$ horizontal, 1408 cm$^{-1}$. Of these only the $A_1$ mode appears in the Raman, as the strong polarized line at 1120 cm$^{-1}$. The calculated values of the
A\textsubscript{1} and E modes given in Table 25 are in fairly good agreement with the assigned values, indicating the calculated values for the B modes are probably not in error by more than 10 percent. The anomalously high value of 1408 cm\textsuperscript{-1} (calculated as 1330 cm\textsuperscript{-1}) for the \textit{E} horizontal bending is apparently connected with the particular nature of the proton motion in this mode, as the other calculated values are derived from the same potential function and are much lower. It is therefore felt that the very weak and diffuse Raman bands at 1350, 1390, 1435, and 1495 cm\textsuperscript{-1} are too high to represent either B mode. There is intense infrared absorption in this range, including that of the 1408 cm\textsuperscript{-1} E band, which supports this conclusion. The only remaining unassigned Raman lines in the range 800-1300 cm\textsuperscript{-1} listed in Table 5 are weak lines at 1170 and 1193 cm\textsuperscript{-1}. However, these appear from visual examination of the film and also the densitometer tracing to be rather definitely polarized, and must therefore represent A\textsubscript{1} overtones or combinations as discussed in section F. They are too far removed from the 1120 cm\textsuperscript{-1} A\textsubscript{1} band to represent boron isotope shifts. Table 5 is based on film No. 62 of Taylor et al., which was their longest exposure of the Raman spectrum of B\textsubscript{12}\textsubscript{H\textsubscript{12}} and in general shows the greatest number of weak lines. Subsequent visual examination of the two exposures on polarization film No. 65 and the corresponding densitometer tracings shows a very weak but sharp line at \approx 1060 cm\textsuperscript{-1} The background on this film is much lower than that on film No. 62. This line appears with the same strength in both exposures and thus appears depolarized. Thus, it is probably not a satellite of the strong 1120 cm\textsuperscript{-1} line (1120-57 = 1063 cm\textsuperscript{-1}) similar to
the 929 and 944 cm\(^{-1}\) satellites of the strong lines at 986 and 1001 cm\(^{-1}\) (see Fig. 7). It could represent an E band as there are infrared absorptions at 1044 and 1081 cm\(^{-1}\), or it may be spurious as it is visible only on film No. 65. In view of these uncertainties, the \(B_1\) vertical and \(B_2\) horizontal \(\text{B-H}\) bending frequencies are assigned the calculated values 1033 and 1114 cm\(^{-1}\), respectively. However, it is recognized that the weak line at \(\sim 1060\) cm\(^{-1}\) may represent the \(B_1\) mode, while the \(B_2\) mode could easily be obscured by the strong polarized line at 1120 cm\(^{-1}\).

The calculated values for the \(B_1\) vertical and \(B_2\) horizontal \(\text{B-D}\) bending frequencies in \(3\,\text{D}_9\) are 876 and 790 cm\(^{-1}\). The calculated and assigned values for \(A_1\) and E vertical \(\text{B-D}\) bending are anomalous because of the interaction and reversal effects discussed in sections C and D. The E horizontal bending is anomalously high for \(3\,\text{D}_9\), just as for \(B_5\,\text{H}_2\). Thus, the calculated values for the \(B_1\) and \(B_2\) modes provide the only reliable estimate of these frequencies. There are no unassigned Raman bands for \(3\,\text{D}_9\) listed in Table 4 over the range 700-1200 cm\(^{-1}\). However, examination of the densitometer tracing of the film exposed 393 hours, which is reproduced in Figure 7, shows weak but fairly definite maxima at 805 and 775 cm\(^{-1}\). Visual examination of the film confirms the presence of very weak bands at these positions. The 775 cm\(^{-1}\) may probably be excluded as a 3 fundamental, because a pronounced shoulder occurs at 770 cm\(^{-1}\) on the very strong 741 cm\(^{-1}\) infrared band. The 805 cm\(^{-1}\) Raman band is probably a 3 fundamental, as there is virtually no infrared absorption at this frequency, and it is therefore assigned to the \(B_2\) horizontal \(\text{B-D}\) bending. The \(B_1\) vertical \(\text{B-D}\) bending is assigned the
calculated value 876 cm$^{-1}$ It may be obscured by the broad E band centered at 846 cm$^{-1}$ but extending over the range 825-875 cm$^{-1}$

