**This dissertation has been
microfilmed exactly as received**

66-10,037

**SCOTT, James Floyd, 1942-
INFRARED ABSORPTION BANDS OF ACETYLENE.**

**The Ohio State University, Ph.D., 1966
Physics, general**

University Microfilms, Inc., Ann Arbor, Michigan

INFRARED ABSORPTION BANDS OF ACETYLENE

DISSERTATION

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

By

James Floyd Scott, A.B.

* * * * *

The Ohio State University
1966

Approved by

K. Narahari Rao

Adviser
Department of Physics

ACKNOWLEDGMENTS

I would like to thank most sincerely Professor K. Narahari Rao, who taught me what spectroscopy is, Professor Harald H. Nielsen, who taught me why some things are as they are, and my wife Carol, who put up with me during the learning period.

I wish to acknowledge also the financial assistance provided through a National Science Foundation Summer Fellowship for Graduate Teaching Assistants, a National Aeronautics and Space Administration Traineeship, and teaching and research assistantships in the Department of Physics.

Finally, I want to thank my fellow graduate students and laboratory coworkers for their many helps, especially Mr. Jan Adams, who performed most of the numerical calculations on the university's IBM 7094.

VITA

May 4, 1942 Born - Beverly, New Jersey

1963 A.B., Harvard University, Cambridge, Massachusetts

1963-1964 Teaching Assistant, Department of Physics,
The Ohio State University, Columbus, Ohio

1964 National Science Foundation Summer Fellow,
The Ohio State University, Columbus, Ohio

1964-1965 Research Assistant, Department of Physics,
The Ohio State University, Columbus, Ohio

1965-1966 National Aeronautics and Space Administration
Trainee, The Ohio State University, Columbus, Ohio

PUBLICATIONS

- J. F. Scott and K. Narahari Rao, "Infrared Absorption Bands of Acetylene. Part I. Analysis of the Bands at 13.7 Microns," J. Mol. Spectry. 16, 15 (1965).
- J. F. Scott and K. Narahari Rao, "Infrared Bands of Acetylene," contributed paper R7, Symposium on Molecular Structure and Spectroscopy, The Ohio State University, Columbus, Ohio, June 16, 1965.
- J. F. Scott and K. Narahari Rao, "Infrared Absorption Bands of Acetylene. Part II. The Effect of Vibrational ℓ -type Doubling," J. Mol. Spectry. 18, 152 (1965).
- J. F. Scott and K. Narahari Rao, "Current Trends in High Resolution Infrared Spectroscopic Research," contributed paper B13, meeting of the Ohio Section of the American Physical Society, Dayton, Ohio, November 13, 1965.
- J. F. Scott and K. Narahari Rao, "Infrared Absorption Bands of Acetylene. Part III. Analysis of the Bands at 3 Microns," J. Mol. Spectry. (in press).
- J. F. Scott and K. Narahari Rao, "Use of Loomis-Wood Plots in Vibration-Rotation Analysis," J. Mol. Spectry. (in press).

CONTENTS

Chapter	Page
I. INTRODUCTION	1
II. ANALYSIS OF THE BANDS AT 13.7 MICRONS	7
III. VIBRATIONAL ℓ -TYPE RESONANCE AND DOUBLING	27
IV. ANALYSIS OF THE BANDS AT 3 MICRONS	53
V. THE USE OF LOOMIS-WOOD DIAGRAMS	97
VI. BANDS IN THE PHOTOGRAPHIC INFRARED	105
APPENDIX	122
REFERENCES	141

LIST OF TABLES

Table	Page
1. Vacuum Wave Numbers (cm^{-1}) of the Rotational Lines of Acetylene - ν_5 fundamental of $^{12}\text{C}_2\text{H}_2$	15
2. Vacuum Wave Numbers (cm^{-1}) of the Rotational Lines of Acetylene - ν_5 fundamental of $^{12}\text{C}^{13}\text{CH}_2$	16
3. Difference Bands of $^{12}\text{C}_2\text{H}_2$ at 13.7μ	17
4. Some of the Band Centers and Rotational Constants of $^{12}\text{C}_2\text{H}_2$ (cm^{-1})	20
5. Vibrational Levels of Acetylene (cm^{-1}).	21
6. Vibrational Interaction Constants of $^{12}\text{C}_2\text{H}_2$	48
7. Transitions Observed at Three Microns	58
8. Rotational Analysis of the Bands ν_3 and $\nu_2 + \nu_4 + \nu_5$ (cm^{-1}).	61
9. Constants Derived from the Bands at 3 Microns	66
10. Rotational Analysis of the Band $\nu_3 + \nu_4 - \nu_4$	82
11. Rotational Analysis of the Band $\nu_3 + \nu_5 - \nu_5$	84
12. Rotational Analysis of the Band $\nu_2 + 2\nu_4^2 + \nu_5^1 - \nu_4^1$	87
13. Rotational Analysis of the Band $\nu_2 + \nu_4^1 + 2\nu_5^2 - \nu_5^1$	90
14. Line Positions of Some Photographic Bands	108
15. Rotation Constants Derived from the Photographic Bands	116

ILLUSTRATIONS

Matrices		Page
I.	Vibration Rotation Submatrix Pertaining to the Levels 00011	30
II.	Vibration Submatrix Pertaining to 00011.	32
III.	Vibration Rotation Submatrix Pertaining to the Levels 00021	34
IV.	Vibration Submatrix Pertaining to 00021.	36
V.	Vibration Rotation Submatrix Pertaining to the Levels 00031	38
VI.	Vibration Submatrix Pertaining to 00031.	40
Figures		
1.	Vibration Rotation Bands of Acetylene at 13.7 Microns	10
2.	Vibration Rotation Bands of Acetylene at 13.7 Microns	12
3.	Vibration Rotation Bands of Acetylene at 13.7 Microns	14
4.	The Energy Levels 00011 and 00021.	42
5.	The Energy Levels 00031	44
6.	An Energy Level Diagram of $^{12}\text{C}_2\text{H}_2$	50
7.	The Spectrum at 3 Microns	55
8.	Transitions Expected at 3 Microns	57
9.	$\nu(m)$ versus m for $\nu_2 + \nu_4 + \nu_5$	69
10.	$R(J-1) + P(J)$ versus J for ν_3	71

ILLUSTRATIONS (Continued)

Figures	Page
11. Submatrix Pertaining to Transitions at 3 Microns . . .	74
12. Graphical Determination of Rotational ℓ -type Doubling Constants	96
13. Loomis-Wood Diagram of the Spectrum at 13.7 Microns. .	100
14. Loomis-Wood Diagram of the Spectrum at 3 Microns . . .	102

INTRODUCTION

In the spectroscopic study of molecules it is customary to measure the positions of observed transitions and to determine from these transitions a set of energy levels compatible with the observations. The energy levels are known to fit a particular functional dependence, since they are eigenvalues of the Hamiltonian for the molecule, and the eigenvalue problems for most molecular geometries have been solved to a high order of approximation. The experimentally determined energy levels are then used to fit the constants which occur in the general eigenvalue expression. The infrared region of the spectrum is most useful for the determination of constants of the energy eigenvalue expression which are associated with rotation and vibration of the molecule.

The infrared absorption spectrum of the acetylene molecule, HCCH, has been analyzed by a large number of investigators from many different laboratories over the past forty years. As a result, quite a lot is known about the molecule; it is linear and symmetric with respect to inversion (1), and its fundamentals have all been unambiguously assigned, although the asymmetric stretch had been misassigned in the literature up until 1964 (2). While many bands have been assigned with certainty, the basic problem of determining a set of

vibrational and rotational constants which will mathematically reproduce the observed spectrum to within the experimental uncertainty remains today.

To a very large extent this difficulty is due to what are loosely termed "resonances," that is, to non-negligible off-diagonal elements in the Hamiltonian, which complicate the eigenvalue problem. Another reason for the difficulty encountered in deriving a good set of vibrational constants for acetylene is the fact that the molecule has a high degree of symmetry, making electric dipole transitions from the ground state to many of the vibrational energy levels forbidden by selection rules, so that many levels have not yet been determined from observed transitions. In addition, the large number of energy levels determined from transitions observed in the visible and photographic infrared regions of the spectrum have been heretofore unusable for determining vibrational constants for the reason that these levels have been thought to involve such high quantum numbers that the cubic terms in the vibrational energy expression, which are negligible in the infrared region, apparently become sizeable. This leads to difficulty since the experimentally determined energy levels yield equations which can be solved simultaneously with vibrational constants as unknowns; if cubic terms must be included, the number of unknowns becomes larger for this molecule than the number of available energy-level equations, thus precluding solution for the unknowns.

It has been my aim in the present study to examine several selected regions of the acetylene spectrum in which one could expect to find transitions involving levels which had not previously been

observed. In particular, analysis has been made of regions of the spectrum in which discrepancies were apparent (3) between observed and calculated vibrational transitions. It is gratifying that in each case considered in the present study, agreement has been obtained between the observed and calculated positions of all the energy levels involved. In one case (4) the assignment of a Q-branch by a previous investigator was a simple error; the transition was thought to have lower state $0000^0_1^1$ but in fact has lower state $0001^1_0^0$. In the three micron region it was found (5) that the inclusion of the effect of vibrational ℓ -type resonance (6), previously neglected by investigators of this region, brings about good numerical agreement of the vibrational levels involved in transitions there. Two bands at about five microns have also been reassigned on this basis. It should be emphasized that the discrepancies in the acetylene spectrum which are reconciled here were not completely ignored by previous workers; it is just that they were unable to treat the problems quantitatively because of their lack of information about certain vibrational levels. The necessary information on levels of interest has been obtained by the analysis of overlapping bands in the 3 and 13.7 micron regions. In the case of the 13.7 micron bands, analysis was made of what apparently is better data than previously obtained for this region of the acetylene spectrum. In the case of the 3 micron region, however, since very recent investigations of this region have been made (2) at the National Bureau of Standards with resolution at least as good as that obtained here, the success in analyzing the spectra

must be attributed to the development and use of the diagram techniques discussed in Chapter V.

In both the 3 and 13.7 micron regions primary interest was in obtaining information about the vibrational constants which are involved in the energy expression when both degenerate modes of the molecule are excited. Previously it had been observed that the only numerical values obtainable for these constants led to inconsistencies (3). The history of the investigation of these constants is very curious. Since 1955, due to Keller's work (7), the diagonal terms of the Hamiltonian for levels involving only the two degenerate modes have been expressed by Eq. (1) below:

$$G_0(v) = \omega_4^0 v_4 + \omega_5^0 v_5 + x_{44} v_4^2 + x_{45} v_4 v_5 + x_{55} v_5^2 + g_{44} l_4^2 + g_{45} l_4 l_5 + g_{55} l_5^2. \quad (1)$$

Previous to Keller's work it was thought, for theoretical reasons, that the constant g_{45} above must be zero (8). His experimental work indicated that the observed energy levels -- that is, energy levels determined directly from observed transitions -- could not be mathematically reproduced without the inclusion of a non-zero g_{45} . Subsequent theoretical reconsiderations showed that g_{45} was, indeed, non-zero. Information about non-zero off-diagonal terms arising from the theoretical reconsiderations of the acetylene molecule has also proved important. Eq. (2) below is an expression for an important Fermi

resonance, important because for several pairs of levels, like 0010^{00} and 0101^{11} , the interaction term is larger than the separation of the unperturbed levels, so that a substantial mixing of the wave functions occurs:

$$\begin{aligned} & (v_1; v_2; v_3; v_4, \ell_4; v_5, \ell_5 | H | v_1; v_2 - 1; v_3 + 1; v_4 - 1, \ell_4 \mp 1; \\ & v_5 - 1, \ell_5 \pm 1) = (-\sqrt{8}) [v_2(v_3 + 1)(v_4 \pm \ell_4)(v_5 \mp \ell_5)]^{1/2} \end{aligned} \quad (2)$$

Eq. (3) is an expression for the terms resulting in what has been called "vibrational ℓ -type resonance" and "vibrational ℓ -type doubling."

Physically, this expression reflects the fact that there are terms which are diagonal in the total vibrational angular momentum, but non-diagonal in the vibrational angular momenta of the individual degenerate modes.

In Eqs. (1-3) the usual notation for vibrational states has been employed; v_i refers to the principal vibrational quantum number of the i -th normal mode of vibration, $i = 1, 2, 3, 4, 5$; ℓ_i refers to the vibrational angular momentum introduced about the figure axis by the i -th transverse mode, $i = 4, 5$. States are designated by the notation $v_1 v_2 v_3 v_4^{\ell_4} v_5^{\ell_5}$, so that 0101^{11} is the state in which $v_1 = 0$, $v_2 = 1$, $v_3 = 0$, $v_4 = 1$, $\ell_4 = 1$, $v_5 = 1$, and $\ell_5 = 1$. It is sometimes desirable to distinguish between such states by the total ℓ -value; hence $0101^{\pm 1 \mp 1}$ is a sigma-state, having a total vibrational angular momentum equal to zero, while $0101^{\pm 1 \pm 1}$ is a delta-state, having a total vibrational angular momentum of magnitude 2 (units are $\hbar$).

$$(v_4, \ell_4; v_5, \ell_5 | H_2^* | v_4, \ell_4 \pm 2; v_5, \ell_5 \mp 2) =$$

(3)

$$1/4 r_{45} [(v_4 \pm \ell_4 + 2)(v_4 \mp \ell_4)(v_5 \mp \ell_5 + 2)(v_5 \pm \ell_5)]^{1/2}$$

The present work concerns itself in part with the evaluation of the constants appearing in Eqs. (1-3). It is the first such attempt known to the author to include the effect of the terms represented by Eq. (3). The inclusion of this effect has led to strikingly different values for the constants x_{45} and g_{45} of Eq. (1) and is discussed in detail in Chapter III.

CHAPTER II

ANALYSIS OF THE BANDS AT 13.7 MICRONS

High resolution infrared spectroscopists have studied many of the vibration rotation bands of the acetylene molecule, and recently Plyler, Tidwell, and Wiggins (3) described an attempt to correlate all the available data for determining a set of vibrational constants for this molecule. In this attempt, these authors encountered some difficulties. In particular, their vibrational constants do not predict the reported (7) measurement for the $0000^0_2^2$ state of $^{12}\text{C}_2\text{H}_2$ any closer than 2 cm^{-1} . Therefore, it seemed that measurement and analysis of the absorption bands of acetylene observed at 13.7μ might provide answers to some of the questions raised by Plyler, Tidwell, and Wiggins, because in this spectral region it is possible to observe not only the ν_5 fundamental vibration rotation band of this molecule (transition $0000^0_1^1 \leftarrow 0000^0_0^0$) but also several "difference" bands including the $2\nu_5^2 - \nu_5$ band (transition $0000^0_2^2 \leftarrow 0000^0_1^1$). In fact, the observed rotational structure has been assigned to five bands of $^{12}\text{C}_2\text{H}_2$ and one (ν_5 fundamental) of $^{12,13}\text{C}^{13}\text{CH}_2$.

EXPERIMENTAL DETAILS

The observational data were obtained by employing a vacuum infrared grating spectrograph. Figs. (1-3) show a tracing of the observed spectrum along with the analysis, and Tables 1, 2, and 3 give vacuum wave numbers (cm^{-1}) of the rotational lines measured for the different bands observed. It may be noted that the previous assignment (7) for the $2\nu_5^2 - \nu_5^1$ band has been revised and it has been shown to be the $(\nu_4 + \nu_5)^2 - \nu_4^1$ band. A different set of rotational lines has been identified as belonging to the $2\nu_5^2 - \nu_5^1$ band.

