THE INFLUENCE OF VIBRATION-ROTATION INTERACTION AND CUBIC ANHARMONICITY ON LINE INTENSITIES IN INFRARED VIBRATION-ROTATION BANDS OF LINEAR SYMMETRIC X-Y-X MOLECULES

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

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1957

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ACKNOWLEDGMENTS

The author wishes to acknowledge his indebtedness to Professors Wave E. Shaffer and Harald H. Nielsen for their assistance and encouragement in this work. For many valuable comments and suggestions, he is obligated to numerous colleagues at Ohio State. Some suggestions by Dr. C. J. Tsao regarding the use of certain properties of the representation coefficients of the three dimensional rotation group have been particularly useful. Much credit is due the previous workers in the field of line intensities whose names are mentioned throughout the text. It has been a pleasure to discuss some of the aspects of this work with one of these workers, Dr. R. C. Herman. The author also wishes to express his gratitude to the Ohio State University Research Foundation for sponsoring a large portion of this work by way of a Research Fellowship.
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The theoretical calculation of spectral line intensities in the infrared bands of molecules is useful for several reasons. There is a relation between the intensity distribution and temperature, population of individual rotational energy states going with a given vibrational energy, nuclear spin, and electric dipole moment, among other molecular properties. The results of intensity calculations, coupled with the information obtained from the frequency distribution of such spectral lines, surely is of aid in the study of these properties for given molecules. Such calculations, in conjunction with present day experimental data, also yield criteria for ascertaining the validity of the general theory involved.

The derivation of line intensity expressions is not new; in 1925, Fowler (1) and Kemble (2) obtained intensities using the old quantum theory and the correspondence principle. Since 1925 the rather cumbersome problem has been treated with increasing refinement. At the present time, nevertheless, satisfactory intensity expressions for only the very simplest molecules have been derived.

The first promising attack based on the new quantum mechanics was that of Oppenheimer (3) in 1926. He treated the band going with the $0 \rightarrow 1$ vibrational transition of the diatomic molecule by applying
matrix mechanics to a model having the electric dipole moment of two equal and opposite point charges and a quadratic vibrational potential function. The model was allowed to rotate and vibration-rotation interaction was considered. His expressions indicate that the P and R branches of the given spectral band should not be equally intense.

Various authors (4 - 6) have carried out calculations on the $0 \rightarrow 1$ and other bands for diatomic models including more general dipole moment expressions, anharmonic potential functions, and the Morse potential function. Some authors have merely applied Oppenheimer's results to specific cases. Also of interest is past work in which only vibration is taken into account (7), work which treats rotation alone (8), and work dealing with the computation of wave functions (9). Herman and Wallis (10), and Herman and Rubin (11), have recently developed theory adequate for interpretation of today's experimental data on vibration-rotation spectra of the diatomic molecule. Work of this sort for polyatomic molecules is just being started.

Nielsen (12), discusses a mechanism involving coriolis coupling to explain the lack of symmetry of the $\omega_3$ band for the $H_2S$ type of molecule. Eggers and Crawford (13), have studied total band intensities of carbon dioxide and nitrous oxide and give expressions from which the line intensities in some of the bands can be calculated. It appears, however, that vibration-rotation interaction can be taken more fully into account than is done in their treatment. Hanson, Nielsen, Shaffer, and Waggoner (14) have presented a systematic method based on the application of a contact transformation for facilitating the evaluation of matrix elements of dipole moment components needed for
intensity calculations, and applied it to the case of the diatomic molecule.

This dissertation is concerned with the application of the contact transformation method to the calculation of vibration-rotation line intensities for the linear symmetric X-Y-X molecule. The Born-Oppenheimer separation of electronic and nuclear motions in the Hamiltonian is employed [See (15); Chapter X of (16)], and electronic spin will be neglected. Nuclear spin will be neglected in the Hamiltonian but its influence on the intensities will be included via the statistical weights of the energy levels and the required symmetries of the wave functions involved. The body fixed reference frame components of the electric dipole moment will be expanded in a power series in terms of the normal coordinates, terms above quadratic being neglected. Quartic and higher terms will be neglected in the vibrational potential function which is also expanded in such a fashion. Of prime interest here are the details of the new method and the effects of vibration-rotation interaction on the intensities.
CHAPTER II

GENERAL THEORY

The Meaning of the Term, "Absorption Line Intensity"

Consider a beam of light incident on and traversing a substance which is essentially homogeneous, in our case a gas enclosed in an absorption cell in an infrared spectrometer. Let $I_{\omega}(0)$ be the intensity of the component of the incident beam having frequency $\omega$ (cm$^{-1}$). In other words $I_{\omega}(0)$ is the energy coming through a unit area taken perpendicular to the beam path per unit time due to photons of frequency $\omega$. It is assumed that the energy flux density is constant over the unit area. Let $I_{\omega}(x)$ be the intensity of the $\omega$ component of the beam after it has gone distance $x$ through the sample. The fractional decrease in the intensity of component $\omega$ as it goes distance $dx$ through the sample is given by the well known relation

$$\frac{dI_{\omega}(x)}{I_{\omega}(x)} = -\alpha_{\omega} dx,$$

(1)

where $\alpha_{\omega}$ is known as the absorption coefficient for component $\omega$.

[See (5); (17).] $\alpha_{\omega}$ depends upon the nature of the absorbing material in a way that we will presently see. For an absorption cell of path length $L$, one obtains upon integrating Eq. (1),

$$I_{\omega}(L) = I_{\omega}(0)e^{-\alpha_{\omega}L} = I_{\omega}(0)\left[1 - \alpha_{\omega}L + \frac{\alpha_{\omega}^2 L^2}{2} - (1/3!)\alpha_{\omega}^3 L^3 + \ldots \right]$$

(2)

The absorption of component $\omega$ by the substance in the cell is then
characterized by the quantity $I_{\text{Absorption}}(\omega)$ given by

$$ I_{\text{Absorption}}(\omega) = \frac{I_w(0) - I_w(L)}{I_w(0)L} = \alpha_w \left[ 1 - \frac{2}{3} \alpha_w L + \frac{1}{3!} \alpha_w^2 L^2 + \ldots \right] $$

If one measures $I_{\text{Absorption}}(\omega)$ over certain ranges of frequency with a spectrometer capable of sufficiently high resolution, using a gas made up of one kind of molecule as an absorbing substance, one obtains frequency distributions such as the vibration-rotation band shown in Fig. 1.