4. **Low Frequency $B_1$ and $B_2$ Modes**

The relatively low frequency $B$ modes remaining to be assigned are the $B_1$ $B-B$ stretchings, the $B_1$ boron skeletal bending mode, and the $B_2$ bridge rocking. The calculated frequencies are given in Table 35. However, not much reliance is placed on these values, except those for $B_2$ B-B stretching which are consistent with the calculated and assigned values for the corresponding $A_1$ and E modes. As shown by the successive columns of Table 25, the greatest difficulty experienced in the normal coordinate calculation of chapter VI lay in finding a potential function which would bring the lowest $B_1$ and $B_2$ frequencies up to values consistent with lowest frequencies observed in the spectra. Calculations I and II represented the assigned $A_1$ and E frequencies with mean errors of less than 3 percent, and yet the lowest $B_1$ and $B_2$ frequencies calculated from the same potential functions were only about 110 and 80 cm$^{-1}$, respectively, or about 1/4 to 1/5 the values of the lowest observed frequencies. In calculation III these frequencies were raised by introducing an additional coordinate, $\theta$, and force constant directly representing bridge rocking, and considerably increasing the force constant for the inter-bridge angle, $\gamma$. This was a rather ad hoc procedure as it is quite possible that additional interaction constants are also required in the potential function. Furthermore, the $\theta$ and $\gamma$ constants were adjusted to bring the $B_1$ skeletal bending and $B_2$ bridge rocking frequencies into reasonable agreement with the 470 and 556 cm$^{-1}$
Raman bands of $B_5^H$, as this was believed to be the most reasonable assignment at the time. An obvious feature of the pyramidal structure is that it should have one relatively low frequency $B_1$ bending mode, and it was natural to assign to this mode the lowest observed frequency of $B_5^H$ at 470 cm$^{-1}$. This was the interpretation of this frequency made by Taylor et al.$^{15}$ when they first observed this frequency in the Raman spectrum and estimated the vibrational entropy. It is also the assignment made by Hrostowski and Pimentel$^{16}$ in Table 35 of their paper, although this is not immediately obvious as they have interchanged the labels for species $B_1$ and $B_2$ in the table. However, these assignments were made before the Raman spectrum of $B_5D_9$ was obtained in the present investigation. The correlation of the observed $B$ frequencies of $B_5^H$ and $B_5D_9$ given in this section indicates that the assignment of the lowest $B_1$ and $B_2$ frequencies should probably be reversed, with the $B_1$ skeletal at 596 cm$^{-1}$ and the $B_2$ bridge rocking at 470 cm$^{-1}$ (Hrostowski and Pimentel made no assignment of the Raman band at 596 cm$^{-1}$ although it is much more intense than the 470 cm$^{-1}$ band). This change in the assignment would have an important beneficial effect if the calculations were repeated and the force constants readjusted to raise the $B_1$ skeletal bending frequency from the calculated value of 415 cm$^{-1}$ in Table 35 to 596 cm$^{-1}$. The most unreasonable of all the calculated frequencies is that of the $B_1B_0$ stretching at 551 cm$^{-1}$ in $B_5^H$ and 498 cm$^{-1}$ in $B_5D_9$, scarcely more than

half the $A_1$ B-B$_0$ stretching frequencies at 986 and 959 cm$^{-1}$, respectively, as definitely established by boron isotope splitting. Raising the $B_1$ skeletal bending frequency by 180 cm$^{-1}$ in B$_5$H$_9$ would very probably force the calculated B-B$_0$ stretching frequency up to a more reasonable value.

The unassigned Raman bands of B$_5$H$_9$ in the low-frequency region under consideration are a very weak 470 cm$^{-1}$ band, medium strength 596 cm$^{-1}$ band, and strong 738 cm$^{-1}$ band. The first is too weak for measurement but the latter two are definitely depolarized. In addition, visual examination of the polarization films shows a broad and strong band of depolarized radiation underlying the very strong and sharp polarized lines at 793 and 803 cm$^{-1}$, but with its center displaced to ~785 cm$^{-1}$.

As there is no significant infrared absorption at these frequencies (other than the 800 cm$^{-1}$ band which is definitely correlated with the polarized 803 cm$^{-1}$ Raman line), the Raman bands at 470, 596, 738, and 785 cm$^{-1}$ are almost certainly B fundamentals.

The Raman bands of B$_5$D$_9$ in the low-frequency range are a medium intensity band at 425 cm$^{-1}$, weak bands at 507 and 537 cm$^{-1}$, and a strong band at 682 cm$^{-1}$. No polarization data were obtained on the first three bands because they are not visible on the polarization film. On visual inspection of the films the 682 cm$^{-1}$ line gives the appearance of being polarized but quantitative calculation based on optical densities yields 0.88 for its depolarization ratio, which is the highest value reported in Table 4. This seems to indicate the unreliability of visual estimates of polarization. Of course, the absolute values of the depolarization ratios reported in Table 4 are questionable as discussed there, but at least the 682 cm$^{-1}$ band is the least polarized line on which measurements
were possible. The infrared spectrum of B$_2$D$_9$ shows a broad absorption extending from 415 to 460 cm$^{-1}$, to which two E fundamentals have been assigned at the somewhat nominal frequencies 439 and 448 cm$^{-1}$, and a band assigned as an $A_1$ fundamental at 512 cm$^{-1}$. In view of this it seems unlikely that the Raman bands at 425 and 507 cm$^{-1}$ should be assigned to B modes. The small shoulder at 668 cm$^{-1}$ on the 638 cm$^{-1}$ infrared band in Figures 3 and 4 is probably connected with the atmospheric CO$_2$ absorption at 667 cm$^{-1}$. As shown by Figure 5 this sometimes appears as a positive and sometimes as a negative absorption with the double beam instrument, probably because of variation of CO$_2$ concentration in the two beams. In any case the 682 cm$^{-1}$ Raman band appears too strong not to be regarded as a fundamental. Furthermore, as no $A_1$ or E fundamentals coincide with the 537 or 682 cm$^{-1}$ Raman bands they must represent 3 fundamentals.