The data shown in Figs. (1-3) were taken with the Pfund-type spectrograph in our laboratory. The absorption pathlength was two meters; the pressure of the gas was one centimeter of mercury; the detector employed was a thermocouple. Some unassigned rotational lines are present, particularly around 725 cm^{-1} . The line at 711 cm^{-1} indicated by an arrow is probably the Q-branch of a transition having the lower state 0002^0_0 or 0002^2_0 ; its assignment remains uncertain.

MOLECULAR CONSTANTS OF ACETYLENE DERIVED FROM THE PRESENT STUDY

Band Centers and Rotational Constants:

Standard techniques (1) have been employed in determining the band centers and rotational constants from the observational data presented in Tables 1 - 3, and the values are summarized in Table 4.

A few comments are of interest regarding the distortion constants of some of the levels of acetylene involved here. Coburn, Rao, and Nielsen (9) have already reported the anomalous nature of the distortion constants evaluated from the observational data pertaining

Figure 1

**Vibration Rotation Bands of Acetylene
at 13.7 Microns**

Figure 2

**Vibration Rotation Bands of Acetylene
at 13.7 Microns**

Figure 3

**Vibration Rotation Bands of Acetylene
at 13.7 Microns**

740

750

760

cm⁻¹

TABLE 1

VACUUM WAVE NUMBERS (cm^{-1}) OF THE ROTATIONAL
LINES OF ACETYLENE

ν_5 fundamental of $^{12}\text{C}_2\text{H}_2$					
J	R(J)	P(J)	J	R(J)	P(J)
0			24	787.71	672.67
1	733.86		25	790.07	670.32
2	736.26	724.45	26	792.40	668.00
3	738.60	722.10	27	794.69	665.58
4	740.93	719.78	28	797.01	663.24
5	743.27	717.38	29	799.37	660.93
6	745.52	715.03	30	801.65	658.58
7	747.91	712.68	31	803.99	646.21
8	750.28	710.32	32	806.29	653.84
9	752.66	707.95	33	808.62	651.50
10	755.05	705.61	34	810.91	649.20
11	757.33	703.24	35	813.23	646.83
12	759.70	700.88	36	815.57	644.48
13	762.02	698.53	37	817.86	642.14
14	764.34	696.17	38	820.15	639.78
15	766.72	693.72	39	822.44	637.47
16	769.06	691.46	40	824.75	635.13
17	771.41	689.10	41	827.02	632.76
18	773.74	686.75	42	829.17	630.47
19	776.07	684.44	43	831.65	628.10
20	778.42	682.10	44	833.91	625.74
21	780.77	679.73	45	836.21	623.45
22	783.07	677.35	46	838.47	
23	785.39	675.01			

TABLE 2

VACUUM WAVE NUMBERS (cm^{-1}) OF THE ROTATIONAL
LINES OF ACETYLENE

ν_5 fundamental of $^{12}\text{C}^{13}\text{CH}_2$					
J	R(J)	P(J)	J	R(J)	P(J)
0			14	762.60	696.17
1			15	764.95	693.90
2	735.13	723.57	16	767.13	
3	737.46	721.34	17	769.50	
4	739.71	719.00	18		687.28
5	741.99	716.77	19		684.94
6	744.28	714.53	20		682.74
7	746.45	712.18	21		680.41
8	748.85	709.98	22		678.24
9	751.25	707.52	23		676.00
10	753.20	705.21	24		673.78
11		702.89	25		670.55
12		700.64	26		668.29
13		698.39			

TABLE 3

DIFFERENCE BANDS OF $^{12}\text{C}_2\text{H}_2$ AT 13.7μ

J	$2\nu_5^0 - \nu_5$		$2\nu_5^2 - \nu_5$		$(\nu_4 + \nu_5)^0 - \nu_4$		$(\nu_4 + \nu_5)^2 - \nu_4$	
	$\Sigma - \Pi$		$\Delta - \Pi$		$\Sigma - \Pi$		$\Delta - \Pi$	
	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)
0								
1	724.70	717.60	733.61		721.06	714.04		
2	727.09	715.34	735.88		723.57	711.72		
3		712.88	738.24	721.77	726.00	709.39		725.02
4		710.57	740.57	719.43		707.04		
5	734.31	708.24	742.93	716.97		704.76	745.85	
6	736.72	705.98	745.39	714.67		702.45	748.27	
7	739.12	703.72	747.66	712.18	735.56	700.14	750.68	715.20
8	741.55	701.40	750.05	709.88	738.00	697.92	753.14	712.82
9	743.99	699.09	752.33	707.52	740.57	695.60	755.65	710.45
10	746.45	696.86	754.68	705.21	742.93	693.27	758.06	
11	748.85	694.63	757.03	702.74		691.03	760.56	

TABLE 3 (Continued)

J	$2\nu_5^0 - \nu_5$		$2\nu_5^2 - \nu_5$		$(\nu_4 + \nu_5)^0 - \nu_4$		$(\nu_4 + \nu_5)^2 - \nu_4$	
	$\Sigma - \Pi$		$\Delta - \Pi$		$\Sigma - \Pi$		$\Delta - \Pi$	
	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)
12	751.25	692.33	759.44	700.47		688.78	763.30	703.72
13	753.54	689.98	761.76	697.92		686.59	765.55	701.52
14	756.20	687.80	764.08	695.60		684.38	768.10	699.29
15	758.67	685.53	766.38	693.23		682.18	770.65	697.06
16	761.12	683.29	768.79	691.03	757.70	679.98		694.89
17	763.60	681.10	771.02	688.60	760.05	677.69		692.70
18	766.05	678.86	773.41	686.26	762.60	675.50		690.39
19	768.51	676.67	775.85	684.14	764.95	673.32		688.19
20	771.02	674.39			767.54	671.14		
21	773.42	672.19			770.10	668.85		
22	775.85	669.94			772.59	666.70		
23		667.62			775.14	664.55		

TABLE 3 (Continued)

J	$2\nu_5^0 - \nu_5$ $\Sigma - \Pi$		$2\nu_5^2 - \nu_5$ $\Delta - \Pi$		$(\nu_4 + \nu_5)^0 - \nu_4$ $\Sigma - \Pi$		$(\nu_4 + \nu_5)^2 - \nu_4$ $\Delta - \Pi$	
	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)	R(J)	P(J)
24		665.40			777.66	662.27		
25		663.17			780.26	660.19		
26		660.96			782.75	657.97		
27	788.00	658.74			785.06	655.82		
28	790.51	656.51			787.56	653.60		
29	792.90	654.22						
30	795.30	652.00						
31	797.72	649.87						
32	800.12	647.51						
33	802.46	645.28						
34	804.86	643.00						
35	807.26							

TABLE 4

SOME OF THE BAND CENTERS AND ROTATIONAL CONSTANTS OF $^{12}\text{C}_2\text{H}_2$ (cm^{-1})

Assignment of band	$(v_1 v_2 v_3 v_4 \ell_{v_5} \ell)'$ - $(v_1 v_2 v_3 v_4 \ell_{v_5} \ell)''$	Species of states	Band center ^a	$B' - B''$
ν_5	$0000^0 1^1 \leftarrow 0000^0 0^0$	$\Pi_u \leftarrow \Sigma_g^+$	729.15	$- 0.00021_4^b$
$2\nu_5^0 - \nu_5$	$0000^0 2^0 \leftarrow 0000^0 1^1$	$\Sigma_g^+ \leftarrow \Pi_u$	720.00	$+ 0.004_3$
$2\nu_5^2 - \nu_5$	$0000^0 2^2 \leftarrow 0000^0 1^1$	$\Delta_g \leftarrow \Pi_u$	728.86	$- 0.001_3$
$(\nu_4 + \nu_5)^0 - \nu_4$	$0001^1 1^1 \leftarrow 0001^1 0^0$	$\Sigma_u^+ \leftarrow \Pi_g$	716.43	$+ 0.004_8$
$(\nu_4 + \nu_5)^2 - \nu_4$	$0001^1 1^1 \leftarrow 0001^1 0^0$	$\Delta_u \leftarrow \Pi_g$	731.23 ^c	$+ 0.008_5$

^a Band centers are believed to be accurate to $\pm 0.02 \text{ cm}^{-1}$. (For instance, the origin ν_5 of $^{12}\text{C}^{13}\text{CH}_2$ determined in the present work compares very well with the value derived in Reference 2.)

^b Although the P and R structure of the ν_5 band has been observed to $J = 45$, the $(D' - D'')$ value has been evaluated to be negligibly small within the accuracy of the present data.

^c The Q branch of this band was identified as belonging to the $2\nu_5^2 - \nu_5$ band in previous work (7).

TABLE 5

VIBRATIONAL LEVELS OF ACETYLENE (cm^{-1})

Energy Level	Observed	Obs.-Calc. I ^a	Obs.-Calc. II ^b
Present work:			
0000 ⁰ ₁ ¹	730.33	0.00	+ 0.05
0000 ⁰ ₂ ⁰	1449.15	0.00	- 0.11
0000 ⁰ ₂ ²	1462.72	0.00	- 0.10
Data from previous work (3,7):			
0000 ⁰ ₃ ¹	2170.31	+ 0.14	+ 0.08
0000 ⁰ ₄ ⁰	2880.55	+ 0.87	+ 0.11
0000 ⁰ ₄ ²	2894.07	+ 0.82	+ 0.06

^aEmploying the observed values for the three levels studied in the present work one obtains $\omega_5^0 = 729.24$, $x_{55} = -2.33$, $g_{55} = 3.42$. "Calculated I" refers to values obtained by using these constants.

^bCombining all the six levels given in this table one obtains $\omega_5^0 = 729.15$, $x_{55} = -2.26$, $g_{55} = 3.39$, and "Calculated II" refers to the values derived by using these constants. For comparison, Plyler et al. (3) give $\omega_5^0 = 729.11$, $x_{55} = -2.27$, $g_{55} = 3.45$.

to the $(\nu_4 + \nu_5)^0$ band of acetylene. Since that paper was written, a few revisions have been made in the formula for the combination relation $R(J-1) + P(J)$ as applied to bands like $(\nu_4 + \nu_5)$ and $2\nu_5$ for which the upper states are combinations of two perpendicular vibrations and are of species sigma. For such a case, Amat and Nielsen (10) have shown that

$$R(J-1) + P(J) = 2\nu_0 + 2(B' - B'')J^2 - \Delta_0 \left\{ \left[1 + \frac{16(q_i^0 + q_i^0)^2}{\Delta_0^2} J^2 (J^2 + 1) \right]^{1/2} - 1 \right\}, \quad (4)$$

where $q_{i,j}^0 = 1/4$ of the $q_{i,j}$ used by Herzberg (1). For the 00011 level

$$\Delta_0 = (\nu_4 + \nu_5)^2 - (\nu_4 + \nu_5)^0 = 2(g_{45} - 2B'') - r_{45}, \quad (5)$$

and for the 00002 level

$$\Delta_0 = 2\nu_5^2 - 2\nu_5^0 = 4(g_{55} - B''). \quad (6)$$

Using the values of the energy levels determined in the present chapter, it is possible to calculate Δ_0 for the 00011 and 00002 levels from Eqs. (5) and (6). These values for Δ_0 can be compared with the ones derived from Eq. (4), using $q_4^0 = 1.30 \times 10^{-3} \text{ cm}^{-1}$, $q_5^0 = 1.15 \times 10^{-3} \text{ cm}^{-1}$ given from theoretical considerations (11), the

measurement of the $(\nu_4 + \nu_5)^0$ band reported earlier, and the $2\nu_5^0 - \nu_5$ band measured in the present work. The results obtained are as follows: for the 00011 level, the value for Δ_0 derived from Eq. (5) is 14.7_8 cm^{-1} , as compared to the value $12.7 \pm 1 \text{ cm}^{-1}$ determined by employing Eq. (4); for the 00002 level the corresponding values are 8.8_4 cm^{-1} and $10.6 \pm 2 \text{ cm}^{-1}$, respectively.

Vibrational Constants ω_5^0 , x_{55} ,
and g_{55} of Acetylene:

The band centers given in Table 4 allow the calculation of some of the energy levels of this molecule, which in turn lead to the evaluation of the vibrational constants given in Eq. (1) in the preceding chapter. The results for the levels which involve the excitation of the ν_5 vibration only have been given in Table 5. In this table "Observed" refers to vibrational band origins, which are related to the band centers of Table 4 in the following manner:

$$\text{Vibrational band origin} = \text{Band center} + B'\ell'^2 - B''\ell''^2. \quad (7)$$

It is indeed true that inclusion of terms like $B\ell^2$ into the vibrational energy formula, as proposed in Herzberg's book (1) makes some matters simpler, however, the notation employed here were chosen to facilitate a comparison with the results published by Plyler (3,12) and by Keller (7). The two sets of calculations given in Table 5 show that slight differences in vibrational constants can lead to large differences in the calculated values of the energy levels. Table 5 shows that the levels

$0000^0_1^1$, $0000^0_2^0$, $0000^0_2^2$, $0000^0_3^1$, $0000^0_4^0$, and $0000^0_4^2$ can be fit to within a calculated-minus-observed disagreement of 0.1 cm^{-1} . This is to be considered very satisfactory in comparison with the observed agreement or lack thereof for other vibrational levels of this molecule. The 0.1 cm^{-1} disagreement is only a bit larger than the uncertainty in some of the energy levels; however, it is not attributable to experimental error; it seems more likely to arise from the presence of the neglected cubic terms, which are apt to be of the order of magnitude of the discrepancies, that is, 0.1 cm^{-1} . The measurement of the transition $(\nu_4 + \nu_5)^2 - \nu_4^1$ allowed us to determine the position of the level $0001^{\pm 1}_1^{\pm 1}$; this delta state had not been determined before, and the knowledge of its position proved invaluable in the calculation of the constants x_{45} and g_{45} . Since this calculation is not as straightforward as that considered above, because of effect of vibrational ℓ -type doubling, it is not considered here and is instead taken up in Chapter III.

ν_5 Band of $^{12}_{13}\text{C}^{13}\text{CH}_2$:

As indicated in Figs. (1-3) and Table 2, the ν_5 fundamental vibration rotation band of the isotopically-substituted molecule $^{12}_{13}\text{C}^{13}\text{CH}_2$ was identified and measured. Analysis of this band allowed us to locate its band center at 728.23 cm^{-1} . This value agrees excellently with the value of 728.233 cm^{-1} quoted by Lafferty (2), who determined it indirectly from difference bands, using an isotopically-enriched sample. In view of this agreement, and also because all the bands used in the present study have been observed in one spectral

region, it is believed that a consistent set of vibrational constants have been obtained for the acetylene molecule.

Ground-state Rotational Constants of $^{12}\text{C}_2\text{H}_2$:

The ground-state rotational constants of this molecule have been evaluated from the observational data for the fundamental. The results obtained are $B_{\text{ground state}} = 1.1766_6 \text{ cm}^{-1}$; $D_{\text{ground state}} = (1.8_1 \pm 0.2) \times 10^{-6} \text{ cm}^{-1}$. The accuracy with which these constants have been determined is limited by the blended nature of many of the rotational lines of the ν_5 band, and the fact that the spectral positions in this work were obtained by employing a grating constant rather than the more modern methods. The present investigation has been done mainly with the intent of identifying the rotational lines of acetylene bands observed at 13.7 microns.

Identification of a Band Pertaining to $^{12}\text{C}_2\text{H}_2$ at 2.5μ :

Combining the results obtained in the present study with the measurement reported for the $[(\nu_1 + \nu_4 + \nu_5)^0 - \nu_4]$ band (12), it has been possible to determine the level $(\nu_1 + \nu_4 + \nu_5)^2$. Based on this calculation, the Q branch reported (12) at 4077.2 cm^{-1} has been assigned to the transition $[(\nu_1 + \nu_4 + \nu_5)^2 - \nu_4]$.