The absorption lines would have width even if the spectrometer were to have infinite resolving power. The theory of this work neglects the causes of this line width. On this account, it turns out that the theoretical expression to be used in this work is accurate only for thin absorbing layers. (Divide the gas up into many successive thin layers. The beam, as it passes through each succeeding layer, has, for a given line with width, a greater and greater ratio of "side" frequencies due to the greater absorption of the latter.) [See p. 20 of (18).] For this reason, when we refer to the "intensity of an absorption line" (actually relative absorption per unit path length), we mean absorption coefficient, which, as is indicated by Eq. (3), is relative absorption per unit path length for sufficiently short path length.
Among the causes of line broadening are Doppler effect associated with velocities of the absorbing molecules in the beam direction, collisions between the molecules and "radiation damping". Discussion of these and other causes of line broadening are to be found in references (19) and (20).

A Theoretical Expression for "Line Intensity" (Absorption Coefficient)

Consider a molecule with electric dipole moment $M$, whose energies $E_n$ are $g_n$-fold degenerate. ($n$ is the aggregate of quantum numbers needed to specify the energies.) Let $\psi_{n_1}, \psi_{n_2}, \ldots, \psi_{n_g}$ be the set of states going with energy $E_n$, where the $s_i$ represent sets of values of the quantum numbers characterizing the molecule but not included in $n$. Consider two such states $E_n$ and $E_{n''}$ with degeneracies $g_{n_1}$ and $g_{n''}$ respectively. Consider now a gas made up of such molecules being exposed to a beam of radiation. Let $N_n$ and $N_{n''}$ be the number of molecules of energies $E_n$ and $E_{n''}$ respectively, enclosed in a volume bounded by two parallel planes a distance $\Delta y$ apart and perpendicular to the path of the incident beam, the other boundaries being parallel to the beam path and such that volume $\Delta y$ is enclosed. If the beam contains photons of frequency $\omega(n'n'') = (E_{n''} - E_n)/hc$, some of the molecules in state $E_n$ will undergo transitions to energy $E_{n''}$, photons of this frequency being absorbed out of the beam. This gives rise to an absorption spectral line of frequency $\omega(n'n'')$, which is made up of components arising from the various possible $\psi_{n_1} \rightarrow \psi_{n''}$ transitions. Born, Dirac, and Slater (21) have, on the basis
of nonrelativistic quantum mechanics and classical radiation theory, obtained an expression for the probability that a system being irradiated while in a state $\psi_{n's_1}$ will undergo a transition to state $\psi_{n''s_i}$ in a very short interval of time. [See p. 452 of (22)] If this transition probability is denoted by $\Pi^{n's_i}_{n's_1}$, their result is

$$\Pi^{n's_i}_{n's_1} = \frac{8\pi^3}{3\hbar^2}\rho \omega \sum_{\beta} |\langle n''s''_j | M_{\beta} | n's_1 \rangle|^2 \quad (4)$$

where $\hbar$ is Planck's constant,

$\rho$ is the energy density of the $w$ component of the incident beam,

$M_\beta$ is the projection of the electric dipole moment on the $\beta$th axis of a "space fixed" reference frame,

and $\langle n''s''_j | M_{\beta} | n's_1 \rangle = \int \psi^{n''s''}_j ^* M_{\beta} \psi^{n's}_1 d\tau$.

The summation is carried over the three axes of the space fixed frame. The energy density $\rho_w$ of the component of the incident beam is related to the intensity $I_w$ as indicated in the relation,

$$\rho_w = I_w/c \quad (5)$$

where $c$ is the velocity of light. (This is seen if one considers that in time $dt$, energy $d\Sigma_w = \rho_w \cdot l \cdot c dt$ passes through a unit area perpendicular to the beam path, and that, for unit area, $I_w = \frac{d\Sigma_w}{dt}$.)

If a very large number, $N_{n's_1}$, of molecules in the thin absorbing layer are in the state $\psi_{n's_1}$, the transition probability $\Pi^{n's_i}_{n's_1}$ is essentially the ratio of the number of molecules undergoing the
transition during a very short time interval to the number of molecules in the original state at the beginning of the interval. Hence the time rate of occurrence of such transitions is given by \( \prod_{n's_i} N_{n's_i} \).

Since energy \( h\omega(n'n\nu) \) is absorbed each transition, the time rate of energy absorption in our thin layer due to molecules undergoing transition \( \psi_{n's_i} \rightarrow \psi_{n's_j} \) is then \( \prod_{n's_i} N_{n's_i} h\omega(n'n\nu) \). Now from statistical mechanics [See Chapter XV of (23); (24)], if \( N_{n's_i} \) is the number of molecules in the layer which are in the state \( \psi_{n's_i} \) of degeneracy \( \varepsilon_{n's_i} \), then

\[
\frac{N_{n's_i}}{N_n} = \varepsilon_{n's_i} e^{-E_n/kT} / \sum_{r} \varepsilon_{n's_r} e^{-E_{n'r}/kT},
\]

where \( r \) goes from 1 to \( \varepsilon_{n's} \). The Boltzmann factor \( e^{-E_n/kT} \) is the same for all the states \( \psi_{n's_r} \) going with energy \( E_{n'r} \). Also, the degeneracies \( \varepsilon_{n's_r} \) are all unity as the \( \psi_{n's_r} \) are by definition non-degenerate. Thus

\[
\frac{N_{n's_i}}{N_n} = \frac{l}{\sum_{r} \varepsilon_{n's_r}} = \frac{l}{\varepsilon_{n's}},
\]