The intensities of the 738 and 682 cm$^{-1}$ Raman bands of B$_2$H$_9$ and B$_2$D$_9$, respectively, suggest that they represent boron modes. Their frequency ratio of .924 supports this assumption. Furthermore, they are in excellent agreement with the calculated B$_2$ 3-B stretching frequencies at 740 and 675 cm$^{-1}$, respectively, and in the same range as the corresponding $A_1$ and E frequencies. These bands are therefore assigned to B$_2$ 3-B stretching.

The order rule then indicates that the 596 cm$^{-1}$ band of B$_2$H$_9$ is correlated with the 537 cm$^{-1}$ band of B$_2$D$_9$, and their frequency ratio of .901 shows that they represent a boron motion. These bands are therefore assigned to the $B_1$ boron skeletal bending mode.
The very weak Raman band of $B_5H_9$ at 470 cm$^{-1}$ must now be assigned to the $B_2$ bridge rocking. The frequency of this mode in $D_9^3$ may now be estimated approximately from the product rule, as all other $3_2$ frequencies have been assigned. This calculation is only approximate because of the uncertainties in the $3_2$ bridge stretching and B-H bending frequencies, for which the calculated values have been used for the most part. However, the calculation is sufficiently accurate to indicate that the frequency ratio for the $3_2$ bridge rocking must be close to the value .707 for a pure hydrogen mode. This ratio lies at or below .712 for this mode in the three calculations of Table 25 despite a five-fold variation in the calculated frequencies, again showing that the $B_2$ bridge rocking is virtually a pure hydrogen motion. Assuming a ratio of .71 yields 335 cm$^{-1}$ as the estimated value of the $B_2$ bridge rocking in $D_9^3$. The failure to observe this frequency in the Raman spectrum of $D_9^3$ in the present investigation because of the unfavorable intensity and background conditions discussed in chapter III, section D.7. The extremely low intensity of the 470 cm$^{-1}$ band of $B_5H_9$ obtained under optimum conditions makes it unlikely that the corresponding band would be visible above background in the spectrum of $D_9^3$. As $B_1$ modes are inactive in the infrared the fact that the present infrared spectra extend only to 400 cm$^{-1}$ is no limitation. The present assignment of the very weak 470 cm$^{-1}$ Raman band of $D_9^3$ to a purely hydrogen mode and the much more intense 596 cm$^{-1}$ band to the boron skeletal bending mode also seems more reasonable from the viewpoint of predicted intensities than the earlier assignments of the 470 cm$^{-1}$ band to the skeletal bending mode as
discussed at the beginning of this section. This completes the assignment of $B_2$ frequencies.

The single remaining $B_1$ mode of $B_5H_9$, the $B-B_0$ stretching, may now be assigned to the one remaining Raman band falling in the possible frequency range for this mode, namely, to the strong depolarized band at 785 cm$^{-1}$. The product rule may now be used to calculate the $B_1$ $B-B_0$ stretching frequency in $B_5D_2$. This yields the value 683 cm$^{-1}$, corresponding to a frequency ratio of 0.870 for this mode. This is essentially coincident with the strong depolarized Raman band of $B_5D_2$ at 682 cm$^{-1}$ which has previously been assigned to the $B_2$ $B-B$ stretching mode and correlated with the 738 cm$^{-1}$ Raman band of $B_5H_9$. However, it should be noted that if the 785 cm$^{-1}$ band of $B_5H_9$ had first been correlated with the 682 cm$^{-1}$ band of $B_5D_2$, which is the only correlation possible with an observed band not yet previously assigned, then the application of the product rule would still have correlated the 738 cm$^{-1}$ band of $B_5H_9$ with the 682 cm$^{-1}$ band of $B_5D_2$. The conclusion is therefore that the $B_1$ $B-B_0$ stretching and $B_2$ $B-B$ stretching frequencies in $B_5D_2$ are nearly coincident at 682 cm$^{-1}$. Of course, the anharmonic errors in the product rule and the errors in other frequencies would allow some separation of these two boron stretching frequencies. However, there is absolutely no theoretical obstacle to even exact degeneracy of modes of two different species. This also accounts for the at first puzzling fact that there is only one Raman band of $B_5D_9$ to be correlated with the two $B_5H_9$ bands at 738 and 785 cm$^{-1}$.
The frequencies which have now been assigned for the $B_1$ and $B_2$ species of $B_5H_9$ and $B_5D_9$ are listed in Table 36, together with their calculated frequency ratios.