INTENSITY ALTERNATION IN ACETYLENE BANDS

Although nothing unexpected or unusual has been noticed in the present data, it is believed that the spectrum shown in Figs. (1-3) provide a good illustration of the intensity alternation expected in

the rotational structure of the vibration rotation bands of the linear symmetric $\text{H}-^{12}\text{C}-^{12}\text{C}-\text{H}$ molecule resulting from the spin ($I = 1/2$) of the H nucleus. It may be noted that in the bands $\nu_5(\Pi_u - \Sigma_g^+)$ and $[(\nu_4 + \nu_5)^0 - \nu_4](\Sigma_u^+ - \Pi_g)$ lines with odd J are stronger, whereas in the band $2\nu_5^0 - \nu_5(\Sigma_g^+ - \Pi_u)$ the lines with even J are the more intense. The $2\nu_5^2 - \nu_5(\Delta_g - \Pi_u)$ and $[(\nu_4 + \nu_5)^2 - \nu_4](\Delta_u - \Pi_g)$ bands show no intensity alternation. Also, as expected, the ν_5 fundamental of $^{12}\text{C}^{13}\text{CH}_2$ shows no intensity alternation.

CHAPTER III

VIBRATIONAL ℓ -TYPE RESONANCE AND DOUBLING

As indicated in Chapter I, there exist terms in the vibrational energy expression for acetylene which are diagonal in the total vibrational angular momentum about the figure axis but are not diagonal in the individual vibrational angular momenta associated with the transverse degenerate modes ν_4 and ν_5 . Because of this, the portion of the Hamiltonian involving levels for which both transverse modes are excited is complicated by the presence of off-diagonal elements when the usual representation, labeling states by the quantum numbers ν_i and ℓ_i , is made. The theoretical aspects of this effect are discussed in Reference 6 by Amat and Nielsen; here only their results are used, as given in Eq. (3) in Chapter I and repeated below:

$$\begin{aligned}
 & (\nu_4, \ell_4; \nu_5, \ell_5; \dots | H_2' | \nu_4, \ell_4 \pm 2; \nu_5, \ell_5 \mp 2; \dots) \\
 & = 1/4 \text{ hcr}_{45} [(\nu_4 \pm \ell_4 + 2)(\nu_4 \mp \ell_4)(\nu_5 \mp \ell_5 + 2)(\nu_5 \pm \ell_5)]^{1/2}.
 \end{aligned} \tag{3}$$

When terms of the form given in the equation above are included in the Hamiltonian and the resulting matrix is then diagonalized, the energy levels obtained are different from those derived ignoring such

terms. When such a term occurs as the matrix element between two states which have different unperturbed energy levels E_1 and E_2 as their diagonal elements, the actual energy levels resulting from the presence of the perturbing off-diagonal element R are $(E_1 + E_2)/2 \pm \{[1/2(E_1 - E_2)]^2 + R^2\}^{1/2}$, as can be easily verified by the diagonalization of the 2X2 matrix involved; this effect is termed "vibrational ℓ -type resonance." When $E_1 = E_2$, the energy levels which result are $E \pm R$ and the effect is termed "vibrational ℓ -type doubling," where "doubling" signifies that the degeneracy of a level has been removed, creating two levels from one. Both the resonance and doubling effects are known in acetylene and are illustrated in Fig. 4. The cases shown are particularly simple in that no other resonances are involved and a maximum of two states are concerned; in the next chapter I shall deal with six states for which neither of these simplifications hold. Fig. 5 presents a somewhat complicated diagram showing the effects of both resonance and doubling within the 00031 states.

The energy level diagrams in Figs. 4 and 5 are most easily understood by reference to the matrices involved. These have been presented as Matrices I - VI. Matrices I, III, and V include both vibrational ℓ -type terms and rotational ℓ -type doubling terms (13); the rotational terms have been included because of the feasibility of inserting the numerical values for the B_v , D_v , q_1 , and all of the vibrational constants, and then numerically diagonalizing these matrices for values of J up to, say, 20 by computer. Discrepancies between these calculated values and the observed rotational line positions of the vibrational levels observed in transitions would be an excellent measure of

Matrix I

**Vibration Rotation Submatrix Pertaining
to the Levels 00011**

	$0001^{+1}1^{+1}$	$0001^{-1}1^{+1}$	$0001^{+1}1^{-1}$	$0001^{-1}1^{-1}$
$0001^{+1}1^{+1}$	$\begin{aligned} &\omega_4^0 + \omega_5^0 + X_{44} \\ &+ X_{45} + X_{55} \\ &+ g_{44} + g_{45} + g_{55} \\ &+ F(J) \end{aligned}$	$2q_4^0 J(J+1)$	$2q_5^0 J(J+1)$	0
$0001^{-1}1^{+1}$	$2q_4^0 J(J+1)$	$\begin{aligned} &\omega_4^0 + \omega_5^0 + X_{44} \\ &+ X_{45} + X_{55} \\ &+ g_{44} - g_{45} + g_{55} \\ &+ F(J) \end{aligned}$	r_{45}	$2q_5^0 J(J+1)$
$0001^{+1}1^{-1}$	$2q_5^0 J(J+1)$	r_{45}	$\begin{aligned} &\omega_4^0 + \omega_5^0 + X_{44} \\ &+ X_{45} + X_{55} \\ &+ g_{44} - g_{45} + g_{55} \\ &+ F(J) \end{aligned}$	$2q_4^0 J(J+1)$
$0001^{-1}1^{-1}$	0	$2q_5^0 J(J+1)$	$2q_4^0 J(J+1)$	$\begin{aligned} &\omega_4^0 + \omega_5^0 + X_{44} \\ &+ X_{45} + X_{55} \\ &+ g_{44} + g_{45} + g_{55} \\ &+ F(J) \end{aligned}$

MATRIX I

Matrix II

Vibration Submatrix Pertaining to 00011

	$0001^{+1}1^{+1}$	$0001^{-1}1^{+1}$	$0001^{+1}1^{-1}$	$0001^{-1}1^{-1}$
$0001^{+1}1^{+1}$	$E_{0001^{+1}}^{\Delta}$	0	0	0
$0001^{-1}1^{+1}$	0	$E_{0001^{+1}}^{\Sigma}$	r_{45}	0
$0001^{+1}1^{-1}$	0	r_{45}	$E_{0001^{+1}}^{\Sigma}$	0
$0001^{-1}1^{-1}$	0	0	0	$E_{0001^{+1}}^{\Delta}$

MATRIX II

Matrix III

**Vibration Rotation Submatrix Pertaining
to the Levels 00021**

$0002^{+2}1^{+1}$	$0002^{+2}1^{-1}$	0002^01^{+1}	0002^01^{-1}	$0002^{-2}1^{+1}$	$0002^{-2}1^{-1}$
$2\omega_4^0 + \omega_5^0 + 4X_{44}$ $+ 2X_{45} + X_{55}$ $+ 4g_{44} + 2g_{45} + g_{55}$ $+ F(J)$	$2q_5^0 J(J+1)$	$2\sqrt{2}q_4^0 J(J+1)$	0	0	0
$2q_5^0 J(J+1)$	$2\omega_4^0 + \omega_5^0 + 4X_{44}$ $+ 2X_{45} + X_{55}$ $+ 4g_{44} - 2g_{45} + g_{55}$ $+ F(J)$	$r_{45}\sqrt{2}$	$2\sqrt{2}q_4^0 J(J+1)$	0	0
$2\sqrt{2}q_4^0 J(J+1)$	$r_{45}\sqrt{2}$	$2\omega_4^0 + \omega_5^0 + 4X_{44}$ $+ 2X_{45} + X_{55}$ $+ g_{55}$ $+ F(J)$	$2q_5^0 J(J+1)$	$2\sqrt{2}q_4^0 J(J+1)$	0
0	$2\sqrt{2}q_4^0 J(J+1)$	$2q_5^0 J(J+1)$	$2\omega_4^0 + \omega_5^0 + 4X_{44}$ $+ 2X_{45} + X_{55}$ $+ g_{55}$ $+ F(J)$	$r_{45}\sqrt{2}$	$2\sqrt{2}q_4^0 J(J+1)$
0	0	$2\sqrt{2}q_4^0 J(J+1)$	$r_{45}\sqrt{2}$	$2\omega_4^0 + \omega_5^0 + 4X_{44}$ $+ 2X_{45} + X_{55}$ $+ 4g_{44} - 2g_{45} + g_{55}$ $+ F(J)$	$2q_5^0 J(J+1)$
0	0	0	$2\sqrt{2}q_4^0 J(J+1)$	$2q_5^0 J(J+1)$	$2\omega_4^0 + \omega_5^0 + 4X_{44}$ $+ 2X_{45} + X_{55}$ $+ 4g_{44} + 2g_{45} + g_{55}$ $+ F(J)$

MATRIX III

Matrix IV

Vibration Submatrix Pertaining to 00021

$0002^{+2}1^{+1}$	$0002^{+2}1^{-1}$	$0002^{0}1^{+1}$	$0002^{0}1^{-1}$	$0002^{-2}1^{+1}$	$0002^{-2}1^{-1}$
$E_{0002^2 1^1}^{\Phi}$	0	0	0	0	0
0	$E_{0002^2 1^1}^{\pi}$	$r_{45}\sqrt{2}$	0	0	0
0	$r_{45}\sqrt{2}$	$E_{0002^0 1^1}^{\pi}$	0	0	0
0	0	0	$E_{0002^0 1^1}^{\pi}$	$r_{45}\sqrt{2}$	0
0	0	0	$r_{45}\sqrt{2}$	$E_{0002^2 1^1}^{\pi}$	0
0	0	0	0	0	$E_{0002^2 1^1}^{\Phi}$

Matrix V

**Vibration Rotation Submatrix Pertaining
to the Levels 00031**

	$0003^{+3}1^{+1}$	$0003^{+3}1^{-1}$	$0003^{+1}1^{+1}$	$0003^{+1}1^{-1}$	$0003^{-1}1^{+1}$	$0003^{-1}1^{-1}$	$0003^{-3}1^{+1}$	$0003^{-3}1^{-1}$
$0003^{+3}1^{+1}$	$3\omega_4^0 + \omega_5^0 + 9X_{44} + 3X_{45} + X_{55} + 9g_{44} - 3g_{45} + g_{55} + F(J)$	$2q_5^0 J(J+1)$	$2\sqrt{3}q_4^0 [J(J+1) - 2J(J+1) - 6]^{1/2}$	0	0	0	0	0
$0003^{+3}1^{-1}$	$2q_5^0 J(J+1)$	$3\omega_4^0 + \omega_5^0 + 9X_{44} + 3X_{45} + X_{55} + 9g_{44} - 3g_{45} + g_{55} + F(J)$	$\sqrt{3}r_{45}$	$2\sqrt{3}q_4^0 [J(J+1) - 2J(J+1) - 6]^{1/2}$	0	0	0	0
$0003^{+1}1^{+1}$	$2\sqrt{3}q_4^0 [J(J+1) - 2J(J+1) - 6]^{1/2}$	$\sqrt{3}r_{45}$	$3\omega_4^0 + \omega_5^0 + 9X_{44} + 3X_{45} + X_{55} + g_{44} + g_{45} + g_{55} + F(J)$	$2q_5^0 J(J+1)$	$4q_4^0 J(J+1)$	0	0	0
$0003^{+1}1^{-1}$	0	$2\sqrt{3}q_4^0 [J(J+1) - 2J(J+1) - 6]^{1/2}$	$2q_5^0 J(J+1)$	$3\omega_4^0 + \omega_5^0 + 9X_{44} + 3X_{45} + X_{55} + g_{44} - g_{45} + g_{55} + F(J)$	$2r_{45}$	$4q_4^0 J(J+1)$	0	0
$0003^{-1}1^{+1}$	0	0	$4q_4^0 J(J+1)$	$2r_{45}$	$3\omega_4^0 + \omega_5^0 + 9X_{44} + 3X_{45} + X_{55} + g_{44} - g_{45} + g_{55} + F(J)$	$2q_5^0 J(J+1)$	$2\sqrt{3}q_4^0 [J(J+1) - 2J(J+1) - 6]^{1/2}$	0
$0003^{-1}1^{-1}$	0	0	0	$4q_4^0 J(J+1)$	$2q_5^0 J(J+1)$	$3\omega_4^0 + \omega_5^0 + 9X_{44} + 3X_{45} + X_{55} + g_{44} + g_{45} + g_{55} + F(J)$	$\sqrt{3}r_{45}$	$2\sqrt{3}q_4^0 [J(J+1) - 2J(J+1) - 6]^{1/2}$
$0003^{-3}1^{+1}$	0	0	0	0	$2\sqrt{3}q_4^0 [J(J+1) - 2J(J+1) - 6]^{1/2}$	$\sqrt{3}r_{45}$	$3\omega_4^0 + \omega_5^0 + 9X_{44} + 3X_{45} + X_{55} + 9g_{44} - 3g_{45} + g_{55} + F(J)$	$2q_5^0 J(J+1)$
$0003^{-3}1^{-1}$	0	0	0	0	0	$2\sqrt{3}q_4^0 [J(J+1) - 2J(J+1) - 6]^{1/2}$	$2q_5^0 J(J+1)$	$3\omega_4^0 + \omega_5^0 + 9X_{44} + 3X_{45} + X_{55} + 9g_{44} - 3g_{45} + g_{55} + F(J)$

MATRIX V

Matrix VI

Vibration Submatrix Pertaining to 00031

	$0003^{+3}1^{+1}$	$0003^{+3}1^{-1}$	$0003^{+1}1^{+1}$	$0003^{+1}1^{-1}$	$0003^{-1}1^{+1}$	$0003^{-1}1^{-1}$	$0003^{-3}1^{+1}$	$0003^{-3}1^{-1}$
$0003^{+3}1^{+1}$	$E_{0003^3 1^1}^{\Gamma}$	0	0	0	0	0	0	0
$0003^{+3}1^{-1}$	0	$E_{0003^3 1^1}^{\Delta}$	$\sqrt{3}r_{45}$	0	0	0	0	0
$0003^{+1}1^{+1}$	0	$\sqrt{3}r_{45}$	$E_{0003^1 1^1}^{\Delta}$	0	0	0	0	0
$0003^{+1}1^{-1}$	0	0	0	$E_{0003^1 1^1}^{\Sigma}$	$2r_{45}$	0	0	0
$0003^{-1}1^{+1}$	0	0	0	$2r_{45}$	$E_{0003^1 1^1}^{\Sigma}$	0	0	0
$0003^{-1}1^{-1}$	0	0	0	0	0	$E_{0003^1 1^1}^{\Delta}$	$\sqrt{3}r_{45}$	0
$0003^{-3}1^{+1}$	0	0	0	0	0	$\sqrt{3}r_{45}$	$E_{0003^3 1^1}^{\Delta}$	0
$0003^{-3}1^{-1}$	0	0	0	0	0	0	0	$E_{0003^3 1^1}^{\Gamma}$

MATRIX VI

Figure 4

The Energy Levels 00011 and 00021

Figure 5

The Energy Levels 00031

the uncertainty in the constants involved. This has not been done in the present work, partly because it would require the use of rotational constants obtained almost entirely from the works of other investigators, and primarily because the vibrational problem has been given greater emphasis. Matrices II, IV, and VI are vibrational submatrices of the Hamiltonian and do not include rotational terms. These three matrices, as is immediately evident, factor to a collection of 1X1 and 2X2 submatrices; hence, for each, the diagonalization is trivial. For the levels 00011 there is one 2X2; its diagonalization produces the doubling shown in Fig. 4. For the levels 00021, the pi-states involve a 2X2 which gives rise to the resonance shown in Fig. 4. The levels 00031 involve 2X2 submatrices both for the case in which $l_4 + l_5 = 0$ and where $l_4 + l_5 = \pm 2$; this gives rise to doubling of the sigma-state and resonance between the delta-states, as shown diagrammatically in Fig. 5.