Hence, the time rate of absorption of energy in the thin layer due to the transition \( \psi_{n's_i} \rightarrow \psi_{n's_j} \) is

\[
\prod_{n's_i} N_{n's_i} \frac{h\omega(n'n\nu)}{\varepsilon_{n's}}.
\]

The time rate of energy absorption in the thin layer due to all possible \( \psi_{n's_i} \rightarrow \psi_{n's_j} \) transitions between \( E_n \) and \( E'_n \) is therefore
\[ \sum_{i=1}^{J} \sum_{j=1}^{J} n_{i}^{n_{j}} \frac{h \omega(n_{i}n_{j})}{E_{n_{i}}} \]

But this is also equal to the decrease in the incident beam intensity, \(-\Delta I_{w}\), as it traverses the thin layer of thickness \(\Delta x\) and unit area facing the beam. Thus, if \(n_{i}^{n_{j}}\) is the number of molecules per unit volume with energy \(E_{n_{i}}\), \(N_{n_{i}} = n_{i}^{n_{j}}\), and

\[ \frac{-\Delta I_{w}(n_{i}n_{j})}{\Delta x} = h \omega(n_{i}n_{j}) \sum_{i=1}^{J} \sum_{j=1}^{J} n_{i}^{n_{j}} \left( \begin{array}{c} \sum_{j=1}^{J} n_{i}^{n_{j}} \left| M_{\beta} | n_{i}^{n_{j}} \rangle \right|^{2} \end{array} \right) \]

From this, equations (1), (4), (5), and the assumption that \(\Delta I_{w}/\Delta x\) is essentially \(dI_{w}/dx\), we obtain for the absorption coefficient

\[ \alpha_{w} = -\frac{1}{I_{w}} \frac{dI_{w}}{dx} \]

the expression,

\[ \alpha_{w}(n_{i}n_{j}) = \frac{6 \pi a_{w}(n_{i}n_{j})}{\beta} \sum_{i=1}^{J} \sum_{j=1}^{J} \left( \begin{array}{c} \sum_{j=1}^{J} n_{i}^{n_{j}} \left| M_{\beta} | n_{i}^{n_{j}} \rangle \right|^{2} \end{array} \right) \]

If \(N\) is the total number of molecules in a unit volume of the gas,

\[ \frac{N_{n_{i}}}{N} = \frac{e^{-E_{n_{i}}/kT}}{\sum_{m} e^{-E_{m}/kT}} \]

where \(m\) signifies a set of values of the quantum numbers needed to specify an energy \(E_{m}\) of the molecule. The sum \(\sum_{m} e^{-E_{m}/kT}\), called the "partition function" or "state sum" is carried over all the possible energy states of the molecule. [See 122f. of (18); Chapter XV of (23); (24).] In our treatment, we will neglect translational motion.
and assume that the energies $E_m$ can be represented as the sum

$$E_m = E_{m\,\text{E}} + E_{m\,\text{VR}} + E_{m\,\text{NS}}$$

where $E_{m\,\text{E}}$ is electronic energy, $E_{m\,\text{VR}}$ is vibration-rotation energy, and $E_{m\,\text{NS}}$ is nuclear spin energy.

In other words, we neglect all interactions except that between vibration and molecular rotation. In this case the degeneracy can be expressed as

$$\varepsilon_m = \varepsilon_{m\,\text{E}} \cdot \varepsilon_{m\,\text{VR}} \cdot \varepsilon_{m\,\text{NS}}$$

We will also assume that all of our molecules are in their ground electronic state, an assumption which upon the comparison of Boltzmann factors is seen to be very close to the truth at $300^\circ\text{K}$. If all the molecules may be considered to be in the same nuclear spin energy state, these assumptions lead to

$$\frac{\mathcal{N}_{n^1}}{\mathcal{N}} = \frac{\varepsilon_{n^1\,\text{VR}} \varepsilon_{n^1\,\text{NS}} e^{-E_{n^1\,\text{VR}}/kT}}{\sum_{m',\,2} \varepsilon_m \varepsilon_m e^{-E_{m\,\text{VR}}/kT}}$$

In the case of the linear $X-Y-X$ molecule, the $E_{m\,\text{VR}}$ can, as we shall demonstrate, be characterized by the quantum numbers

$$\{ v_1 v_2^1 v_3 J M \},$$

where

$$\{ v_1 v_2 v_3 \}$$

characterize the energy due to vibrational motion,

$$l_2$$

characterizes vibrational angular momentum,

$$J$$

characterizes total angular momentum,

$$M$$

characterizes the possible projections of total angular momentum along a space-fixed axis were
the molecule to be placed in a space-fixed perturbing field.

It happens that the energies are, to our degree of approximation, independent of \( M \), which, for a given \( J \) can take on the \((2J+1)\) values \( J, J-1, \ldots, -J \). (See p. 60.) We will then take \( s_{\text{NS}} = (2J+1) \).

A method for finding the \( s_{\text{NS}} \) for linear symmetric molecules has been worked out by Placzek and Teller. [See p. 17 of (25); (26).] They consider the linear symmetric configuration,

\[
X_k 
- X_2 
- X_1 
- Y 
- X_1 
- X_2 
- \cdots 
- X_k,
\]

where \( X_i \) nuclei have spin \( I_i \), i.e., spin angular momentum \( \sqrt{I_i(I_i+1)} \), and the center nucleus, \( Y \), which may or may not be present, has spin \( I_Y \). Using their method, one must determine the "resultant statistics" of the configuration (and hence the "symmetry" of its complete wave functions) from a consideration of the statistics followed by the individual nuclei. It happens that a nucleus with integer spin (even mass number) follows "Bose statistics" while one having half integer spin (odd mass number) follows "Fermi statistics". If the side configuration, \(-X_1 
- X_2 
- \cdots 
- X_k\) has within it an odd number of nuclei following Fermi statistics, the resultant statistics for \(X_k 
- X_2 
- X_1 
- Y 
- X_1 
- X_2 
- \cdots 
- X_k\) is Fermi. In all other cases the resultant statistics is Bose. For Bose resultant statistics, the complete wave function must remain unchanged if all the nuclei \( X_i \) on the right of the \( Y \) nucleus or center of symmetry are simultaneously interchanged with the corresponding \( X_i \) nuclei on the left. On the other hand, if the resultant statistics is Fermi, the complete wave function must
change sign if the above interchange is made. Wave functions which remain unchanged under the above symmetry operation (equivalent to a reflection of the configuration in the symmetry plane perpendicular to the internuclear axis) will be called "symmetric" while wave functions which change sign will be called "antisymmetric". In our determination of statistical weights it will be assumed that the complete wave function $\psi_{\text{Complete}}$ can be expressed to a sufficient degree of accuracy as the product $\psi_{\text{Electronic}} \psi_{\text{Vibration}} \psi_{\text{Rotation}} \psi_{\text{Nuclear Spin}}$, the factors of which are either symmetric or antisymmetric with respect to the above reflection. [See p. 355 of (16); p. 135 of (18).]