### Table 36

**Assigned Values of $B_1$ and $B_2$ Frequencies for $B_5H_9$ and $B_5D_9**

<table>
<thead>
<tr>
<th>Species</th>
<th>Description of Mode</th>
<th>Frequencies (cm$^{-1}$)</th>
<th>Ratio $\left(\frac{\nu'(B_5D_9)}{\nu(B_5H_9)}\right)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_1$</td>
<td>$B-H$ stretching</td>
<td>2598 (1596)</td>
<td>.748</td>
</tr>
<tr>
<td></td>
<td>Unsymmetrical bridge stretching</td>
<td>1944 (1129)</td>
<td>.712</td>
</tr>
<tr>
<td></td>
<td>$B-H$ vertical bending</td>
<td>1033 (683)</td>
<td>.848</td>
</tr>
<tr>
<td></td>
<td>$S-B_0$ stretching</td>
<td>785 (685)</td>
<td>.970</td>
</tr>
<tr>
<td></td>
<td>Boron skeletal bending</td>
<td>596 (337)</td>
<td>.901</td>
</tr>
<tr>
<td>$B_2$</td>
<td>Symmetrical bridge stretching</td>
<td>(1651) (1275)</td>
<td>.772</td>
</tr>
<tr>
<td></td>
<td>$B-H$ horizontal bending</td>
<td>(1114) 905</td>
<td>.723</td>
</tr>
<tr>
<td></td>
<td>$B-B$ stretching</td>
<td>735 (635)</td>
<td>.924</td>
</tr>
<tr>
<td></td>
<td>Bridge rocking</td>
<td>470 (335)</td>
<td>.713</td>
</tr>
</tbody>
</table>

An alternative assignment of the low frequency $B_1$ and $B_2$ modes is indicated in Table 37. This has the advantage of not making use of any unobserved frequencies. However, it is still necessary to assign two fundamentals to a single band of $B_5D_9$, in this case the 537 cm$^{-1}$. If the 470 and 425 cm$^{-1}$ bands are assigned to boron skeletal bending as indicated, it is not possible to correlate the 596 and 425 cm$^{-1}$ bands and assign them to bridge rocking. For it would then be necessary by the order rule to correlate the 735 with the 537 cm$^{-1}$ band, which yields in effect two low-frequency hydrogen modes, and makes it impossible to satisfy the product rule. Thus, the 596 and 537 cm$^{-1}$ bands have to be
correlated and identified as a boron stretching mode. The most reasonable assignment for bridge rocking is then the 73° and 537 cm\(^{-1}\) bands. But in order to avoid using 537 cm\(^{-1}\) for two fundamentals of the same species it is then necessary to assign the 596 and 537 cm\(^{-1}\) pair to \(B_1\) 3-3\(\sigma\) stretching. Finally, the remaining pair of bands at 785 and 682 must be assigned as \(B_2\) 3-3 stretching. This leads to anomalously low values for the \(B_1\) 3-3\(\sigma\) stretchings, which seem physically unreasonable, although admittedly they are indicated by the results of the normal coordinate calculation in Table 35. However, the \(B_2\) 3-3 stretching frequencies now agree less well with the calculated values, and the \(B_2\) bridge rockings are in very poor agreement with these values. On the whole, it is felt that the assignment in Table 36 is more reasonable. However, it will be noted that both assignments yield the same frequencies as fundamentals for \(B_5H_9\), so that the use of the alternative assignment would not alter the statistical values of the thermodynamic

<table>
<thead>
<tr>
<th>Species</th>
<th>Description of Mode</th>
<th>Frequency (cm(^{-1}))</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>(B_1)</td>
<td>3-3(\sigma) stretching</td>
<td>596</td>
<td>537</td>
</tr>
<tr>
<td></td>
<td>Boron skeletal bending</td>
<td>470</td>
<td>425</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>.901</td>
</tr>
<tr>
<td>(B_2)</td>
<td>3-3 stretching</td>
<td>73°</td>
<td>537</td>
</tr>
<tr>
<td></td>
<td>Bridge rocking</td>
<td>73°</td>
<td>537</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>.904</td>
</tr>
</tbody>
</table>
functions calculated for \( \text{B}_5\text{H}_9 \) in the next chapter. The thermodynamic functions for \( \text{B}_5\text{D}_9 \) would be very significantly different for the two assignments, because of the marked difference in the assignment of several of the lowest frequencies to which the entropy is particularly sensitive. Unfortunately, a third law entropy is not available for \( \text{B}_5\text{D}_9 \).

F. Overtones and Combinations

In the preceding sections of this chapter the fundamental vibrational frequencies of normal and deuterated pentaborane have been assigned. However, not all of the observed infrared and Raman bands have been assigned as fundamentals. In particular in the infrared spectra of \( \text{B}_5\text{H}_9 \) and \( \text{B}_5\text{D}_9 \) and the Raman spectrum of \( \text{B}_5\text{H}_9 \), the number of observed bands exceeds the expected number of active fundamentals. Of course, this is not surprising as the many weak and the few medium strength bands which have not been assigned as fundamentals are reasonably interpreted as overtones or combinations of the fundamentals. The purpose of this section is to offer a plausible explanation of these bands.