By the diagonalization of these three matrices, algebraic relations for the actual perturbed vibrational energy levels have been obtained. The positions of these energy levels determined from the measurement of observed transitions have then been used to calculate the constants, diagonal and nondiagonal, involved.

Upon diagonalizing Matrix II we obtain a modification of Eq. (1):

$$G_0(v) = \omega_4^0 + \omega_5^0 + x_{44} + x_{45} + x_{55} + g_{44} - g_{45} + g_{55} \pm r_{45}, \quad (8)$$

where the plus sign refers to the Σ^+ state and the minus sign to the Σ^- state; and for the Δ state,

$$G_0(v) = \omega_4^0 + \omega_5^0 + x_{44} + x_{45} + x_{55} + g_{44} + g_{45} + g_{55}. \quad (9)$$

Chapter I discusses the measurement of both the $(\nu_4 + \nu_5)^0 - \nu_4$ and $(\nu_4 + \nu_5)^2 - \nu_4$ bands, and from the data given there one can arrive at the following two relations, using Eqs. (8-9), (units are cm^{-1}):

$$[(\nu_4 + \nu_5)^0 - \nu_4] - \nu_5 = x_{45} - g_{45} + r_{45} = -15.03, \quad (10)$$

$$[(\nu_4 + \nu_5)^2 - \nu_4] - \nu_5 = x_{45} + g_{45} = +4.47. \quad (11)$$

Another pair of useful levels for evaluating the constants x_{45} , g_{45} , and r_{45} are the states 0002^0_1 and 0002^2_1 . For these levels, the work of Amat and Nielsen (6) leads to the following expression^a for the vibrational term values:

$$\begin{aligned} \frac{\epsilon_v}{hc} = \frac{\epsilon_v^0}{hc} + 2\omega_t^0 + \omega_t^0 + 4x_{tt} + 2x_{tt} + x_{t,t} + 2x_{l_t l_t} - x_{l_t l_t} \\ + x_{l_t l_t} \pm \{(-2x_{l_t l_t} + x_{l_t l_t})^2 + 2r_{tt}\}^{1/2}. \end{aligned} \quad (12)$$

^aEquation (12) corrects the error in Reference 6 where the r_{tt} term was raised to only a single power.

In the notation of the present paper, Eq. (12) becomes

$$G_0(v) = 2\omega_4^0 + \omega_5^0 + 4x_{44} + 2x_{45} + x_{55} + 2g_{44} - g_{45} + g_{55} \quad (13)$$

$$\pm \{(-2g_{44} + g_{45})^2 + 2r_{45}^2\}^{1/2},$$

where the plus sign is taken for the $0002^0 1^1$ level, and the minus sign for $0002^2 1^1$. The above is, of course, simply the result obtained by the diagonalization of Matrix IV. Inserting into Eq. (13) the experimental data of Plyler et al., for the $2\nu_4^{0,2} + \nu_5$ bands^b and the value for the level $0002^2 0^0$ obtained from the work of Innes (14), it is deduced that

$$[(2\nu_4^0 + \nu_5)] - (2\nu_4^2) - (\nu_5) = 2x_{45} - 2g_{44} - g_{45} \quad (14)$$

$$+ \{(g_{45} - 2g_{44})^2 + 2r_{45}^2\}^{1/2} = -4.52,$$

$$[(2\nu_4^2 + \nu_5)] - (2\nu_4^2) - (\nu_5) = 2x_{45} - 2g_{44} - g_{45} \quad (15)$$

$$- \{(g_{45} - 2g_{44})^2 + 2r_{45}^2\}^{1/2} = -24.23.$$

^bThe $\pm$ signs in Eq. (12) are associated with the wrong levels in Reference 6; this may be verified by setting $r_{tt} = 0$ in Eq. (12) and noting that the expressions reduce to the correct form for the unperturbed energy levels given by the $\pm$ assignments following Eq. (13). With this consideration, Eq. (12) indicates that the assignment of these bands given by Plyler et al. must be reversed, and we have done so in Eqs. (14) and (15).

It is of interest to mention that the investigations by Innes deal with the electronic bands of the acetylene molecule. Figure 6 presents an energy level diagram wherein the levels of interest to the present paper are drawn. It is easy to see that the electronic transitions marked (i) and (ii) in the figure originate from the same upper electronic level and terminate in the levels $0002^2_0^0$ and the ground state $0000^0_0^0$.

The simultaneous solution of Eqs. (10), (11), (13), (14) and (15) yields the roots given below in Table 6:

TABLE 6

	Set A	Set B
g_{45}	7.92	6.35
x_{45}	- 3.45	- 1.88
r_{45}	- 3.66	- 6.80
g_{44}	- 0.22	2.13 (cm^{-1})

It was hoped that a choice between the two sets of roots given above could be made on the basis of an independent determination of the constant g_{44} . Such a determination is afforded by the observational data of Innes (14) on the levels $0002^2_0^0$, $0003^1_0^0$, and $0004^0_0^0$ and the level $0001^1_0^0$ known (1) from work in the infrared. The value obtained from Innes' levels, however, is $g_{44} = 1.36 \text{ cm}^{-1}$ and is about equally far from each of the roots in Table 6, offering no help in the choice between them. The reason that Innes' value does not agree better with the results given here is probably as follows: the levels $0001^1_0^0$, $0002^2_0^0$, $0003^1_0^0$, $0004^0_0^0$ appear to yield a set of four equations in

Figure 6

An Energy Level Diagram of $^{12}\text{C}_2\text{H}_2$

the three unknowns ω_4^0 , x_{44} , and g_{44} , but actually one of the equations involved is linearly dependent upon the others; hence, while all three constants can be calculated, and the fourth equation shows the self-consistency of the experimental data, there is no real check, algebraically speaking, on the value of g_{44} ; moreover, since the levels involved do not include a pair such as 0002^0_0 and 0002^2_0 or 0003^1_0 and 0003^3_0 , from which g_{44} can be determined directly, this calculation is, in fact, rather insensitive to the value of g_{44} , which is very much smaller than that of ω_4^0 . Therefore the disagreement of both of our values of g_{44} with that obtainable from Innes' work is not too disturbing.

An additional means of distinguishing between the true and extraneous roots in Table 6 was to be found, it had been hoped, in the levels 00031 presented in Fig. 5 and Matrix VI. The sigma-plus level of 0003^1_1 has been observed by others (3) and yields the following algebraic expression upon diagonalization of Matrix VI:

$$G_0(v) = 3\omega_4^0 + \omega_5^0 + 9x_{44} + 3x_{45} + x_{55} + g_{44} - g_{45} + g_{55} + 2r_{45}. \quad (16)$$

This leads to the relation (using constants in Table 6)

$$[(3v_4 + v_5)^0] - 3v_4 - v_5 = 3x_{45} - g_{45} + 2r_{45} = -25.59. \quad (17)$$

Inserting the observational data for the infrared bands $(3\nu_4 + \nu_5)^0$ and ν_5 along with the value for the level 0003^1_0 determined from the studies of the electronic bands, the left-hand side of Eq. (17) is evaluated as -25.50 which compares excellently with the value of -25.59 based on the constants x_{45} , g_{45} , and r_{45} . Unfortunately, this expression is linearly dependent upon the expressions in Eqs. (10-11) and therefore offers no way of choosing between the two sets of roots in Table 6; it is satisfied equally well by each. It does serve to demonstrate the self-consistency of our equations, however, illustrating that the theoretically-derived equations are completely compatible with the data. Many other levels have been reported for acetylene involving the vibrational modes ν_4 and ν_5 . All these have one of the combinations $\nu_4 + \nu_5$, $2\nu_4 + \nu_5$, or $3\nu_4 + \nu_5$ occurring in them and therefore do not provide us with any more information than that discussed above insofar as the effect of r_{45} term is concerned.

The next chapter shows, however, that the constants in Set A of Table 6 are much more likely to approximate the true values than are those in Set B. This conclusion is drawn from the consideration of several levels involved as the upper states of difference bands in the three micron region. Since the calculations involve resonating triads which exhibit combined Fermi and vibrational ℓ -type resonance, the effect is not simply that discussed in this chapter, and the details are presented in the next chapter, following the analysis of the bands involved.

CHAPTER IV

ANALYSIS OF THE BANDS AT THREE MICRONS

Acetylene bands occurring in the three micron region of the spectrum have been studied by a number of different investigators (1,2,3,6). In this region, one observes the bands ν_3 , $\nu_2 + \nu_4 + \nu_5$ and several overlapping "hot" bands (see Fig. 7), one of which was previously assigned (3) as $\nu_2 + 2\nu_4^0 + \nu_5 - \nu_4$. There are seven "hot" bands which are expected to be of detectable intensity at normal temperatures; they are given in Fig. 8. Since all are of the $\Pi - \Pi$ variety and are expected to exhibit resolvable rotational ℓ -type doubling, the spectrum is very complex. In the present work, it has been possible to analyze six bands of $^{12}\text{C}_2\text{H}_2$, including four "hot" bands, and two bands of $^{12}\text{C}^{13}\text{CH}_2$; the carbon-13 transitions were comparable in intensity to the $^{12}\text{C}_2\text{H}_2$ "hot" bands, although an unenriched sample of acetylene was used.

Fig. 7 shows a fast scan of the spectrum in the region around three microns, with the rotational assignments given for ν_3 and $\nu_2 + \nu_4 + \nu_5$. Slow scans with complete assignment of overlapping rotational structure are given in Appendix I.

Table 7 is a complete list of transitions observed at three microns.

Figure 7

The Spectrum at 3 Microns

C_2H_2 at 3μ

Figure 8

Transitions Expected at 3 Microns

$$U_1 + U_4^1 - U_5^1$$

$$\left. \begin{aligned} U_3 + U_4^1 - U_4^1 \\ U_2 + 2U_4^0 + U_5^1 - U_4^1 \\ U_2 + 2U_4^2 + U_5^1 - U_4^1 \end{aligned} \right\} \text{Group I}$$

$$\left. \begin{aligned} U_3 + U_5^1 - U_5^1 \\ U_2 + U_4^1 + 2U_5^0 - U_5^1 \\ U_2 + U_4^1 + 2U_5^2 - U_5^1 \end{aligned} \right\} \text{Group II}$$

TABLE 7

TRANSITIONS OBSERVED AT THREE MICRONS

UPPER STATE	LOWER STATE	BAND CENTER (cm^{-1})
$0010^0_0^0$	$0000^0_0^0$	3294.822
$0101^1_1^1$	$0000^0_0^0$	3281.894
$0011^1_0^0$	$0001^1_0^0$	3285.44
$0010^0_1^1$	$0000^0_1^1$	3269.55
$0102^2_1^1$	$0001^1_0^0$	3269.70
$0101^1_2^2$	$0000^0_1^1$	3286.39

TRANSITIONS FROM THE GROUND STATE

Bands of $^{12}\text{C}_2\text{H}_2$:

The bands ν_3 and $\nu_2 + \nu_4 + \nu_5$ have been most recently re-assigned by Lafferty and Thibault (2). A Fermi resonance given by Eq. (18) occurs between the upper states with the notable result that the intensities of the two bands are approximately the same; the band at the higher wave number is assigned as ν_3 .

Both of these bands have been measured up to approximately $J = 50$ in the present work. It has been observed, in agreement with the results in Reference (2), that the rotational energies of the upper states, 0010^0_0 and 0101^1_1 , cannot be expressed as $F'(J) = B'J(J+1) - D'J^2(J+1)^2$. An additional term or terms was required to fit the observed combination differences $R(J) - P(J)$ and $R(J-1) + P(J)$. On the other hand, the use of additional terms did not improve the rms deviation of the fit for the ground state combination difference $R(J-1) - P(J+1)$; this demonstrates that the need for additional terms arises from effects in the upper states and not from any possible errors in calculating the dispersion curve.

Lafferty found that the addition of an H' terms, resulting in the expression for P- and R-branch line positions given below in Eq. (17), gave a satisfactory fit of the observed data.

$$\begin{aligned} \nu(m) = & \nu_0 + (B' + B'')m + (B' - B'' - D' + D'')m^2 - (2D' + 2D'' - H')m^3 \\ & - (D' - D'' - 3H')m^4 + 3H''m^5 + H'm^6 \end{aligned} \quad (17)$$

The line positions (vacuum cm^{-1}) calculated in this way are given in Table 8, along with the observed values. Table 9 compares the constants determined with those obtained by Lafferty, using the same kind of fit. The extent of agreement is good; although the calculated uncertainties of the constants do not overlap, these uncertainties are not in any sense absolute in that only random, and not systematic errors are included in such calculations. In particular, there is a shift of about 0.03 cm^{-1} between Lafferty's data and ours over most of the region measured, as is reflected in our values for the band centers given in Table 9. To help clarify this matter, the bands were measured with both HCl and CO calibration; with each standard we obtained the same result for the band centers to within $\pm 0.002 \text{ cm}^{-1}$. A single-pen system was used to eliminate pen lag. The acetylene data were recorded interspersed with HCl or CO lines, which were recorded by changing the prism order. It is doubtful that this system would allow a band center error of 0.03 cm^{-1} .