We neglect $\psi_{\text{Translation}}$ but it is readily seen that our symmetry operation will have no effect on it. Such complete wave functions $\psi_{\text{Complete}}$ containing an odd number of antisymmetric factors will be antisymmetric. For all other cases the complete wave function is symmetric. The various possible symmetries of the components of complete wave functions are tabulated below in Table 1. [See Chapter I of (25).]

It is appropriate to note here that electronic and vibrational wave functions for linear molecules are, by convention, characterized by such symbols as

$$\Sigma^+, \Sigma^-, \Pi^+ , \Delta^+$$

[See Chapters V, VI of (18); Chapters II, IV of (25).] The symbols $\Sigma, \Pi, \Delta, \ldots$ refer in the electronic case to states in which the molecular electronic orbital angular momentum quantum number $\Lambda$ is 0, 1, 2, \ldots respectively. For the vibrational case these symbols refer to states where the internal angular momentum quantum number $\ell$ is
0, 1, 2 ..., respectively. The superscript + means that the vibrational or electronic wave function is symmetric with respect to a reflection in a plane passing through all the nuclei. (We shall not be concerned with this symmetry operation here.)

The subscripts \{ g, u \} mean that the electronic or vibrational wave function is \{ symmetric, antisymmetric \} with respect to an inversion of rectangular coordinates through the center of symmetry at the molecule. In this work, our symmetric X-Y-X molecule will be assumed, as has been mentioned, to be in its ground electronic state. For convenience, we shall let \( \psi_{EVR} \) denote the product \( \psi_{Elec}. \psi_{Vib}. \psi_{Rot.} \), i.e., the non nuclear portion of \( \psi \). We shall not treat the case in which \( A \neq 0 \) in the ground state. This situation does occur for the diatomic molecule, NO. [See p. 121 of (18).] If the electronic state has \( A \neq 0 \), the electronic wave function can be either symmetric or antisymmetric with respect to inversion of coordinates, and the two possibilities occur as two slightly separated energy levels. [See p. 129 of (18).]
<table>
<thead>
<tr>
<th>Wave Function</th>
<th>Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\psi_{\text{Elec.}}$ (Ground State)</td>
<td>Symmetric</td>
</tr>
<tr>
<td>$\psi_{\text{Vib.}}$</td>
<td></td>
</tr>
<tr>
<td>$\Sigma^+_g, \Pi_g, \Delta_g, \ldots$</td>
<td>Symmetric</td>
</tr>
<tr>
<td>$\Sigma^+_u, \Pi_u, \Delta_u, \ldots$</td>
<td>Antisymmetric</td>
</tr>
<tr>
<td>$\psi_{\text{Rot.}}$</td>
<td></td>
</tr>
<tr>
<td>J even</td>
<td>Symmetric</td>
</tr>
<tr>
<td>J odd</td>
<td>Antisymmetric</td>
</tr>
<tr>
<td>$\psi_{\text{Nuc. Spin}}$</td>
<td></td>
</tr>
<tr>
<td>(1) Symmetric</td>
<td></td>
</tr>
<tr>
<td>(If $\psi_{\text{Complete}}$ and $\psi_{\text{EVR}}$ are both symmetric or both antisymmetric)</td>
<td></td>
</tr>
<tr>
<td>(2) Antisymmetric</td>
<td></td>
</tr>
<tr>
<td>(If $\psi_{\text{Complete}}$ and $\psi_{\text{EVR}}$ have opposite symmetries)</td>
<td></td>
</tr>
<tr>
<td>$\psi_{\text{Complete}}$</td>
<td></td>
</tr>
<tr>
<td>Symmetric</td>
<td></td>
</tr>
<tr>
<td>(For Bose resultant statistics)</td>
<td></td>
</tr>
<tr>
<td>Antisymmetric</td>
<td></td>
</tr>
<tr>
<td>(For Fermi resultant statistics)</td>
<td></td>
</tr>
</tbody>
</table>

($\psi_{\text{EVR}} = \psi_{\text{Elec.}} \psi_{\text{Vib.}} \psi_{\text{Rot.}}$)
For our \( X_k \ldots X_2X_1Y-X_1X_2 \ldots X_k \) configuration in its ground electronic state, it turns out \([\text{See p. 17 of (25).}]\) that the nuclear spin statistical weight \( g_{mNS} \) for an energy level going with a complete wave function whose nuclear spin portion is symmetric is

\[
\frac{1}{2}(2I_Y+1)\left[ \prod_{i=1}^{k} (2I_i+1)^2 + \prod_{i=1}^{k} (2I_i+1) \right]
\]

while \( g_{mNS} \) for an energy level going with a complete wave function whose nuclear spin portion is antisymmetric is

\[
\frac{1}{2}(2I_Y+1)\left[ \prod_{i=1}^{k} (2I_i+1)^2 - \prod_{i=1}^{k} (2I_i+1) \right].
\]

\([\text{In the absence of a central } Y \text{ nucleus, the factor } (2I_Y+1) \text{ becomes } 1.\]