Overtones, sum, and difference bands arise due to anharmonic terms in the potential energy. An excellent discussion of these bands has been given by Herzberg.\(^{17}\) Overtones and combination bands for which

\[
\sum |\Delta \nu_i| = 2, \quad \text{where} \quad \Delta \nu_i \quad \text{is the change in the vibrational quantum number of the } i\text{th normal mode, are called binary combinations, for} \\
\sum |\Delta \nu_i| = 3, \text{ ternary combinations, etc. In general binary}
\]

\(^{17}\) Herzberg, op. cit.
combinations are weaker than fundamentals, ternary combinations weaker than binary combinations, etc. For this reason only binary combinations will be considered in this section as possible explanations of the observed bands. Binary combinations are expected to be weaker than the corresponding fundamentals, since the anharmonic terms in the potential function are much smaller than the harmonic terms. Difference bands are further reduced in intensity since the relative number of molecules in the excited initial state is reduced by the thermal distribution, and is considerably smaller than the number of molecules in the ground state. The latter is the initial state for overtone or sum bands. For a difference band of frequency \((\nu_k - \nu_1)\), the fraction of molecules in the initial state relative to the number in the ground state is given by the Boltzmann factor, \(e^{-\left(\frac{hc \nu_1}{kT}\right)}\). Here \(\nu_1\) is the frequency of the \(i\)th normal mode in wave numbers, \(h\) is Planck's constant, \(k\) is Boltzmann's constant, and \(c\) the velocity of light. From these considerations, it is clear that difference bands of frequency \((\nu_k - \nu_1)\) will be observed only if \(\nu_1\) is relatively low. Although the above statements concerning the intensity of binary combinations are generally correct, it should be pointed out that the intensity of a combination can be greatly increased by Fermi resonance with a fundamental.

The symmetry of overtones and combinations for molecules belonging to the point group \(C_{\nu\nu}\) have been given in Table 3. Combining these results with the infrared and Raman selection rules discussed in chapter IV and summarized in Table 6, the activity of any binary combination can be determined. Since a few of the combinations observed in the Raman
spectrum of $B_5H_9$ appear to be polarized, it should be noted that only binary combinations of two modes of the same symmetry species or even (sometimes odd) harmonics give rise to $A_1$ or polarized Raman lines.

In some molecules, a study of the overtone and combination bands can give information about frequencies which are inactive as fundamentals, but whose overtones or combinations have symmetries such that they are active. However, in pentaborane with 25 active fundamentals and 2 inactive $A_2$ modes, there is little possibility of obtaining any information about the inactive modes. The number of possible frequencies resulting from the combinations and overtones of observed fundamentals is extremely large and offers a reasonable explanation of virtually any observed bands which have not been assigned as fundamentals. In many cases more than one explanation is possible. As it is extremely difficult to make any accurate estimates of the expected intensities of combination bands, little attempt has been made to differentiate between the several possible explanations of the same band. However, sum and overtone bands have been favored over difference bands. In Table 38, the observed infrared and Raman bands which have not been assigned as fundamentals are listed. In the second column at least one explanation of each band as an overtone or combination is given. The principal purpose of this table is to explain as combinations those unassigned bands having frequencies less than the highest fundamentals, or in the present case $B-H$ or $B-D$ stretching frequencies. Therefore bands which lie above 2600 cm$^{-1}$ in $B_5H_9$ or 2000 cm$^{-1}$ in $B_5D_9$ have not been included. As a result of anharmonic effects, and errors in determining band centers, the observed values for overtone and
combination bands will not usually be an exact agreement with the values calculated by addition of the fundamental frequencies, but the differences should not exceed about 2 percent. However, Fermi resonance between excited states of the same symmetry species can occasionally produce much larger displacements from the calculated positions.
### Table 3A

**Possible Assignments as Overtones or Combinations of Bands of $\text{B}_3\text{H}_9$ and $\text{B}_5\text{D}_9$ Not Assigned as Fundamentals**

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Infrared Frequency (cm$^{-1}$)</th>
<th>Raman Frequency (cm$^{-1}$)</th>
<th>Overtone or Combination</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{B}_3\text{H}_9$</td>
<td>1081</td>
<td>470 + 614 = 1084</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1143</td>
<td>2(568) = 1136</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1170 p†</td>
<td>568 + 596 = 1164</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1193 p†</td>
<td>568 + 614 = 1182</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1348</td>
<td>2(568) = 1192</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1350</td>
<td>2(614) = 1228</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1493</td>
<td>883 + 470 = 1353</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1495</td>
<td>614 + 738 = 1352</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1733</td>
<td>793 + 568 = 1361</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1730</td>
<td>1044 + 700 = 1744</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1916</td>
<td>1120 + 700 = 1734</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>936 + 738 = 1724</td>
<td></td>
</tr>
<tr>
<td>$\text{B}_5\text{D}_9$</td>
<td>1289</td>
<td>1493 + 596 = 1499</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1274</td>
<td>2(568) = 1276</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1506</td>
<td>2(1044) = 2088</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1492</td>
<td>1408 + 700 = 2108</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1626</td>
<td>1626 + 568 = 2194</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2240</td>
<td>1626 + 614 = 2240</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2(1120) = 2240</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2460</td>
<td>1408 + 1044 = 2452</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1830 + 614 = 2444</td>
<td></td>
</tr>
</tbody>
</table>
IX. THERMODYNAMIC FUNCTIONS OF PENTABORANE

In this chapter the thermodynamic functions of normal pentaborane will be calculated from the vibrational assignment of the previous chapter. In addition to providing useful thermodynamic data, this calculation provides a check of the vibrational assignment, as the third law entropy of normal pentaborane at 295° K has been measured by Johnston et al. Since the vibrational contribution to the entropy at room temperature is relatively small compared to the rotational and translational contributions and since high frequency vibrations do not contribute significantly to the vibrational entropy at this temperature, the experimental value of the entropy provides a check only on the assignment of the low frequency modes.