While the expression in Eq. (17) fits our data with an rms deviation which approximates the experimental uncertainty of measurement, the data is not sufficient to conclude that such a dependence is involved. Firstly, the term $3H^*m^5$ is dominated at low J-values by the m^4 and lower order terms and at high J-values by the m^6 term, so that the data can be fitted to $\nu(m) = A + Bm + Cm^2 + Dm^3 + Em^4 + Gm^6$ about as well as they can to Eq. (17). Secondly, the addition of a seventh-order term did lower the standard deviation of fit slightly for our data. These two points indicate that functional dependence given by Eq. (17) is not justified by the data. In the absence of a theoret-

TABLE 8

ROTATIONAL ANALYSIS OF THE BANDS ν_3 AND $\nu_2 + \nu_4 + \nu_5$ (cm^{-1})

*denotes blend

J	ν_3				$\nu_2 + \nu_4 + \nu_5$			
	P(J)		R(J)		P(J)		R(J)	
	OBSERVED	O-C	OBSERVED	O-C	OBSERVED	O-C	OBSERVED	O-C
0			3297.16	- 0.01			3284.23	0.00
1	3292.49	+ 0.02	3299.51	+ 0.01	3279.55	+ 0.01	3286.56	- 0.01
2	3290.13	+ 0.02	3301.81	- 0.02	3277.20	+ 0.02	3288.91	+ 0.01
3	3287.74	0.00	3304.14	- 0.01	3274.81	0.00	3291.21	- 0.01
4	3285.40	+ 0.04	3306.48	+ 0.02	3272.43	0.00	3293.53	0.00
5	3282.99	+ 0.01	3308.75	- 0.01	3270.06	+ 0.01	3295.82	- 0.01
6	3280.59	+ 0.01	3311.07	+ 0.01	3267.67	+ 0.01	3298.13	+ 0.01
7	3278.19	+ 0.01	3313.34	0.00	3265.26	0.00	3300.40	- 0.01
8	3275.77	0.00	3315.62	+ 0.01	3262.84	- 0.01	3302.69	0.00
9	3273.34	- 0.01	3317.86	- 0.01	3260.43	0.00	3304.95	0.00

TABLE 8 (Continued)

J	ν_3				$\nu_2 + \nu_4 + \nu_5$			
	P(J)		R(J)		P(J)		R(J)	
	OBSERVED	O-C	OBSERVED	O-C	OBSERVED	O-C	OBSERVED	O-C
10	3270.90	- 0.02	3320.12	- 0.01	3258.00	0.00	3307.23	+ 0.02
11	3268.47	- 0.01	3322.39	+ 0.02	3255.58	+ 0.01	3309.45	- 0.01
12	3266.02	- 0.01	3324.60	0.00	3253.12	0.00	3311.71	+ 0.01
13	3263.56	0.00	3326.82	+ 0.01	3250.67	0.00	3313.92	0.00
14	3261.09	0.00	3329.03	+ 0.01	3248.20	- 0.01	3316.14	0.00
15	3258.60	- 0.00	3331.23	+ 0.02	3245.74	0.00	3318.35	0.00
16	3256.11	- 0.01	3333.43	+ 0.04*	3243.24	- 0.02	3320.55	+ 0.01
17	3253.61	0.00	3335.57	+ 0.01*	3240.77	0.00	3322.74	+ 0.01
18	3251.09	0.00	3337.69	- 0.02*	3238.29*	+ 0.02	3324.92	+ 0.02
19	3248.58	+ 0.02	3339.81	- 0.03*	3235.74*	- 0.01	3327.05	- 0.01
20	3246.04	+ 0.02	3341.97	+ 0.01	3233.25	+ 0.02	3329.20	- 0.01

TABLE 8 (Continued)

J	ν_3				$\nu_2 + \nu_4 + \nu_5$			
	P(J)		R(J)		P(J)		R(J)	
	OBSERVED	O-C	OBSERVED	O-C	OBSERVED	O-C	OBSERVED	O-C
21	3243.47	+ 0.01	3344.06	- 0.01	3230.70	0.00	3331.32	- 0.02
22	3240.88	- 0.01	3346.15	0.00	3228.16	0.00	3333.43	- 0.03*
23	3238.29*	- 0.02	3348.22	- 0.01	3225.60	0.00	3335.57	0.00*
24	3235.74*	+ 0.03	3350.26	- 0.02	3223.04	0.00	3337.69	+ 0.02*
25	3233.09	- 0.01	3352.30	- 0.01	3220.48	+ 0.02	3339.81	+ 0.06*
26	3230.47	0.00	3354.33	0.00	3217.87	0.00	3341.83	+ 0.01
27	3227.82	0.00	3356.31	- 0.02	3215.26	- 0.01	3343.88	+ 0.01
28	3225.16	0.00	3358.28	- 0.03	3212.66	0.00	3345.91	0.00
29	3222.48	0.00	3360.26	- 0.01	3210.04	+ 0.01	3347.93	0.00
30	3219.78	- 0.01	3362.21	0.00	3207.39	0.00	3349.93	- 0.01
31	3217.09	+ 0.01	3364.19	+ 0.06	3204.74	0.00	3351.94	+ 0.01

TABLE 8 (Continued)

J	ν_3				$\nu_2 + \nu_4 + \nu_5$			
	P(J)		R(J)		P(J)		R(J)	
	OBSERVED	O-C	OBSERVED	O-C	OBSERVED	O-C	OBSERVED	O-C
32	3214.36	0.00	3366.04	0.00	3202.08	0.00	3353.90	- 0.01
33	3211.61	0.00	3367.91	- 0.01	3199.40	0.00	3355.86	- 0.01
34	3208.84	- 0.02	3369.78	- 0.01	3196.68	- 0.03	3357.82	+ 0.01
35	3206.08	0.00	3371.65	+ 0.02	3194.00	0.00	3359.74	0.00
36	3203.35	+ 0.06	3373.47	+ 0.01	3191.29	0.00	3361.66	+ 0.01
37	3200.49	0.00	3375.29	+ 0.01	3188.56	0.00	3363.56	+ 0.01
38			3377.09	+ 0.02	3185.82	0.00	3365.43	0.00
39	3194.82	- 0.01	3378.87	+ 0.01	3183.07	+ 0.01	3367.29	0.00
40	3191.98	- 0.01	3380.63	+ 0.01	3180.28	- 0.01	3369.15	+ 0.01
41	3189.13	+ 0.01	3382.36	- 0.02	3177.52*	+ 0.01	3370.96	- 0.01
42	3186.24	- 0.01	3384.10	- 0.02	3174.71*	- 0.01	3372.84	+ 0.06

TABLE 8 (Continued)

J	ν_3				$\nu_2 + \nu_4 + \nu_5$			
	P(J)		R(J)		P(J)		R(J)	
	OBSERVED	O-C	OBSERVED	O-C	OBSERVED	O-C	OBSERVED	O-C
43	3183.34	- 0.02	3385.89	+ 0.03			3374.57	- 0.01
44			3387.54	- 0.04				
45	3177.52*	- 0.04	3389.24	- 0.07	3166.27	0.00	3378.11	- 0.02
46	3174.71*	+ 0.06						
47			3392.72	- 0.03			3381.65	+ 0.02
48			3394.47	0.00				
49			3396.18	- 0.03				
50			3398.00	+ 0.05				
51								
52			3401.49	0.00				

TABLE 9

CONSTANTS DERIVED FROM THE BANDS AT 3 MICRONS

	ν_3 $^{12}\text{C}_2\text{H}_2$		$\nu_2 + \nu_4 + \nu_5$ $^{12}\text{C}_2\text{H}_2$		ν_3 $^{12}\text{C}^{13}\text{CH}_2$	
	(Present Work)	(Lafferty)	(Present Work)	(Lafferty)	(Present Work)	(Lafferty)
ν_0	3294.822 ± 0.004	3294.853 ± 0.002	3281.894 ± 0.003	3281.919 ± 0.002	3284.1 ₈	3284.205 ± 0.001
$B'-B''$ $\times 10^3$	- 4.085 ± 0.020	- 4.305 ± 0.014	- 4.068 ± 0.016	- 4.182 ± 0.010	- 5.4 ₂	- 5.545 ± 0.005
$D'-D''$ $\times 10^6$	1.71 ± 0.02	1.42 ± 0.02	0.81 ± 0.02	0.70 ± 0.01		- 1.04 ± 0.04
$H' \times 10^{10}$	3.67 ± 0.06	2.69 ± 0.06	1.17 ± 0.06	0.86 ± 0.03		
	(Present Work)		(Lafferty and Thibault)			
B_0 weighted average	1.17655 $\pm$ 0.00008		1.17660 $\pm$ 0.00003			
D_0 weighted average $\times 10^6$	1.57 $\pm$ 0.07		1.564 $\pm$ 0.009			

ically derived expression for the higher-order rotational effects of the Fermi resonance between the two upper states in question, it seems premature to represent the data by an expression involving an H' term, even an H' (effective).

The data do clearly show that the effect present in the two bands under discussion can be approximated very well by $F'(J) = B'J(J+1) - D'J^2(J+1)^2 + kJ^6$. This is shown in Figs. 9 and 10.

Bands of $^{12}\text{C}^{13}\text{CH}_2$:

The bands ν_3 and $\nu_2 + \nu_4 + \nu_5$ of this molecule were observed, although an unenriched sample of acetylene was used. It was possible to measure ν_3 up to about $J = 20$ for both P- and R- branches, although the R-branch lines were more often blended. Constants derived from this band are given in Table 9. While our data for this species are less extensive than that which Lafferty obtained with an enriched sample, the determination of the band center in our work was sufficiently accurate to show the 0.03 cm^{-1} shift discussed above.

$\nu_2 + \nu_4 + \nu_5$ is weaker than ν_3 and could only be observed on the long wavelength side of the 3 micron bands, where it was not as badly overlapped. P(7) through P(34) of this band were observed. No band center is given for this band in Table 9 because of the extrapolation it would require from our data.

Figure 9

$\nu(m)$ versus m for $\nu_2 + \nu_4 + \nu_5$

$$\nu_2 + \nu_4 + \nu_5$$

$$\begin{aligned} \nu(M) = & \nu_0 + (B' + B'')M \\ & + (B' - B'' - D' + D'')M^2 \\ & - 2(D' + D'')M^3 + (D'' - D')M^4 \\ & \text{vs. } M \end{aligned}$$

Figure 10

$R(J-1) + P(J)$ versus J for ν_3

TRANSITIONS FROM OTHER LEVELS: "HOT" BANDS

Vibrational Analysis:

The two groups of resonating triads in Fig. 8 are of particular theoretical interest in that each should show both Fermi resonance of the form given in Eq. (18) (2).

$$\begin{aligned}
 (v_1; v_2; v_3; v_4, l_4; v_5, l_5 \parallel v_1; v_2 - 1; v_3 + 1; v_4 - 1, l_4 \mp 1; \\
 v_5 - 1, l_5 \pm 1) = (-\gamma/8) [v_2(v_3 + 1)(v_4 \pm l_4)(v_5 \mp l_5)]^{1/2}
 \end{aligned}
 \tag{18}$$

and vibrational l -type resonance of the form (6) given in Eq. (19)

$$\begin{aligned}
 (v_4, l_4; v_5, l_5 \parallel v_4, l_4 \pm 2; v_5, l_5 \mp 2) = \\
 1/4 r_{45} [(v_4 \pm l_4 + 2)(v_4 \mp l_4)(v_5 \pm l_5 + 2)(v_5 \mp l_5)]^{1/2}
 \end{aligned}
 \tag{19}$$

The resulting matrix for the energy levels in the first group in Fig. 8 is given in Fig. 11; the same matrix describes the energy levels in the second group in Fig. 8 if the levels 0102^0_1 , 0011^1_0 , 0102^2_1 are replaced by 0101^1_2 , 0010^0_1 , and 0101^1_2 , respectively. Here E_1 , E_2 , and E_3 are the unperturbed energy levels of the states designated by the quantum numbers given.

E_1 , E_2 , and E_3 are calculated numerically below by use of the most recently determined values of the vibrational constants involved (3,4,5); γ is known numerically from the work of Lafferty and

Figure 11

Submatrix Pertaining to Transitions at 3 Microns

0102⁰1¹

0011¹0⁰

0102⁰1¹

0102⁰1¹

0011¹0⁰

0102²1¹

E_1	$-\frac{1}{4}\gamma$	$\sqrt{2}r_{45}$
$-\frac{1}{4}\gamma$	E_2	$-\frac{1}{8}\gamma$
$\sqrt{2}r_{45}$	$-\frac{1}{8}\gamma$	E_3

Thibault (2), and r_{45} was obtained in our last paper of this series (15,16). These values allow us to numerically diagonalize the matrix in Fig. 11. Since earlier calculations (6) (see Chapter III) yielded two alternate sets of values for the constants g_{45} , x_{45} , and r_{45} , this numerical diagonalization was performed with the values of E_1 , E_3 , and r_{45} calculated from each set.

Set A	Set B
$g_{45} = 7.92$	$g_{45} = 6.35$
$x_{45} = -3.45$	$x_{45} = -1.88$
$r_{45} = -3.66$	$r_{45} = -6.80$
$g_{44} = -0.22$	$g_{44} = 2.13$

Using the values given above, together with values of energy levels determined directly from observed transitions (2,3,4,15) by means of the Ritz Combination Principle, the following is obtained (other constants from Ref. 3):

$$\begin{aligned}
 E_1 = 0102 \begin{smallmatrix} 0 & 1 \\ 1 & \end{smallmatrix} \text{ (unperturbed)} &= (\nu_2) + (2\nu_4^2) + (\nu_5) - 4g_{44} \\
 &+ 2x_{24} + 2x_{45} + x_{25} = 1973.99 + 1235.07 + 730.34 + 0.88 \\
 &- 25.40 - 6.90 - 1.38 = 3906.60 \qquad \text{Set A} \qquad (20)
 \end{aligned}$$

$$\begin{aligned}
 &= 1973.99 + 1235.07 + 730.34 - 8.52 - 25.40 - 3.76 - 1.38 \\
 &= 3900.34 \qquad \text{Set B} \qquad (21)
 \end{aligned}$$

$$\begin{aligned}
 E_2 &= 0011^1_0^0 \text{ (unperturbed)} = (v_{3 \text{ unperturbed}}) + (v_4) + x_{34} \\
 &= 3288.66 + 612.88 - 8.19 = 3893.35
 \end{aligned} \tag{22}$$

$$\begin{aligned}
 E_3 &= 0102^2_1^1 \text{ (unperturbed pi state)} = (v_2) + (2v_4^2) + (v_5) \\
 &\quad + 2x_{24} + 2x_{45} + x_{25} - 2g_{45} = 1973.99 + 1235.07 + 730.34 \\
 &\quad - 25.40 - 6.90 - 1.38 - 15.84 = 3888.88 \quad \text{Set A}
 \end{aligned} \tag{23}$$

$$\begin{aligned}
 &= 1973.99 + 1235.07 + 730.34 - 25.40 - 3.76 - 1.38 - 12.70 \\
 &= 3896.16 \quad \text{Set B}
 \end{aligned} \tag{24}$$

Therefore, for these levels, the matrix in Fig. 11 becomes

	$0102^0_1^1$	$0011^1_0^0$	$0102^2_1^1$	
$0102^0_1^1$	3906.60	6.46	- 5.18	
$0011^1_0^0$	6.46	3893.35	9.14	Set A
$0102^2_1^1$	- 5.18	9.14	3888.88	

and

	$0102^0_1^1$	$0011^1_0^0$	$0102^2_1^1$	
$0102^0_1^1$	3900.34	6.46	- 9.62	
$0011^1_0^0$	6.46	3893.35	9.14	Set B
$0102^2_1^1$	- 9.62	9.14	3896.16	

Upon diagonalization, these matrices yield the perturbed energy levels compared below with those determined from observed transitions by means of the Ritz Combination Principle:

Set A	Set B	"Observed"
3909.35	3908.15	-----
3900.17	3902.27	3898.32
3879.31	3879.43	3882.63

Set A is seen to yield slightly better agreement with the "observed" values. If the value of gamma is now changed from Lafferty's value of 25 cm^{-1} to 20 cm^{-1} , one obtains:

Set A	"Observed"	Set B
3908.73	-----	3908.12
3898.44	3898.32	3899.84
3881.66	3882.63	3881.89

A similar calculation is performed below for the other resonating triad:

$$\begin{aligned}
 E_1 &= 0101^1_2^0 \text{ (unperturbed)} = (\nu_2) + (\nu_4) + (2\nu_5^0) + x_{24} + 2x_{25} \\
 &\quad + 2x_{45} \\
 &= 1973.99 + 612.88 + 1449.15 - 12.70 - 2.76 - 6.90 = 4013.66 \\
 &\quad \text{Set A} \quad (25) \\
 &= 1973.99 + 612.88 + 1449.15 - 12.70 - 2.76 - 3.76 = 4016.80 \\
 &\quad \text{Set B} \quad (26)
 \end{aligned}$$

$$\begin{aligned}
 E_2 &= 0010^0 1^1 \text{ (unperturbed)} = (\nu_{3 \text{ unperturbed}}) + (\nu_5) + x_{35} \\
 &= 3288.66 + 730.34 - 8.68 = 4010.32 \quad (27)
 \end{aligned}$$

$$\begin{aligned}
 E_3 &= 0101^1 2^2 \text{ (unperturbed pi state)} = (\nu_2) + (\nu_4) + (2\nu_5^2) \\
 &\quad + x_{24} + 2x_{25} + 2x_{45} - 2g_{45} = 1973.99 + 612.88 + 1462.72 \\
 &\quad - 12.70 - 2.76 - 6.90 - 15.84 = 4011.39 \quad \text{Set A} \quad (28)
 \end{aligned}$$

$$\begin{aligned}
 &= 1973.99 + 612.88 + 1462.72 - 12.70 - 2.76 - 3.76 - 12.70 \\
 &= 4017.67 \quad \text{Set B} \quad (29)
 \end{aligned}$$