Hence, from our remarks on pp. 10 and 11 \([\text{taking as complete statistical weight the product } g_{mVR} g_{mNS} \text{ since we assume Eq. (13) is valid for our purposes}].\), energy levels going with complete wave functions whose nuclear spin portions are symmetric have statistical weight

\[
g(1) = \frac{1}{2}(2I_Y+1)\left[ \prod_{i=1}^{k} (2I_i+1)^2 + \prod_{i=1}^{k} (2I_i+1) \right] (2J+1) \quad (14)
\]

while energy levels going with complete wave functions whose nuclear spin portions are antisymmetric have statistical weight

\[
g(2) = \frac{1}{2}(2I_Y+1)\left[ \prod_{i=1}^{k} (2I_i+1)^2 - \prod_{i=1}^{k} (2I_i+1) \right] (2J+1). \quad (15)
\]

A summary of the cases which can occur for the symmetric linear molecule in the ground electronic state is presented in Table 2.

\[
( \prod_{i=1}^{k} a_i \equiv a_1a_2 \ldots a_k )
\]
Table 2

Types of Complete Wave Functions and Statistical Weights of Energy Levels Going with Them for a Linear Symmetric Molecule \( X_1 - X_2 - X_1 - \cdots \) in Its Ground Electronic State

(For all cases, \( \Psi_{\text{Elec.}} \) is \( s \) (symmetric); \( a \) means antisymmetric)

<table>
<thead>
<tr>
<th>Case</th>
<th>Resultant Statistics</th>
<th>Characterization of Wave Functions</th>
<th>Statistical Weight of Energy Level Going with ( \Psi_{\text{Complete}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Bose</td>
<td>( s ), ( \Sigma_+^g, \pi_g, \Delta_3 ), ...</td>
<td>( J ) even, ( s ), ( s )</td>
</tr>
<tr>
<td>2</td>
<td>&quot;</td>
<td>&quot;</td>
<td>( J ) odd, ( a ), ( a )</td>
</tr>
<tr>
<td>3</td>
<td>&quot;</td>
<td>&quot;</td>
<td>( J ) even, ( a ), ( a )</td>
</tr>
<tr>
<td>4</td>
<td>&quot;</td>
<td>&quot;</td>
<td>( J ) odd, ( s ), ( s )</td>
</tr>
<tr>
<td>5</td>
<td>Fermi</td>
<td>( a ), ( \Sigma_+^g, \pi_g, \Delta_3 ), ...</td>
<td>( J ) even, ( s ), ( a )</td>
</tr>
<tr>
<td>6</td>
<td>&quot;</td>
<td>&quot;</td>
<td>( J ) odd, ( a ), ( s )</td>
</tr>
<tr>
<td>7</td>
<td>&quot;</td>
<td>&quot;</td>
<td>( J ) even, ( a ), ( a )</td>
</tr>
<tr>
<td>8</td>
<td>&quot;</td>
<td>&quot;</td>
<td>( J ) odd, ( s ), ( a )</td>
</tr>
</tbody>
</table>

where \( \varepsilon(1) = \frac{1}{8}(2I_1+1)^3 \left[ \frac{1}{\pi} \prod_{i=1}^{k} (2I_1+1)^2 + \frac{1}{\pi} \prod_{i=1}^{k} (2I_1+1) \right] (2J+1) \) where \( I_1 \) is spin of nucleus \( X_1 \), \( I_y \) that of \( Y \).

\( \varepsilon(2) = \frac{1}{8}(2I_1+1)^3 \left[ \frac{1}{\pi} \prod_{i=1}^{k} (2I_1+1)^2 - \frac{1}{\pi} \prod_{i=1}^{k} (2I_1+1) \right] (2J+1) \)
Now if all the spins $I_q$ are zero, $g(2) = 0$, and energy states having this statistical weight don't exist for the system. (Recall that the statistical weight for an energy level is its degeneracy, the lowest degeneracy for an existing state being 1.) In this case our original assumption (p. 6) that the states exist is false and we cannot with assurance use expression (9) in determining absorption coefficients. However, it is safe to say that if an energy state doesn't exist, no transitions involving it can occur. Thus, if for energy level $E_n$, $\varepsilon_n = 0$, or $\varepsilon_n$ for $E_n$ is zero, absorption coefficient

$$\alpha_w(n',n) = 0.$$ 

Also, we have not taken into account the fact that molecules in excited states are continually returning to lower energy levels so that the net absorption of radiation by the gas is decreased. This process occurs spontaneously, but can also be induced by the incident beam of radiation. In the spontaneous case, the net re-emitted energy from molecules in the gas comes off in all directions such that only a small portion of it gets through the spectrometer. For this reason, the effect of spontaneous re-emission is usually neglected. However, emitted radiation from induced transitions is directed in the beam direction.

[See references (5), (6), and (27).] According to Crawford and Dinsmore (6), the factor $\left[ 1-e^{-h\sigma(n')/kT} \right]$ must be multiplied into our expression for $\alpha_w(n',n)$ to correct for this effect. Table 3 should give the reader an indication of when this induced re-emission should be taken into account.
Table 3

Some Approximate Values of $e^{-\hbar c w / k T} = e^{-\frac{1}{1.4} \frac{w}{T}}$

<table>
<thead>
<tr>
<th>$T$ (°K)</th>
<th>$\omega$ (cm$^{-1}$)</th>
<th>$e^{-\hbar c w / k T}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>10</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.62</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>0.0083</td>
</tr>
<tr>
<td></td>
<td>10000</td>
<td>$1.7 \times 10^{-21}$</td>
</tr>
<tr>
<td>30</td>
<td>10</td>
<td>0.62</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.0083</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>$1.7 \times 10^{-21}$</td>
</tr>
<tr>
<td>1000</td>
<td>10</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.87</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td>10000</td>
<td>$5.6 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

Most of the difficulties encountered in intensity calculations such as ours arise in the evaluation of the quantities

$$\Pi_{s_1}^{n_1} = \sum_i \sum_j \sum_{s} \left| \langle n'' s'' | M_{s_i} | n' s_i \rangle \right|^2 .$$