The equations for the calculation of the thermodynamic functions from the vibrational frequencies and the structural parameters of a molecule are well known. For the derivation of these equations, the reader is referred to any book on statistical thermodynamics (for example, Hill). The basic assumptions, which are usually made and which produce only very small errors in the thermodynamics functions


at ordinary temperatures, are (1) the translational, rotational, 
vibrational, and electronic eigenfunctions are separable, (2) transla­
tion and rotation can be treated classically, (3) the rotation is that 
of a rigid rotor, (4) the vibrations are harmonic, and (5) excited elec­
tronic states may be neglected. The errors due to assumption (2) 
become important only for very light molecules at very low temperatures, 
but assumptions (3) to (5) may introduce significant errors for ordinary 
molecules at high temperatures. However, with these assumptions the 
contributions of translation, rotation, and vibration to the thermo­
dynamic functions may be calculated separately.

The formulas for the translational contributions to the thermo­
dynamic functions may be put in the form
\[
\frac{(H^0 - E^0)}{T} = C_P^0 = 4.9680,
\]
\[
-(F^0 - E^0)/T = 6.8635 \log M + 7.2830 - 11.4392 \log T,
\]
\[
S^0 = 6.8635 \log M - 2.3150 + 11.4392 \log T,
\]
where \( M \) is the molecular weight and \( T \) the absolute temperature. The 
numerical values given in these and the following formulas have been 
calculated from the values of the fundamental constants given by Rossini 
et al.\(^3\) The values obtained for the thermodynamic functions refer to a 
gas in the thermodynamic standard gaseous state of unit fugacity (1 
atmosphere).

---

\(^3\) F. D. Rossini, F. T. Gucker, Jr., H. L. Johnston, L. Pauling, 
The rotational contributions to the thermodynamic functions are given by

\[
\frac{H^0 - E^0}{T} = 2.980^a
\]

\[
\frac{- (F^0 - E^0)}{T} = 2.2878 \log (I_x I_y I_z x 10^{117}) - 4.5757 \log \sigma + 3.0141 + 5.9635 \log T
\]

\[
S^0 = 2.2878 \log (I_x I_y I_z x 10^{117}) - 4.5757 \log \sigma + 0.3333 + 6.8635 \log T
\]

where \(I_x, I_y,\) and \(I_z\) are the three principal moments of inertia and \(\sigma\) is the symmetry number (the number of ways the molecule may be superimposed upon itself by rotation of the entire molecule).

There is no basic difficulty in calculating the vibrational contributions from the Einstein functions for an harmonic oscillator. However, this is not necessary, as an extensive tabulation of harmonic oscillator contributions to the thermodynamic functions is given by Johnston, Savedoff, and Belzer.\(^4\) This table gives the principal thermodynamic functions as a function of \(\sqrt{\gamma}/T\) at intervals of 0.001 up to \(\sqrt{\gamma}/T = 3.00\) and at intervals of 0.01 up to \(\sqrt{\gamma}/T = 10.43\) The vibrational contributions to the thermodynamic functions are obtained by summing the contribution of each fundamental frequency of the molecule. If a given frequency is of degeneracy \(g\), it is necessary to include it \(g\) times in the summation.

For normal pentaborane, \( M = 63.182 \text{ g mole}^{-1} \), \( \sigma = 4 \), \( I_x = I_y = 71.30 \), and \( I_z = 101.9 \) (see Table 9). The following vibrational frequencies were used for the calculation of the vibrational contributions (frequencies in parentheses are not observed and were calculated from the normal coordinate analysis of chapter VI):

- \( A_1 \): 700, 798, 986, 1123, 1842, 2598, 2610
- \( A_2 \): (866), (1776)
- \( B_1 \), \( B_2 \): 470, 596, 738, 785, (1033), (1114), (1586), (1651), 2598
- \( E \): 567, 615, 700, 833, 1034, 1413, 1621, 1801, 2598

There are a few differences between the precise values of the above frequencies and the frequencies assigned in the preceding chapter, as a result of further refinement of the assignment following these calculations. However, these small discrepancies are well within the accuracy of the assigned frequencies. The translational, rotational, and vibrational contributions and their sum are given in Table 39 for the principal thermodynamic functions of normal pentaborane, at 296, 298.15, and eight temperatures ranging from 500 to 2500°K.