Therefore, for these levels, matrix I becomes:

	$0101^1 2^0$	$0010^0 1^1$	$0101^1 2^2$	
$0101^1 2^0$	4013.66	6.46	- 5.18	
$0010^0 1^1$	6.46	4010.32	9.14	Set A
$0101^1 2^2$	- 5.18	9.14	4011.39	

	$0101^1 2^0$	$0010^0 1^1$	$0101^1 2^2$	
$0101^1 2^0$	4016.80	6.46	- 9.62	
$0010^0 1^1$	6.46	4010.32	9.14	Set B
$0101^1 2^2$	- 9.62	9.14	4017.67	

Upon diagonalization these matrices yield the perturbed energy levels compared below with those determined from observed transitions from the Ritz Combination Principle:

Set A	Set B	"Observed"
4020.17	4043.91	-----
4017.72	4026.64	4016.71
3997.48	4004.24	3999.89

As with the triad involving $0011^1_0^0$, it is again seen that a better fit is obtained using the vibrational constants in Set A. When the value of gamma is again reduced from Lafferty's value of 25 cm^{-1} to 20 cm^{-1} , the results shown below are obtained:

Set A	"Observed"	Set B
4018.12	-----	4042.56
4017.26	4016.71	4026.71
3999.99	3999.89	4017.67

As can be seen from the above discussion, the vibrational constants listed in Set A give a very nice fit to those four levels determined from observed transitions when the Fermi resonance parameter gamma is taken as 20 cm^{-1} ; this allows a choice between the two sets of vibrational constants and a determination of which set is most nearly correct, it allows a determination of the gamma, and it allows the assignment of the upper states of the observed hot bands in the three micron region. It appears that the vibrational calculations here are somewhat more sensitive to the value of gamma than were Lafferty's calculations; because of this, the value derived here more nearly approximates the true value. The constants determined from the dis-

cussion above are listed below with observed and calculated vibrational levels:

State	Energy Level (cm^{-1})	"Observed"	O-C
$0101^1_2^2$	4017.26	4016.71	- 0.55
$0010^0_1^1$	3999.99	3999.89	+ 0.10
$0102^2_1^1$	3881.66	3882.63	- 0.97
$0011^1_0^0$	3898.44	3898.32	+ 0.12

$$x_{45} = - 3.45 \quad g_{45} = 7.92 \quad r_{45} = - 3.66 \quad g_{44} = - 0.22 \quad \gamma = 20$$

It would seem that the above agreement of calculated and observed values is reasonable in view of the uncertainty in the values of some of the anharmonic constants involved in the calculation. x_{34} and x_{35} are not known with great accuracy, and this leads to an uncertainty in the unperturbed values of E_2 ($0011^1_0^0$ and $0010^0_1^1$), hence to errors in the calculated perturbed values. Two questions seem to remain with regard to the above discussion, however. The first is the difference between the value of g_{44} and that of 1.36 cm^{-1} determined by Innes from the levels $0001^1_0^0$, $0002^2_0^0$, 0003^1_0 , and $0004^0_0^0$. With regard to this matter, it should be pointed out that Innes' four levels do not involve a pair such as $0002^0_0^0$ and $0002^2_0^0$ or $0004^0_0^0$ and $0004^2_0^0$ and are consequently relatively insensitive to the calculation of g_{44} ; moreover, the consistency of his values for these levels may be due in part to the fact that they provide a system of three equations in three unknowns

$(\omega_4^0, x_{44}, g_{44})$, and not four equations, since that for 0004^0_0 is linearly dependent upon those for 0001^1_0 and 0003^1_0 . For these reasons, the two values $g_{44} = -0.22$ and $+1.36 \text{ cm}^{-1}$ are perhaps equally inaccurate or equally accurate. The second point is that the transitions to the uppermost level of each resonating triad were not observed. For the triad involving 0011^1_0 this is quite understandable since the unperturbed energy level 0102^0_1 is quite a bit higher than the other two; the operator which diagonalizes these three levels shows clearly that the mixing of 0102^0_1 with 0011^1_0 is rather slight, so that the naturally strong intensity of $\nu_3 + \nu_4 - \nu_4$ is not expected to be shared with $\nu_2 + 2\nu_4^0 + \nu_5 - \nu_4$. On the other hand, the zero-order wave functions designated by 0101^1_2 , 0101^1_2 , and 0010^0_1 are all quite thoroughly mixed, owing to the extreme nearness of the unperturbed levels. Therefore, the fact that no band was observed which could be interpreted as $\nu_2 + \nu_4 + 2\nu_5^0 - \nu_5$ is puzzling.

Rotational Analysis:

Rotational assignments for the four $\Pi - \Pi$ transitions observed are given in Tables 10 through 13, along with the derived constants. Calculated values were determined by fitting fourth-order curves to the wave numbers of each subband as a function of m-number. This fit yields the parameters B and D. In addition, the ℓ -type splittings of each rotational line were fit to $\Delta\nu = (q' + q'')m + (q' - q'')m^2$, where q is the rotational ℓ -type doubling constant defined by Herzberg (1) and used by Plyler et al. (12). Some deviation of the ℓ -type splittings from the quadratic dependence given above seems to be in evidence,

TABLE 10

ROTATIONAL ANALYSIS OF THE BAND $\nu_3 + \nu_4 - \nu_4$

Q-branch at 3285.44 (All units cm^{-1})						
J	P(J) ^a	O-C ave.	R(J)	O-C	R(J)	O-C
1			3290.13	0.00		
2	3280.71	- 0.02			3292.49	0.00
3	3278.34	- 0.02	3294.79	+ 0.02		
4	3275.96	- 0.02			3297.16	+ 0.03
5	3273.60	+ 0.01	3299.39	+ 0.02		
6	3271.18	- 0.01			3301.71	- 0.03
7	3268.79	0.00	3303.94	+ 0.01		
8	3266.36	- 0.01	3306.17	- 0.03	3306.36	+ 0.04
9	3263.96	+ 0.02	3308.47	+ 0.02		
10	3261.50	- 0.01	3310.70	0.00	3310.88	+ 0.03
11	3259.08	+ 0.01	3312.92	- 0.01	3313.06	- 0.05
12	3256.62	+ 0.01	3315.15	0.00	3315.36	+ 0.01
13	3254.17	+ 0.02	3317.32	- 0.04	3317.59	0.00
14	3251.69	+ 0.01	3319.53	- 0.03	3319.80	- 0.01
15	3249.23	+ 0.03	3321.76	+ 0.01	3322.05	+ 0.03
16	3246.70	0.00	3323.93	+ 0.01	3324.23	+ 0.01
17	3244.22	+ 0.02	3326.08	0.00	3326.43	+ 0.02
18	3241.70	+ 0.01	3328.24	+ 0.01	3328.60	+ 0.01
19	3239.17	0.00	3330.36	0.00	3330.79	+ 0.04

TABLE 10 (Continued)

J	P(J)	O-C ave.	R(J)	O-C	R(J)	O-C
20	3236.63	0.00	3332.47	- 0.01	3332.91	0.00
21	3234.09	+ 0.01	3334.61	+ 0.02	335.03	- 0.01
22	3231.52	0.00	3336.72	+ 0.04	3337.18	+ 0.02
23	3228.95	+ 0.01	3338.73	- 0.02	3339.28	+ 0.01
24	3226.35	- 0.01	3340.85	+ 0.04	3341.33	- 0.03
25	3223.75	- 0.01	3342.85	- 0.01	3343.42	- 0.02
26	3221.10	- 0.04	3344.85	- 0.03	3345.49	- 0.01
27	3218.50	- 0.01	3346.85	- 0.04	3347.56	+ 0.02
28	3215.88	+ 0.01	3348.88	0.00	3349.56	0.00
29	3213.15	- 0.06	3350.84	- 0.01	3351.57	- 0.00
30	3210.50	- 0.04	3352.78	- 0.02	3353.56	0.00
31	3207.90	+ 0.05	3354.73	0.00	3355.52	0.00
32	3205.20	+ 0.07	3356.64	0.00	3357.47	0.00
33	3202.38	- 0.02	3358.57	+ 0.04	3359.38	- 0.01
34			3360.53	+ 0.13	3361.29	0.00
35						
36					3365.15	+ 0.13
37					3366.89	+ 0.04

CONSTANTS DERIVED: band center = 3285.455 ± 0.006

$$(B' - B'')_{\text{ave.}} = - 4.21 \times 10^{-3}$$

$$(D' - D'') = 0.96 \times 10^{-6}$$

$$q' = 5.55 \times 10^{-3} \quad q_4 = q'' = 5.14 \times 10^{-3}$$

^a ℓ -doublets unresolved

TABLE 11

ROTATIONAL ANALYSIS OF THE BAND $\nu_3 + \nu_5 - \nu_5$

Q-branch at 3269.55 (All units cm^{-1})								
J	P(J)	O-C	P(J)	O-C	R(J)	O-C	R(J)	O-C
1						3274.22	- 0.03 ^a	
2		3264.86	+ 0.02 ^a			3276.54	- 0.04	
3		3262.45	- 0.01				3278.86	- 0.01
4		3260.05	- 0.03		3281.24	- 0.02	3281.16	- 0.01
5		3257.69	0.00		3283.57	- 0.01	3283.44	- 0.02
6		3255.30	+ 0.01		3285.88	- 0.01	3285.73	- 0.01
7		3252.89	0.00		3288.24	+ 0.05	3287.99	- 0.02
8		3250.52	+ 0.05		3290.51	+ 0.03	3290.23	- 0.04
9		3248.09	+ 0.04		3292.79	+ 0.02	3292.49	- 0.03
10					3295.08	+ 0.04	3294.79	+ 0.03
11							3297.03	+ 0.04
12							3299.22	+ 0.01
13							3301.42	+ 0.01

TABLE 11 (Continued)

J	P(J)	O-C	P(J)	O-C	R(J)	O-C	R(J)	O-C
14	3235.92	+ 0.01					3303.64	+ 0.03
15	3233.45	- 0.01					3305.82	+ 0.02
16	3231.01	+ 0.01					3308.01	+ 0.03
17	3228.56	+ 0.03					3310.16	+ 0.01
18	3226.10	+ 0.05					3312.30	0.00
19	3223.54	- 0.03					3314.45	0.00
20	3221.10	+ 0.02					3316.57	- 0.02
21	3218.57	- 0.01	3217.93	+ 0.01			3318.68	- 0.03
22	3216.08	+ 0.01			3321.51	+ 0.02		
23	3213.55	0.00	3212.72	- 0.01	3323.63	+ 0.02		
24	3211.04	+ 0.02			3325.73	+ 0.01		
25	3208.48	0.00	3207.51	+ 0.01	3327.77	- 0.03		
26	3205.93	- 0.01	3204.86	- 0.01	3329.86	- 0.01		
27	3203.35	- 0.03	3202.23	+ 0.01	3331.90	- 0.02		
28	3200.81	0.00	3199.56	0.00	3333.96	0.00		

TABLE 11 (Continued)

J	P(J)	O-C	P(J)	O-C	R(J)	O-C	R(J)	O-C
29	3198.19	- 0.04	3196.86	- 0.03	3335.96	- 0.01		
30	3195.61	- 0.02	3194.20	- 0.01	3337.98	+ 0.02		
31	3193.01	- 0.02	3191.50	- 0.01				
32	3190.40	- 0.01	3188.78	- 0.01				
33	3187.77	- 0.01	3186.07	0.00				
34	3185.13	0.00	3183.34	+ 0.01				
35	3182.50	+ 0.03	3180.60	+ 0.03				
36	3179.82	+ 0.03						

CONSTANTS DERIVED: band center = 3269.560 ± 0.010

$$(B' - B'')_{\text{ave.}} = - 4.11 \times 10^{-3}$$

$$(D' - D'') = 0.88 \times 10^{-6}$$

$$q' = 6.00 \times 10^{-3} \quad q_5 = q'' = 4.60 \times 10^{-3}$$

^a *l*-doublets unresolved

TABLE 12

 ROTATIONAL ANALYSIS OF THE BAND $\nu_2 + 2\nu_4^2 + \nu_5^1 - \nu_4^1$

Q-branch at 3269.70 (All units cm^{-1})						
J	P(J)	O-C	P(J)	O-C	R(J) ^a	O-C ave.
1					3274.50	+ 0.07
2		3265.05	+ 0.03 ^a			
3		3262.65	0.00		3279.11	+ 0.03
4		3260.27	0.00		3281.49	+ 0.10
5		3257.88	0.00		3283.71	+ 0.02
6					3285.88	- 0.10
7					3288.24	- 0.02
8					3290.51	- 0.02
9					3292.78	- 0.01
10					3295.08	+ 0.03
11	3243.47	- 0.01			3297.29	0.00
12	3241.02	- 0.04			3299.51	0.00
13	3238.59	- 0.03	3238.24	- 0.08	3301.71	- 0.02
14	3236.18	0.00	3235.83	- 0.01	3303.94	0.00
15	3233.72	- 0.01	3233.28	- 0.06	3306.17	+ 0.04
16	3231.25	- 0.03	3230.81	- 0.03	3308.31	0.00
17	3228.81	0.00	3228.31	- 0.02	3310.49	+ 0.01

TABLE 12 (Continued)

J	P(J)	O-C	P(J)	O-C	R(J)	O-C ave.
18	3226.35	+ 0.01	3225.79	- 0.02	3312.59	- 0.04
19	3223.86	- 0.01	3223.28	0.00	3314.74	- 0.03
20	3221.40	+ 0.02	3220.73	- 0.01	3316.87	- 0.02
21	3218.87	- 0.01	3218.20	+ 0.01	3318.97	- 0.03
22	3216.38	0.00	3215.64	+ 0.01		
23	3213.88	+ 0.01	3213.05	- 0.01	3323.20	+ 0.02
24	3211.36	+ 0.01	3210.50	+ 0.02	3325.27	+ 0.02
25	3208.84	+ 0.02	3207.90	+ 0.01	3327.31	+ 0.01
26	3206.27	- 0.01	3205.30	+ 0.01		
27	3203.70	- 0.03	3202.70	+ 0.03		
28	3201.17	0.00	3200.07	+ 0.02		
29	3198.59	0.00	3197.43	+ 0.01		
30	3196.09	+ 0.08	3194.82	+ 0.05		
31	3193.47	+ 0.05	3292.11	0.00		
32	3190.80	- 0.01	3189.44	0.00		
33	3188.17	- 0.02	3186.76	0.00		
34	3185.54	- 0.02	3184.06	- 0.01		
35			3181.35	- 0.01		
36	3180.22	- 0.03	3178.62	- 0.02		
37			3175.90	0.00		
38			3173.15	- 0.01		

TABLE 12 (Continued)