The bulk of this dissertation is concerned with obtaining them. As has already been mentioned, provision has not been made to include nuclear spin, electronic motions, and translational motion in the Hamiltonian (and hence the wave functions) we use. Aside from symmetry considerations, the validity of such a procedure as far as the calculation of our dipole moment matrix elements for vibration-rotation transitions is concerned hinges upon the smallness of the interactions of the omitted motions with vibration and rotation. [See p. 138, (18); Chapter X of (15).] We then neglect these interactions. However, if $\psi_{\text{Complete}}$ can be written as the product $\psi_{\text{EHR}} \psi_{\text{Nuc. Spin}}$ (in other words, if we can
neglect the interaction between nuclear spin and the rest of the motion), then the orthogonality of spin wave functions of opposite symmetry and the nondependence of electric dipole moment on spin lead to vanishing probabilities for transitions in which the symmetry of \( \psi_{\text{Nuc. Spin}} \) changes. [See p. 135 of (18).] We will thus, with the help of Table 2 (p. 16) eliminate vibration-rotation transitions for which a change occurs in the symmetry of the nuclear spin wave function, and concern ourselves with the evaluation of the quantities

\[
\prod_{n_{\text{VR}}}^{n_{\text{VR}}} = \sum_{i=1}^{3} \sum_{j=1}^{3} \sum_{\alpha} \left| \langle n_{\text{VR}}^n s_{\text{VR}}^f | M_{\beta} | n_{\text{VR}}^n s_{\text{VR}}^f \rangle \right|^2
\]

where \( n_{\text{VR}} \) is a set of the quantum numbers characterizing the vibration-rotation energies \( E_{n_{\text{VR}}} \) and \( s_{\text{VR}} \) is a set of values of the quantum numbers not included in \( n_{\text{VR}} \) but needed to specify the vibration-rotation wave functions \( \psi_{n_{\text{VR}} s_{\text{VR}}} \).

For convenience we change notation, letting \( \gamma = n_{\text{VR}}, \gamma' = s_{\text{VR}} \), and \( \zeta = s_{\text{VR}} \), summing over \( \zeta' \) and \( \zeta'' \) rather than \( i \) and \( j \) keeping in mind that each summation is carried over only the \( \varepsilon_{n_{\text{VR}}} \) substates for the vibration-rotation level involved. Then the above expression for \( \prod_{n_{\text{VR}}}^{n_{\text{VR}}} \) becomes

\[
\prod_{\gamma}^{\gamma''} = \sum_{\zeta'} \sum_{\zeta''} \sum_{\alpha} \left| \langle \gamma'' \zeta'' | M_{\beta} | \gamma' \zeta' \rangle \right|^2.
\]  

(16)

Also, if we let \( \varepsilon_{\gamma} = \varepsilon_{n_{\text{VR}}} \varepsilon_{n_{\text{Nuc. Spin}}} \), the values of which are to be obtained from the last column of Table 2 on page 16, Equation (13) becomes
\[
\frac{n_{\nu'}}{n} = \frac{n_{\nu}}{n} = \frac{g_\nu e^{-E_\nu/kT}}{\sum \eta g_\eta e^{-E_\eta/kT}} \tag{17}
\]

It is well to bear in mind at this point that this expression is valid only if all the molecules can be considered to be in the ground electronic state and in the same nuclear spin energy state.

Thus, if our assumptions are valid, the absorption coefficient ("line intensity") for a vibration-rotation spectral line caused by all the possible transitions \(\psi^{\nu'} \rightarrow \psi^{\nu''}\) of molecules in our gas from energy \(E^{\nu}\) with statistical weight \(g^{\nu}\) to energy state \(E^{\nu''} (> E^{\nu'})\) with statistical weight \(g^{\nu''}\) is given by

\[
\alpha_w(\nu''|\nu') = \begin{cases} 
\frac{3h^3 w(\nu''|\nu')}{\hbar^2} \left[ 1 - e^{-\hbar \omega(\nu''|\nu')/kT} \right] \frac{n e^{-E^{\nu'}/kT}}{\mathcal{Z}(T)} \Pi^\nu'' \\
\text{if } g^{\nu'} \text{ and } g^{\nu''} \neq 0, \text{ and the symmetry of} \\
\psi_{\text{Nuc. Spin}} \text{ does not change;} \\
0 \text{ if } g^{\nu'} \text{ and/or } g^{\nu''} = 0, \text{ or the symmetry} \\
\text{of } \psi_{\text{Nuc. Spin}} \text{ changes.}
\end{cases} \tag{18}
\]

where \(w(\nu''|\nu') = (E^{\nu''} - E^{\nu'})/hc = \text{the frequency of the spectral line in cm}^{-1}\);

\(N = \text{the number of molecules per unit volume of the gas;}
\)

\(T = \text{the absolute temperature of the gas;}
\)

\(\mathcal{Z}(T) = \sum \eta g_\eta e^{-E_\eta/kT}\), where the summation is carried over all of the vibration-rotation states for the molecule involved;
The calculation of the quantities

\[ \langle \eta, \xi | M_\beta | \eta', \xi' \rangle \]

is cumbersome because the (corrected) wave functions are complicated. For vibrating rotating molecules, perturbation theory is normally used to obtain these functions. For a molecule with Hamiltonian

\[ H = H_0 + H_1 + \epsilon^2 H_2 + \ldots \]

whose zero order eigenfunctions are denoted by \( \psi_0 \) (i.e.,

\[ H_0 \psi_0 = E_0 \psi_0 \]

the wave functions according to degenerate perturbation theory can be represented by the expression

\[ II_{\eta''} = \sum \sum \frac{\langle \eta'', \xi'' | M_\beta | \eta', \xi' \rangle^2}{h} \]
\[ \psi_{\gamma} = \psi_{\gamma} + \varepsilon \left\{ \sum_{\gamma'} \sum_{\gamma''} \frac{(\gamma | H_{\gamma''} \gamma'')}{E_{\gamma'} - E_{\gamma''}} \psi_{\gamma'} \right\} + \sum_{\gamma'} \sum_{\gamma''} \sum_{\gamma'''} \frac{(\gamma | H_{\gamma'''}, \gamma'') (\gamma''' | H_{\gamma''}, \gamma)}{(E_{\gamma'} - E_{\gamma''})} \left[ \left( \gamma | H_{\gamma}, \varepsilon H + \cdots \gamma \right) \right]_{\gamma'} \] 

where the \( E_{\gamma} \) are the zero order eigenvalues, \( \varepsilon \) is an appropriate smallness parameter, and

\[ (\gamma | H_{\gamma}, \varepsilon H + \cdots \gamma) = \int_{0}^{\infty} \psi_{\gamma}^{*} H_{\gamma} \psi_{\gamma}, \text{ etc.} \]

the wave functions here being the zero order ones. [See p. 34 of (28).]