The only experimental value with which to compare the calculated values is the calorimetric value of Johnston et al. for the entropy at 296°K. The measured value of the entropy of the actual gas at 296°K and 190.2 mm Hg pressure is 68.43 cal. deg.\(^{-1}\) mole\(^{-1}\). The Berthelot equation is used to correct this value to that of the ideal gas at 760 mm Hg, which gives the value 65.75 cal. deg.\(^{-1}\) mole\(^{-1}\). Although the critical constants in the Berthelot equation may not be very accurate, they have only a small effect on the correction to the entropy, as the use of the ideal gas equation in place of the Berthelot equation changes
### TABLE 39

**Thermodynamic Functions of Normal Pentaborane**

<table>
<thead>
<tr>
<th>$T$ (°K)</th>
<th>Heat Capacity, $C^\circ_p$ (cal. deg.$^{-1}$ mole$^{-1}$)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Trans.</td>
<td>Rot.</td>
<td>Vibr.</td>
<td>Total</td>
</tr>
<tr>
<td>296</td>
<td>4.97</td>
<td>2.98</td>
<td>14.98</td>
<td>22.93</td>
</tr>
<tr>
<td>298.15</td>
<td>4.97</td>
<td>2.98</td>
<td>15.15</td>
<td>23.13</td>
</tr>
<tr>
<td>500</td>
<td>4.97</td>
<td>2.98</td>
<td>31.65</td>
<td>39.60</td>
</tr>
<tr>
<td>800</td>
<td>4.97</td>
<td>2.98</td>
<td>47.08</td>
<td>55.03</td>
</tr>
<tr>
<td>1000</td>
<td>4.97</td>
<td>2.98</td>
<td>53.33</td>
<td>61.31</td>
</tr>
<tr>
<td>1200</td>
<td>4.97</td>
<td>2.98</td>
<td>57.68</td>
<td>65.63</td>
</tr>
<tr>
<td>1500</td>
<td>4.97</td>
<td>2.98</td>
<td>61.98</td>
<td>69.98</td>
</tr>
<tr>
<td>1800</td>
<td>4.97</td>
<td>2.98</td>
<td>64.49</td>
<td>72.44</td>
</tr>
<tr>
<td>2000</td>
<td>4.97</td>
<td>2.98</td>
<td>65.59</td>
<td>73.64</td>
</tr>
<tr>
<td>2500</td>
<td>4.97</td>
<td>2.98</td>
<td>67.67</td>
<td>75.61</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$T$ (°K)</th>
<th>Enthalpy, $(h^\circ - E^\circ) / T$ (cal. deg.$^{-1}$ mole$^{-1}$)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Trans.</td>
<td>Rot.</td>
<td>Vibr.</td>
<td>Total</td>
</tr>
<tr>
<td>296</td>
<td>4.97</td>
<td>2.98</td>
<td>4.26</td>
<td>12.21</td>
</tr>
<tr>
<td>298.15</td>
<td>4.97</td>
<td>2.98</td>
<td>4.33</td>
<td>12.28</td>
</tr>
<tr>
<td>500</td>
<td>4.97</td>
<td>2.98</td>
<td>12.22</td>
<td>20.17</td>
</tr>
<tr>
<td>800</td>
<td>4.97</td>
<td>2.98</td>
<td>22.58</td>
<td>30.53</td>
</tr>
<tr>
<td>1000</td>
<td>4.97</td>
<td>2.98</td>
<td>28.23</td>
<td>36.18</td>
</tr>
<tr>
<td>1200</td>
<td>4.97</td>
<td>2.98</td>
<td>32.85</td>
<td>40.75</td>
</tr>
<tr>
<td>1500</td>
<td>4.97</td>
<td>2.98</td>
<td>39.23</td>
<td>46.18</td>
</tr>
<tr>
<td>1800</td>
<td>4.97</td>
<td>2.98</td>
<td>42.41</td>
<td>50.35</td>
</tr>
<tr>
<td>2000</td>
<td>4.97</td>
<td>2.98</td>
<td>44.57</td>
<td>52.62</td>
</tr>
<tr>
<td>2500</td>
<td>4.97</td>
<td>2.98</td>
<td>49.10</td>
<td>57.05</td>
</tr>
</tbody>
</table>
### TABLE 39 (contd.)

**Free Energy, \(- (F^0 - E^0)/T\) (cal. deg.\(^{-1}\) mole\(^{-1}\))**

<table>
<thead>
<tr>
<th>T (°K)</th>
<th>Trans.</th>
<th>Rot.</th>
<th>Vibr.</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>296</td>
<td>33.34</td>
<td>18.94</td>
<td>1.30</td>
<td>53.56</td>
</tr>
<tr>
<td>298.15</td>
<td>33.70</td>
<td>18.94</td>
<td>1.33</td>
<td>53.95</td>
</tr>
<tr>
<td>500</td>
<td>35.95</td>
<td>20.48</td>
<td>5.42</td>
<td>61.85</td>
</tr>
<tr>
<td>1000</td>
<td>39.39</td>
<td>22.54</td>
<td>19.21</td>
<td>81.14</td>
</tr>
<tr>
<td>1200</td>
<td>40.30</td>
<td>23.09</td>
<td>24.77</td>
<td>88.16</td>
</tr>
<tr>
<td>1500</td>
<td>41.41</td>
<td>23.75</td>
<td>32.70</td>
<td>97.96</td>
</tr>
<tr>
<td>1800</td>
<td>42.31</td>
<td>24.79</td>
<td>40.36</td>
<td>103.66</td>
</tr>
<tr>
<td>2000</td>
<td>42.94</td>
<td>24.61</td>
<td>44.53</td>
<td>112.07</td>
</tr>
<tr>
<td>2500</td>
<td>43.95</td>
<td>25.27</td>
<td>55.13</td>
<td>124.35</td>
</tr>
</tbody>
</table>