CONSTANTS DERIVED: band center = 3269.74 ± 0.01

$$(B' - B'')_{\text{ave.}} = -4.34 \times 10^{-3}$$

$$(D' - D'') = 0.61 \times 10^{-6}$$

$$q' = 4.36 \times 10^{-3} \quad q_4 = q'' = 5.49 \times 10^{-3}$$

^a_l-doublets unresolved

TABLE 13

ROTATIONAL ANALYSIS OF THE BAND $\nu_2 + \nu_4^1 + 2\nu_5^2 - \nu_5^1$

Q-branch at 3286.39 (All units cm^{-1})								
J	P(J)	O-C	P(J)	O-C	R(J)	O-C	R(J)	O-C
1					3291.08	+ 0.04		
2					3293.40	+ 0.05		
3	3279.27	- 0.02						
4	3276.88	- 0.02						
5	3274.50	- 0.01						
6	3272.09	- 0.01			3302.56	+ 0.05		
7	3269.70	+ 0.01						
8	3267.25	- 0.01			3307.05	+ 0.03		
9	3264.86	+ 0.04			3309.28	+ 0.02	3309.61	+ 0.01
10	3262.37	0.00			3311.51	+ 0.03	3311.86	- 0.03
11	3259.90	- 0.01			3313.69	- 0.01	3314.15	- 0.01

TABLE 13 (Continued)

J	P(J)	O-C	P(J)	O-C	R(J)	O-C	R(J)	O-C
12	3257.42	- 0.01			3315.91	+ 0.01	3316.44	0.00
13	3254.93	- 0.02			3318.07	- 0.02	3318.68	- 0.02
14	3252.43	- 0.02			3320.25	- 0.02		
15					3322.39	- 0.04	3323.20	0.00
16	3247.39	- 0.03	3247.79	0.00	3324.60	+ 0.02	3325.45	+ 0.01
17	3244.87	- 0.02	3245.31	- 0.01			3327.66	- 0.01
18	3242.32	- 0.02	3242.84	- 0.01	3328.87	+ 0.02	3329.86	- 0.04
19	3239.74	- 0.04	3240.37	+ 0.01	3330.99	+ 0.03	3332.12	+ 0.01
20	3237.19	- 0.01	3237.86	- 0.01	3333.07	0.00	3334.33	+ 0.02
21	3234.62	0.00	3235.37	- 0.01	3335.14	0.00	3336.53	+ 0.02
22	3232.02	0.00	3232.86	- 0.01	3337.18	- 0.03	3338.73	+ 0.04

TABLE 13 (Continued)

J	P(J)	O-C	P(J)	O-C	R(J)	O-C	R(J)	O-C
23	3229.41	+ 0.01	3230.39	+ 0.03	3339.28	+ 0.01	3340.85	- 0.02
24	3226.80	+ 0.02			3341.33	+ 0.02		
25							3345.22	+ 0.04
26	3221.51	+ 0.03			3345.34	+ 0.01	3347.35	+ 0.02
27	3218.87	+ 0.06			3347.35	0.00	3349.46	0.00
28	3216.19	+ 0.07			3349.29	- 0.04	3351.57	- 0.01
29					3351.29	0.00	3353.67	- 0.02
30	3210.70	0.00			3353.20	- 0.03		
31					3355.16	0.00		
32	3205.20	- 0.02			3357.05	- 0.03		
33	3202.38	- 0.07			3359.00	+ 0.03		

TABLE 13 (Continued)

J	P(J)	O-C	P(J)	O-C	R(J)	O-C	R(J)	O-C
34					3360.84	0.00	3361.94	- 0.06
35								
36								
37								
38					3368.18	+ 0.03		

CONSTANTS DERIVED: band center = 3286.36 ± 0.01

$$(B' - B'')_{\text{ave.}} = - 4.38 \times 10^{-3}$$

$$(D' - D'') = 0.50 \times 10^{-6}$$

$$q' = 6.88 \times 10^{-3} \quad q_5 = q'' = 4.60 \times 10^{-3}$$

although Fig. 12 shows that the formula above is a good approximation; because of the apparent deviation at high J-values, however, the calculated values in Tables 10 - 13 do not involve the constraint imposed by the Δv formula.

Some blended lines are listed in the tables; these were not included in determining the constants. Lines for which no values are given in the tables were not observed, usually due to blending.

The values of q_5 determined agree extremely well with those of previous investigators (12). Those for q_4 are not quite as accurate, due primarily to the fact that our data resolved the doubling on only one branch for the two bands having lower state 00010; this leads to greater inaccuracy in the determination of q' and q'' for those bands than arises when doubling is measured in both branches.

Figure 12

**Graphical Determination of Rotational ℓ -type
Doubling Constants**

CHAPTER V

LOOMIS-WOOD DIAGRAMS FOR POLYATOMIC INFRARED SPECTRA

In Chapters II and IV the regions of the two active fundamentals, three and fourteen microns, were investigated. Both of the fundamentals are badly overlapped at normal temperatures, due to the presence of transitions from the low-lying vibrational states associated with the two bending modes. Since many of the upper states involved in these difference bands do not yield infrared-active transitions from the ground state, there is considerable interest in the analysis of these overlapping bands. It has been found that the diagram method originally described by Loomis and Wood (1,17) is very helpful in sorting out the overlapping bands.

In the spectra of linear molecules usually a series of evenly-spaced lines stand out clearly as belonging to the same band in an overlapped region. By forming first and second differences for the band and keeping the second difference constant, the expected positions of additional lines belonging to this band may be calculated. If the series of lines is indeed a band, then further lines will be found at each of the calculated positions, with a regular intensity pattern evident. These lines may then be numbered by assignment of an arbi-

trary running number m ; they form the abscissa axis of our diagram. For each line of the calculated band, differences are formed with all the neighboring spectral lines; these differences are plotted versus the running number m , as shown on the accompanying figures.

Fig. 13 is a diagram of the spectra at 13.7 microns. P and R branch lines of the ν_5 fundamental were used as running numbers since their intensity made this an easy choice. Differences between each line of ν_5 and its neighbors are plotted above or below the point on the abscissa representing that ν_5 line. The result is a series of smooth curves, each consisting of a single band. The curvature of the plots is due to the term $(B'_v - B''_v)J^2$, and is very noticeable for most of the bands in this figure. Band B does not exhibit such curvature, indicating that B' is very nearly equal to B'' for this band; the negative slope of this band shows that for it the term $(B'_v + B''_v)$ is much less than $B' + B''$ of the band (ν_5) used as abscissa -- and points out that band B is due to the isotopic species involving carbon-13. This was a surprising observation, since a natural, un-enriched sample of acetylene had been used. Fig. 13 shows more clearly the effect of $B' + B''$ and $B' - B''$ values than most similar diagrams do. This is because the band chosen as abscissa has B' very nearly equal to B'' and because the band centers of the overlapping bands are all near the band center of ν_5 . In general it is not quite so easy to pick out isotopic transitions, or to locate band centers -- which are at the apex of each parabolic curve in Fig. 13. Fig. 14 demonstrates this quite well.

Figure 13

**Loomis-Wood Diagram of the Spectrum at
13.7 Microns**

A ν_5 of ¹²C ¹³CH₂
 B ν_5
 C $2\nu_5^0 - \nu_5$

D $2\nu_5^2 - \nu_5$
 E $(\nu_4 + \nu_5)^0 - \nu_4$
 F $(\nu_4 + \nu_5)^2 - \nu_4$

Figure 14

Loomis-Wood Diagram of the Spectrum at 3 Microns

LOOMIS-WOOD DIAGRAM OF 3μ C_2H_2 SPECTRA

Fig. 14 shows a diagram involving approximately 700 lines measured in the three micron region. As in Fig. 13, the dots which do not fall on drawn curves generally correspond to spectral lines of very weak intensity which were not identified. In Fig. 14, m -values of the P and R branch lines of the strong combination band $\nu_2 + \nu_4 + \nu_5$ were used as running numbers. Since $B' \neq B''$ for this band, and since the band centers of the overlapping bands are not close together, the effect of $B' + B''$ and $B' - B''$ terms seen in Fig. 13 is not obvious here. Nevertheless, the bands do fall on smooth curves, and the main job of analysis can be done as well as in Fig. 13. The most striking feature of Fig. 14 is the presence of $\Pi - \Pi$ bands C, E, F and G. These transitions all exhibit resolved rotational ℓ -type doubling which manifests itself as discernible splitting on the P-branch side, R-branch side, or both. Band C has been discussed in the past by Plyler et al. (12); the others are previously unreported. Note that band G exhibits extremely large doubling in both P and R branches; this is due to the large difference $q' - q''$ between the rotational ℓ -type doubling constants of the upper and lower states.

It has been found that this diagram method has been helpful in analyzing overlapping bands of C_2D_2 and of CO_2 , in addition to those cases shown here. Moreover, it can also readily be used for analysis of parallel bands of symmetric top molecules; it was found, using data on ND_3 , that the K-subbands could be treated exactly as overlapping bands of a linear molecule. The present interest in "hot" bands of

symmetric tops and the problem of vibrational ℓ -type doubling in such molecules led to consideration of this; it appears that the diagram techniques discussed here might aid in the initial analysis of such spectra.

CHAPTER VI

BANDS IN THE VISIBLE AND PHOTOGRAPHIC INFRARED

The present chapter is concerned with the analysis of nine vibration rotation bands of $^{12}\text{C}_2\text{H}_2$ which occur in the visible and near infrared regions of the spectrum. All of these bands have been observed before; however, band centers and B-values have not been determined for them using modern techniques. Further, there has been a lack of knowledge of numerical values of the vibrational constants involved in the expressions for the upper states of the transitions considered here. Because of this, the assignment of two of these bands has been viewed as very uncertain (1).

The data presented in this chapter were obtained with a ten-meter spectrograph^a in a Czerny-Turner mounting. For all of the bands presented here, a path length of forty meters was used, with pressures from 100 mm. to 1 atm. Iron arc emission standards were used for calibration; a third-order dispersion curve was determined for each plate by means of a least-squares fit of the iron lines.

Because fewer lines are observable in vibration rotation bands of acetylene occurring in the photographic region than are encountered

^aThanks are due Dr. E. S. Fishburne for obtaining the spectra used in this study.

in the infrared bands, calculation of rotational constants B and D is not as accurate. If one has only fifteen or twenty lines, calculation of B and D by means of least-squares fits to combination differences is apt to be very unsatisfactory; and, in cases such as those encountered in the present work at 8640 and 6850 Å, where only three or four lines are measurable on the P-branch side, combination differences are completely useless. On the other hand, a fourth-order fit to $\nu(m)$, given by the first five terms of Eq. (17) uses every data point; its disadvantage, compared to the combination differences, is that it fits the data to five constants (ν_0 , B' , B'' , D' , D'') and not two or three, with a high uncertainty resulting for each constant. Because of this problem, a third method, described below, has been employed to determine rotational constants from the observational data.

With the single exception of the $\Pi - \Pi$ transition at 12618 cm^{-1} , all of the bands analyzed here are transitions from the ground state. The B_0 , D_0 values for the ground state are very well known (see Table 9 of Chapter IV). If the expression for $\nu(m)$ is rearranged as

$$\begin{aligned} \nu(m) - B''(m-m^2) - D''(-2m^3 + m^4) = \nu_0 + B'(m + m^2) \\ + D'(2m^3 + m^4), \end{aligned} \quad (30)$$

where the fact that $D \ll B$ for acetylene allows the terms Dm^2 to be dropped (compare with Eq. (17)), then the $B'' = B_0$ and $D'' = D_0$ terms can be calculated and the left side of Eq. (30) can be fitted to only three

unknowns. This has, in fact, been done with the data of this chapter.

A multiple regression procedure developed by Mr. J. Luce of our laboratory has been used to fit the data to the expression in Eq. (30). This program employs an iterative matrix inversion and double precision arithmetic and exceeds the accuracy of the usual least squares fits. With it the constants given in Table 15 were determined from the data tabulated in Table 14. The uncertainty listed with each band center, B, or D value is the standard deviation; Table 15 shows that a high level of accuracy and small confidence interval was obtained with relatively few data points.

Assignment of the bands at 11570.73 and 11586.43 cm^{-1} is discussed below. The upper states of these bands had been assigned by Funke (18) as 2a, 2, 2s and 1a, 3, 4s in the notation of his day, where the quantum numbers are $V_{\text{C-H}}$, $V_{\text{C-C}}$, and V_{bend} and the letters indicate asymmetric or symmetric. Herzberg (1), however, lists them as $[1212^0_0^0 ?]$ and $[1303^1_1^1 ?]$. The two notations refer to the same state in the first case, although Funke's is somewhat ambiguous; however, Funke's assignment of the latter state would be $0314^0_0^0$ in our notation. The data presented in this chapter agree perfectly with Herzberg's assignment.

The vibrational constants required for the calculations pursued here are known reasonably well from Reference 3 and the previous chapters. Conspicuous by its absence from lists in these two places is x_{22} . Since x_{22} is important in the photographic bands, it is calculated here. The calculation below uses the value of $(00100_{\text{unperturbed}})$

TABLE 14

LINE POSITIONS OF SOME PHOTOGRAPHIC BANDS

ROTATIONAL ANALYSIS OF THE BAND $5\nu_3$ (All units cm^{-1})				
J	P(J)	O-C	R(J)	O-C
0				
1				
2				
3	15592.89	0.00	15608.93	0.00
4	15590.36	- 0.01	15610.96	+ 0.01
5	15587.74	- 0.01	15612.92	+ 0.02
6	15585.06	0.00	15614.80	+ 0.01
7	15582.32	+ 0.01		
8	15579.54	+ 0.04	15618.35	- 0.02
9	15576.64	+ 0.02	15620.05	- 0.01
10	15573.67	0.00	15621.64	- 0.04
11	15570.70	+ 0.04	15623.23	- 0.01
12	15567.58	0.00	15624.73	0.00
13	15564.44	+ 0.01	15626.16	+ 0.01
14	15561.23	+ 0.01	15627.51	0.00
15	15557.97	+ 0.02	15628.80	- 0.01
16			15630.02	- 0.01
17			15631.17	- 0.02

TABLE 14 (Continued)

ROTATIONAL ANALYSIS OF THE BAND $5\nu_3$ (All units cm^{-1})				
J	P(J)	O-C	R(J)	O-C
18	15547.73	- 0.01		
19	15544.21	+ 0.01		
20			15634.28	0.00
21	15537.00	+ 0.06		
22				
23	15529.44	+ 0.02	15636.75	- 0.02
24				
25			15638.10	- 0.01

ROTATIONAL ANALYSIS OF THE BAND $\nu_1 + 3\nu_2 + 3\nu_4^1 + \nu_5^1$ (All units cm^{-1})				
J	P(J)	O-C	R(J)	O-C
0				
1			11591.00	- 0.03
2				
3	11579.32	+ 0.05	11595.49	0.00
4			11597.69	+ 0.02
5	11574.37	+ 0.05	11599.85	+ 0.04
6			11601.90	- 0.01

TABLE 14 (Continued)

ROTATIONAL ANALYSIS OF THE BAND $\nu_1 + 3\nu_2 + 3\nu_4^1 + \nu_5^1$ (All units cm^{-1})				
J	P(J)	O-C	R(J)	O-C
7	11569.07	- 0.15	11603.96	- 0.01
8	11566.53	- 0.09	11605.99	0.00
9	11563.99	+ 0.01	11607.96	- 0.01
10			11609.91	+ 0.01
11	11558.56	- 0.01	11611.80	0.00
12				
13			11615.37	- 0.06
14				
15			11618.90	+ 0.04
16				
17			11622.07	0.00
18				
19			11624.99	- 0.03

TABLE 14 (Continued)