Following the method of Hanson, Nielsen, Shaffer, and Waggoner (14), simplification of the calculation of

\[ \int_{\gamma}^{\gamma'} M_{\beta} \psi_{\beta}, \text{ etc.} \]

can be brought about by a judicious application of an appropriate contact transformation \( T \). If the inverse of \( T \) is \( T^{-1} \), i.e. \( T^{-1}T = 1 \), then surely

\[ \int_{\gamma}^{\gamma'} M_{\beta} \psi_{\beta}, \text{ etc.} = \int_{T^{-1}T} M_{\beta} T^{-1}T \psi_{\beta}, \text{ etc.} \]

where

\[ M_{\beta}^{-1} \equiv T M_{\beta} T^{-1} \]
Now the $\psi_s$ are the solutions of the Schrodinger equation,

$$H\psi_s = E_s \psi_s,$$  \hspace{1cm} (22)

so one can write

$$THT^{-1}\psi_s = T\psi T^{-1}\psi_s = E_s T\psi_s.$$  \hspace{1cm} (23)

It is seen that the

$$T\psi_s = \psi_s$$  \hspace{1cm} (24)

are the eigenfunctions of the operator

$$THT^{-1} = H',$$  \hspace{1cm} (25)

whose eigenvalues are those of $H$. Also note that

$$\delta_{s,s'} = \int \psi^{*}_s \psi_{s'} \, dt = \int \psi^{*}_s T^{-1} \psi_{s'} \, dt$$

$$= \int \psi^{*}_s T^{-1} \psi_{s'} \, dt,$$  \hspace{1cm} (26)

so that $\psi^{*}_s T^{-1}$ is "equivalent" to $\psi^{*}_{s'}$. The calculation of our matrix elements

$$\int \psi^{*}_s M_\beta \psi_{s'} \, dt$$

will be simplified if $T$ is chosen in such a way as to make $\psi^{*}_s$ sufficiently less complicated than $\psi_{s'}$ to the order of approximation to be used. The method is most useful when, upon applying it, one obtains an integrand $\psi^{*}_s M_\beta \psi_{s'}$, consisting of one summation arising from $M_\beta$. 

rather than the original integrand containing the product of two multiple summations arising from the two original wave functions. Since the are the eigenfunctions of the transformed Hamiltonian $H'$, they can be expressed in terms of the (transformed zero order wave function) matrix elements of terms occurring in

$$H' = H'_0 + \epsilon H'_1 + \epsilon^2 H'_2 + \ldots$$

in the manner indicated in Equation (19), and it is seen that a transformation $T$ which will make $H'_1$ such as to be zero or to have only diagonal (transformed zero order wave function) matrix elements will make $\psi'$ equal to $\psi_0'$ for first order calculations. Later (see the middle of p. 25), $\psi_0'$ will be shown to be equal to $\psi_0$ for the type of contact transformation we use, so that to first order,

$$\int \psi_0^* \psi_0' \, d\tau = \int \psi_0^* \psi_0' \, d\tau. \quad (27)$$

It should be pointed out here that one cannot always find a $T$ which diagonalizes $H_1$ or makes it go over to zero, but, even if one cannot, a $T$ can usually be found which causes the desired effect on part of $H_1$ and simplifies matters. Later on we will present a scheme for handling the problem to higher orders of approximation.

Contact transformations have proven to be useful in energy calculations for quite some time, the application procedure, however, being somewhat different from that described above. First to use them in such calculations were Van Vleck in 1929 (29) in a study of "sigma-type doubling" and electron spin, and Johndahl in 1934 (30) in a paper on magnetic susceptibility. [See also p. 394f. of (22).] Shaffer, Mielson, and Thomas (31), Thomas (32), and others (33-38)
have found and applied such transformations in the calculation of the vibration-rotation energies of polyatomic molecules. Although the details of their application are different from ours, the transformation functions they have obtained suit our purposes and will be the ones we use. These transformations $T$ are of the form

$$T = e^{i\xi S} = 1 + i\xi S - \frac{1}{2} \xi^2 S^2 - \frac{i}{3!} \xi^3 S^3 + \ldots$$

and the transformed Hamiltonian can be expressed as

$$H' = H_0' + \xi^2 H_1' + \xi^3 H_2' + \xi^3 H_3' + \ldots = THT^{-1}$$

where $H''_0 = H_0$

$$H''_1 = H_1 + i\left[ S, H_0 \right]$$

$$H''_2 = H_2 + i\left[ S, H_1 \right] + \frac{1}{2!} \left[ S, \left[ S, H_0 \right] \right] = H_2 + i\left[ S, H_1 + H_0' \right]$$

$$H''_3 = H_3 + i\left[ S, H_2 \right] + \frac{1}{3!} \left[ S, \left[ S, H_1 \right] \right] + \frac{i}{3!} \left[ S, \left[ S, \left[ S, H_0 \right] \right] \right]$$

where $\left[ S, H_1 \right] = sH_1 - H_1 S$, etc.

From this it is seen that, since $H''_0 = H_0$, $\psi'' = \psi''$, so that equation (27) is valid to first order.