**Entropy, S\(^0\) (cal. deg.\(^{-1}\) mole\(^{-1}\))**

<table>
<thead>
<tr>
<th>T (°K)</th>
<th>Trans.</th>
<th>Rot.</th>
<th>Vibr.</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>296</td>
<td>38.31</td>
<td>21.09</td>
<td>5.56</td>
<td>65.77</td>
</tr>
<tr>
<td>298.15</td>
<td>38.35</td>
<td>21.92</td>
<td>5.66</td>
<td>65.93</td>
</tr>
<tr>
<td>500</td>
<td>40.92</td>
<td>23.46</td>
<td>17.54</td>
<td>92.12</td>
</tr>
<tr>
<td>1000</td>
<td>44.36</td>
<td>25.52</td>
<td>47.44</td>
<td>117.32</td>
</tr>
<tr>
<td>1200</td>
<td>45.27</td>
<td>26.07</td>
<td>57.57</td>
<td>128.89</td>
</tr>
<tr>
<td>1500</td>
<td>46.38</td>
<td>26.73</td>
<td>70.93</td>
<td>194.03</td>
</tr>
<tr>
<td>1800</td>
<td>47.28</td>
<td>27.29</td>
<td>82.46</td>
<td>157.02</td>
</tr>
<tr>
<td>2000</td>
<td>47.80</td>
<td>27.59</td>
<td>89.30</td>
<td>164.69</td>
</tr>
<tr>
<td>2500</td>
<td>48.91</td>
<td>28.25</td>
<td>104.24</td>
<td>181.40</td>
</tr>
</tbody>
</table>
the correction by only 0.07 cal. deg.\(^{-1}\) mole\(^{-1}\). The statistically calculated value for the entropy in Table 39 is 65.77 cal. deg.\(^{-1}\) mole\(^{-1}\), which is in excellent agreement with the experimental value of 65.75 cal. deg.\(^{-1}\) mole\(^{-1}\).

The thermodynamic functions of pentaborane have also been calculated by Evans, Prosen, and Wagman\(^5\) based on the vibrational assignment of Hrostowski and Pimentel.\(^6\) Although there are considerable differences between the present assignment and that of Hrostowski and Pimentel, the differences in the thermodynamic functions resulting from the two assignments are not very large. In general the values for the thermodynamic functions calculated from the present assignment are slightly larger than those calculated by Evans, Prosen, and Wagman. The average difference of the values at nine temperatures (Evans, Prosen, and Wagman did not calculate the thermodynamic functions at 296\(^\circ\) K) are 0.45 for the heat capacity, 0.47 for the enthalpy, 0.56 for the free energy, and 1.05 cal. deg.\(^{-1}\) mole\(^{-1}\) for the entropy. In part, the explanation of the relatively small differences lies in the fact that the contribution of a vibrational frequency to the thermodynamic functions depends only on the degeneracy of the symmetry species to which the frequency is assigned, and not on the symmetry species itself.

---


In spite of the relatively good agreement of the calculated thermodynamic functions, the present assignment is based on considerably more spectral data and a much more detailed theoretical analysis than that of Hrostowski and Pimentel. They did not have available the Raman data for $\mathbf{D}_9$, and had only a brief summary of the Raman data for $\mathbf{H}_9$. In addition they did not carry out a normal coordinate calculation as a check on their assignment. In fact, for the most part they simply assigned the observed bands to symmetry species, without attempting a detailed assignment of frequencies to dynamical modes. The excellent agreement they obtained between their statistical entropy and the calorimetric entropy is of little significance, as they had the inactive $A_2$ frequencies as adjustable parameters, and in fact assigned an unreasonably low value of $500 \text{ cm}^{-1}$ to one $A_2$ frequency. In the present assignment the relatively small fraction of frequencies not observed are calculated from the product rule or from a potential function based on observed frequencies.

It should be noted that the assumptions made in the calculation of the thermodynamic functions are valid to a considerable degree of approximation at room temperature. Several of the assumptions become less valid at high temperatures. Therefore the calculated thermodynamic functions given in Table 39 are undoubtedly less accurate at high temperatures than the agreement with the calorimetric entropy would indicate.
AUTobiography

I, Sam Ray Coriell, was born December 21, 1935, in Greenfield, Ohio. I received my elementary and high school education in the Greenfield public schools. In 1956, I received the B. Sc. degree with a major in chemistry from the Ohio State University. I entered the Graduate School of the Ohio State University and was a teaching assistant in physical and general chemistry for three years. I was a University Fellow in 1959-1960 and an NSF Cooperative Graduate Fellow in 1960-61. When I complete my Ph.D. requirements, I will become a postdoctoral fellow at the National Bureau of Standards.