ROTATIONAL ANALYSIS OF THE BAND $2\nu_1 + \nu_2 + \nu_3$ (All units cm^{-1})				
J	P(J)	O-C	R(J)	O-C
0				
1			11787.48	+ 0.03
2				
3	11775.71	+ 0.02	11791.80	0.00
4	11773.12	- 0.05		
5	11770.63	0.00	11795.95	0.00
6	11768.02	0.00	11797.97	+ 0.02
7	11765.38	+ 0.01	11799.93	+ 0.03
8	11762.67	+ 0.02	11801.80	+ 0.01
9	11759.87	- 0.03	11803.65	0.00
10	11757.09	- 0.02	11805.36	- 0.08
11	11754.21	- 0.03	11807.21	+ 0.02
12	11751.36	+ 0.02	11808.94	+ 0.04
13	11748.35	- 0.04	11810.59	+ 0.05
14	11745.33	- 0.05	11812.18	+ 0.03
15	11742.30	- 0.04	11813.75	+ 0.04
16			11815.19	- 0.02
17			11816.69	+ 0.01
18				
19			11819.46	+ 0.01
20			11820.79	+ 0.02
21			11822.02	- 0.03

TABLE 14 (Continued)

ROTATIONAL ANALYSIS OF THE BAND $\nu_1 + 2\nu_2 + \nu_3 + 2\nu_4^0$ (All units cm^{-1})				
J	P(J)	O-C	R(J)	O-C
0				
1			11575.34	+ 0.03
2				
3			11579.69	- 0.02
4			11581.80	- 0.05
5	11558.56	+ 0.02	11583.92	- 0.03
6	11556.04	+ 0.07	11585.95	- 0.05
7			11587.90	- 0.09
8			11589.99	+ 0.04
9			11591.86	+ 0.01
10			11593.74	+ 0.02
11			11595.49	- 0.03
12			11597.31	+ 0.03
13			11599.01	+ 0.03
14				
15			11602.21	0.00
16				
17			11605.15	- 0.06
18				
19			11607.96	+ 0.01
20				
21			11610.44	+ 0.02

TABLE 14 (Continued)

ROTATIONAL ANALYSIS OF THE BAND $\nu_1 + \nu_2 + 3\nu_3$ (All units cm^{-1})				
J	P(J)	O-C	R(J)	O-C
0				
1	14614.75	- 0.06		
2	14612.40	0.00		
3	14610.00	+ 0.07		
4	14607.45	+ 0.05		
5	14604.81	- 0.01	14630.04	- 0.02
6	14602.14	- 0.03	14632.03	+ 0.01
7	14599.48	0.00	14633.90	- 0.01
8	14596.70	- 0.02	14635.76	0.00
9	14593.92	0.00	14637.57	+ 0.01
10	14591.06	0.00	14639.31	+ 0.01
11	14588.14	- 0.01	14641.01	+ 0.01
12	14585.20	0.00	14642.62	- 0.03
13	14582.20	+ 0.01	14644.26	0.00
14	14579.20	+ 0.05		
15	14576.04	- 0.02	14647.40	+ 0.04
16	14572.90	+ 0.03		
17	14569.78	+ 0.02	14650.34	+ 0.01
18				
19	14563.28	- 0.06	14653.19	+ 0.02

TABLE 14 (Continued)

ROTATIONAL ANALYSIS OF THE BAND $2\nu_2 + 3\nu_3 + 2\nu_4^0$
 (All units cm^{-1})

J	P(J)	O-C	R(J)	O-C
0				
1				
2				
3			14605.99	+ 0.03
4			14608.08	+ 0.03
5	14584.69	- 0.09	14610.00	- 0.08
6			14612.15	+ 0.08
7	14579.42	- 0.08	14614.01	+ 0.01
8	14576.84	+ 0.07	14615.96	+ 0.08
9	14574.00	0.00	14617.73	+ 0.02
10				
11	14568.29	- 0.02	14621.26	+ 0.03
12				
13			14624.58	+ 0.03
14			14626.04	- 0.10
15			14627.67	- 0.02
16			14629.10	- 0.10
17			14630.78	+ 0.12

TABLE 14 (Continued)

ROTATIONAL ANALYSIS OF THE BAND $\nu_2 + 3\nu_3$ (All units cm^{-1})				
J	P(J)	O-C	R(J)	O-C
0				
1			11604.69	+ 0.01
2			11606.88	- 0.02
3	11592.91	0.00	11609.07	0.00
4	11590.42	- 0.01	11611.20	+ 0.01
5	11587.90	+ 0.01	11613.26	- 0.02
6	11585.33	+ 0.02	11615.37	+ 0.05
7	11582.68	- 0.01	11617.29	- 0.03
8	11580.01	- 0.02	11619.29	+ 0.01
9	11577.33	0.00	11621.18	- 0.02
10	11574.59	0.00		
11	11571.83	+ 0.02		

perturbed at higher J-values

TABLE 15

ROTATION CONSTANTS DERIVED FROM THE PHOTOGRAPHIC BANDS

(All values are vac. cm^{-1} ; uncertainties are standard deviations)

UPPER STATE	LOWER STATE	BAND CENTER	B'	$D' \times 10^6$
1212 ⁰ ₀	00000	11570.729 $\pm$ 0.02	1.15533 $\pm$ 0.0002	6.4 $\pm$ 0.4
1303 ¹ ₁	00000	11586.431 $\pm$ 0.02	1.15922 $\pm$ 0.0003	7.9 $\pm$ 0.8
01300	00000	11600.110 $\pm$ 0.01	1.15375 $\pm$ 0.0006	5.2 $\pm$ 5.0
21100	00000	11782.894 $\pm$ 0.01	1.15125 $\pm$ 0.0001	4.5 $\pm$ 3.0
10310	00010	12618.520 $\pm$ 0.05	1.15055 $\pm$ 0.0011	6.9 $\pm$ 4.5
10300	00000	12675.691 $\pm$ 0.01	1.15132 $\pm$ 0.0001	1.0 $\pm$ 0.2
0232 ⁰ ₀	00000	14597.082 $\pm$ 0.04	1.14990 $\pm$ 0.0007	1.8 $\pm$ 2.1
11300	00000	14617.165 $\pm$ 0.01	1.14729 $\pm$ 0.0002	5.9 $\pm$ 0.4
00500	00000	15600.176 $\pm$ 0.008	1.14345 $\pm$ 0.00006	1.30 $\pm$ 0.10

from Reference 2 and the level 03100. This level was chosen since it appears to be free of resonance; unlike many of the upper levels of photographic bands, it cannot exhibit Darling-Dennison resonance, and the Fermi resonance with 0401^1_1 is apparently very weak, since no neighboring band is in evidence which could be assigned as 04011 .

$$01000 = \omega_2 + x_{22} = 1973.99 \quad (31)$$

$$\begin{aligned} 03000 &= 03100 - (00100_{\text{unperturbed}}) - 3x_{23} \\ &= 9151.70 - 3288.66 + 8.46 = 5871.30 \\ &= 3\omega_2 + 9x_{22} \end{aligned} \quad (32)$$

Eqs. (31) and (32) yield $\omega_2 = 1990.88$ and $x_{22} = -16.89 \text{ cm}^{-1}$. These values are considered superior to those presented elsewhere. With them, 1303^1_1 is calculated as

$$\begin{aligned} 1303^1_1 &= (0003^1_1) + (03000) + (10000) + 3x_{12} \\ &\quad + 3x_{14} + x_{15} + 3x_{25} + 9x_{24} \\ &= 2560.59 + 5871.30 + 3372.83 - 39.27 - 49.62 \\ &\quad - 10.85 - 4.14 - 114.30 = 11586.54 \text{ cm}^{-1}, \end{aligned} \quad (33)$$

compared to the value of 11586.43 observed.

Similarly,

$$\begin{aligned}
 1212^0_0^0 &= 11100 + 01000 + 0002^2_0^0 - 4g_{44} \\
 &\quad + x_{12} + x_{23} + 4x_{24} + 2x_{14} + 2x_{34} + 2x_{22} \\
 &= 8512.10 + 1973.99 + 1235.07 + 0.88 \\
 &\quad - 1309 - 2.82 - 50.80 - 33.08 - 16.44 \\
 &\quad - 33.78 = 11572.03 \text{ cm}^{-1},
 \end{aligned} \tag{34}$$

compared to 11570.73 cm^{-1} observed. Since the value of g_{44} used above is relatively uncertain (see Chapter IV), this agreement is quite satisfactory.

Comparison of calculated and observed values of $B' - B''$ for these bands is made below, using the data from Table 15 and the α 's from Reference 3:

Band	Obs. ($B' - B''$) $\times 10^3$	Calc. $\times 10^3$	O-C $\times 10^3$
$1212^0_0^0 - 00000$	21.27 ± 0.20	22.42	$- 1.15 \pm 0.20$
$1303^1_1^1 - 00000$	17.38 ± 0.30	17.58	$- 0.20 \pm 0.30$

The agreement is very good. The calculated value for $1303^1_1^1$ was obtained as $B' - B'' = \alpha_1 + 3\alpha_3 + (\alpha_{\text{effective}}) 0003^1_1^1$, where $\alpha_{\text{effective}} = B' - B_0$ for the band $0003^1_1^1$. This was done so that the rotational effects of the off-diagonal elements due to vibrational and

rotational ℓ -type effects and shown in Matrix V are completely included.

This is an important point, since the rotational ℓ -type doubling constants q_i in Matrix V make $(\alpha_{\text{effective}})^{0003^1 1^1}$ differ from $3\alpha_4 + \alpha_5$ by 2.04×10^{-3} , a large amount compared to the O-C differences above.

The $(B' - B'')$ values for the other six transitions studied are given below (cm^{-1}):

Transition	Obs. $(B' - B'') \times 10^3$	Calc. $\times 10^3$	O-C $\times 10^3$
01300 - 00000	22.85 ± 0.60	23.10	$- 0.25 \pm 0.60$
21100 - 00000	25.35 ± 0.10	25.54	$- 0.19 \pm 0.10$
10300 - 00000	25.38 ± 0.10	23.62	1.76 ± 0.10
02320 - 00000	26.70 ± 0.70	26.80	$- 0.10 \pm 0.70$
11300 - 00000	29.31 ± 0.20	29.92	$- 0.61 \pm 0.20$
00500 - 00000	33.15 ± 0.06	28.00	5.15 ± 0.06

Here the discrepancy observed for the B-value of the 00500 state is presumably due to the need for higher order terms caused by the large quantum number; that is, $B' = B_0 - \alpha_3 v_3 - \beta_3 v_3^2$. If this is the case, our data yield $\alpha_3 = 5.35 \times 10^{-3} \text{ cm}^{-1}$ and $\beta_3 = 0.25 \times 10^{-3} \text{ cm}^{-1}$ when combined with the values in Reference 3. This calculation does not yield very reliable values, however, and is given only to show the order of magnitude of the extra β -term required.

The discrepancy indicated by the O-C value for 10300 is worthy of note. This band is influenced by an extremely strong rotational perturbation described by Funke (17). The constants given above were de-

terminated by fitting the observed line positions up to $J = 26$ to the formula discussed in this chapter. At about $J = 26$ a crossing of states apparently takes place, with extra lines resulting; $J = 18$ of the 10300 level is split into two levels (R(17) and P(19) of 10300 - 00000 are doublets), indicating a crossing of states at that point also.

With the exception of these two bands, all of the observed B values agree extremely well with those calculated using the α_i given in Reference 3.

The agreement of observed and calculated B-values for the other states indicates that the linear expression for this inertial coefficient remains good for the vast majority of levels which occur as upper states of transitions in the photographic region. It suggests that future evaluation of the α_i constants can include measured B-values from the photographic bands without the necessary inclusion of non-linear terms in the expression used.

Most of the bands observable in the photographic region involve excitation of ν_3 to $v = 2$ or more and consequently require consideration of Darling-Dennison resonance as well as Fermi resonance of the form $(\nu_3 \parallel \nu_2 + \nu_4 + \nu_5)$. Because of this, the vibrational calculations are complicated to a degree which makes them undesirable at this time. The band centers presented in this work, however, should aid in such calculations in the near future, when more levels have been determined from observed transitions. Most important, the vibrational calculations included here for the purposes of identifying the transitions to 1212^0_0 and 1303^{11}_1 gave such good results that it appears unlikely that any

cubic vibrational terms need be included in the calculation of upper states for bands occurring throughout most of the photographic region; highly excited levels such as 00500 are probable exceptions.

The conclusion to be drawn from these observations is that it is not justifiable to use only data observed in the region beyond the photographic (3) in the determination of the best set of rotational and vibrational constants for $^{12}\text{C}_2\text{H}_2$. Data from the visible and near infrared apparently satisfy the linear approximation for B-values and the quadratic vibrational expression for band centers, as long as resonance terms are properly included. Since this appears to be so, the inclusion of such data in future summaries, such as that given in 1963 in Reference 3, is strongly recommended and should aid in the numerical evaluation of off-diagonal elements, such as the Darling-Dennison resonance parameter. Additional studies of photographic bands involving ν_1 and ν_3 need to be made before this analysis can be performed with sufficient accuracy to justify the labor involved. Measurement of 10200, 00400 and 40000 would help; this could be done, in principle, by observation of the transitions to these levels from the 00001 lower state.

APPENDIX

The acetylene absorption bands observed in the three micron region:

Band A	ν_3
Band B	$\nu_2 + \nu_4^1 + \nu_5^1$
Band C	$\nu_3 + \nu_4^1 - \nu_4^1$
Band D	$\nu_3 (^{12}\text{C}^{13}\text{CH}_2)$
Band E	$\nu_2 + 2\nu_4^2 + \nu_5^1 - \nu_4^1$
Band F	$\nu_3 + \nu_5^1 - \nu_5^1$
Band G	$\nu_2 + \nu_4^1 + 2\nu_5^2 - \nu_5^1$
Band H	$\nu_2 + \nu_4^1 + \nu_5^1 (^{12}\text{C}^{13}\text{CH}_2)$

The traces show the spectrum observed at different pressures.

REFERENCES

- 1 G. Herzberg, "Molecular Spectra and Molecular Structure, Vol. II," Van Nostrand, Princeton, New Jersey, 1945.
- 2 W. J. Lafferty and R. J. Thibault, J. Mol. Spectry. 14, 79 (1964).
- 3 E. K. Plyler, E. D. Tidwell, and T. A. Wiggins, J. Opt. Soc. Am. 53, 589 (1963).
- 4 J. F. Scott and K. Narahari Rao, J. Mol. Spectry. 16, 15 (1965).
- 5 J. F. Scott and K. Narahari Rao, J. Mol. Spectry. (in press).
- 6 G. Amat and H. H. Nielsen, J. Mol. Spectry. 2, 152 (1958).
- 7 F. L. Keller, Ph.D. dissertation, University of Tennessee, 1955.
- 8 W. H. Shaffer and A. H. Nielsen, J. Chem. Phys. 9, 847 (1941).
- 9 T. J. Coburn, K. Narahari Rao, and H. H. Nielsen, J. Chem. Phys. 25, 607 (1956).
- 10 G. Amat and H. H. Nielsen, J. Mol. Spectry. 2, 163 (1958).
- 11 H. H. Nielsen, G. Amat, and M. Goldsmith, J. Chem. Phys. 26, 1060 (1957).
- 12 T. A. Wiggins, E. K. Plyler, and E. D. Tidwell, J. Opt. Soc. Am. 51, 1219 (1961).
- 13 H. H. Nielsen and W. H. Shaffer, J. Chem. Phys. 11, 140 (1943).
- 14 K. K. Innes, J. Chem. Phys. 22, 863 (1954).
- 15 J. F. Scott and K. Narahari Rao, J. Mol. Spectry. 18, 152 (1965).
- 16 J. F. Scott and K. Narahari Rao, J. Mol. Spectry. 18, 451 (1965).
- 17 F. W. Loomis and R. W. Wood, Phys. Rev. 32, 223 (1928).
- 18 G. W. Funke, Zeits. f. Physik 104, 169 (1936).