Now $H_1$ usually consists of a sum of terms which we will denote by

$$H_1 = \sum_k H_{1k}$$

In such a case it is convenient to express the $S$-function also as a sum,

$$S = \sum_k S_k$$

so that

$$H'_1 = \sum_k H_{1k} + \left[ \sum_k S_k, H_0 \right]$$

$$= \sum_k \left\{ H_{1k} + \left[ S_k, H_0 \right] \right\}.$$
Thus, for each $H_{1k}$, we desire to find an $S_k$ such that

$$H_{1k} + i \left[ S_k, H_0 \right]$$

equals zero or has no off diagonal (zero order wave function) matrix elements. In molecular vibration-rotation problems, the zero order Hamiltonian is often of the form

$$H_0 = H_0^\text{Rot.} + \sum_j h c \left\{ \omega_j \left( \frac{p_j^2}{\hbar^2} + q_j^2 \right) \right\}$$

where the $q_j$ are properly chosen normal vibration coordinates and the $p_j$ are the quantum mechanical operators $-ih \frac{\partial}{\partial q_j}$ associated with the momentum associated with the respective $q_j$. $H_0^\text{Rot.}$ contains total angular momentum operators and coordinates usually independent of the $p_j$ and $q_j$. (However, in our $H_0$ for the linear X-Y-X molecule, $H_0^\text{Rot.}$ involves the arc tangent of a ratio of the two perpendicular mode $q_j$ coordinates.) For an $H_0$ given by equation (39),

$$H_{1k}' = H_{1k} + i \left[ S_k, H_0 \right] \text{Vib.} + i \left[ S_k, H_0 \right] \text{Rot.}$$

where

$$H_0 \text{Vib.} = \sum_j h c \omega_j \left\{ \frac{p_j^2}{\hbar^2} + q_j^2 \right\} .$$

$S_k$ functions which make $i \left[ S_k, H_0 \right] \text{Vib.}$ equal to various $H_{1k}$ are given below in Table 4. They were obtained from p. 456 of (36) and derived on the basis of the commutation properties of the $p_j$ and $q_j$. In most cases encountered, $i \left[ S_k, H_0 \right] \text{Rot.} = 0$, and usually, the part of $S_k$ (the factor $A$ in Table 4), which sometimes contains total angular momentum operators, gives rise to no difficulty. However, for the case of our $H_0$ for the linear molecule, both of these factors must be looked into.
Table 4

$S_k$ and Their $i [S_k, H_{oVib.}]$

<table>
<thead>
<tr>
<th>$S_k$</th>
<th>$i [S_k, H_{oVib.}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{A}{\hbar \omega_j} \frac{p_j^4}{4}$</td>
<td>$A q_j$</td>
</tr>
<tr>
<td>$\frac{2A}{\hbar \omega_j} \left{ \frac{p_j^4}{3\hbar^3} + \frac{1}{2\hbar} q_j p_j q_j \right}$</td>
<td>$A q_j^3$</td>
</tr>
<tr>
<td>$\frac{A}{\hbar \omega_j (4\omega_j^2 - \omega_j^2)} \left{ (2\omega_j^2 - \omega_j^2) \frac{1}{\hbar} q_j^2 p_j + \omega_j^2 \frac{1}{\hbar} (p_j q_j + q_j p_j) q_j + 2\omega_j^2 \frac{1}{\hbar^3} p_j^2 p_j \right}$</td>
<td>$A q_j q_j^2$</td>
</tr>
<tr>
<td>$\frac{A \hbar}{\hbar c (\omega_j^2 - \omega_j^2)} \left{ \omega_j q_j q_j + \omega_j \frac{1}{\hbar^2} p_j p_j \right}$</td>
<td>$A q_j p_j$</td>
</tr>
<tr>
<td>$\frac{A \hbar}{\hbar \omega_j} q_j$</td>
<td>$A p_j$</td>
</tr>
</tbody>
</table>
It turns out that for one of the $S_k$, $i \left[ S_k, H_{\text{Rot}} \right] \neq 0$. Fortunately, the respective $H_{\text{el}}$ will be seen to have no off diagonal (zero order wave function) matrix elements so that for this term, no $S_k$ is needed in the first place.

Once the appropriate $S = \sum_k S_k$ is found, one proceeds to obtain the transformed electric dipole moment components $\left\{ M_{+}, M_{-}, M_{Z} \right\}$, or, to facilitate calculations later on, the quantities $\left\{ M_{+}, M_{-}, M_{Z} \right\}$ where, before transformation,

$$
M_{+} = \frac{1}{\sqrt{2}} (M_{X} + i M_{Y}) \\
M_{-} = \frac{1}{\sqrt{2}} (M_{X} - i M_{Y}) \quad (4.0) \\
M_{Z} = M_{Z}
$$

If the subscripts $+, -, \text{and } Z$ are denoted by $\gamma$, it can be readily shown by direct operation that

$$
\sum_{\beta} \left| \left\langle \gamma' \gamma | M_{\beta} | \gamma' \gamma' \right\rangle \right|^2 = \sum_{\gamma'} \left| \left\langle \gamma' \gamma | M_{\gamma} | \gamma' \gamma' \right\rangle \right|^2 \quad (4.1)
$$

If $T = e^{i \epsilon S}$, then

$$
M_{\gamma}' = TM_{\gamma} T^{-1} = M_{\gamma} + \epsilon i \left[ S, M_{\gamma} \right] - \frac{\epsilon^2}{2} \left[ S, \left[ S, M_{\gamma} \right] \right] + \ldots, \quad (4.2)
$$

and the $\left\langle \gamma' \gamma | M_{\gamma} | \gamma' \gamma' \right\rangle$ are obtained to first order by taking the zero wave function matrix elements of the first two terms.

A formal scheme for incorporating higher order terms in the Hamiltonian makes use of a contact transformation of the form
\[ J = e^{i(\xi L + \xi L + \xi L + \cdots)} \]

\[ = 1 + \xi i L + \xi \left\{ i \left( \frac{1}{2} L^2 \right) \right\} + \xi^3 \left\{ i \left( \frac{1}{2} L^2 \right) \left( \frac{1}{2} L^2 + \frac{1}{2} \right) \left( \frac{1}{2} L^2 + \frac{1}{2} \right) \right\} + \cdots \quad (43) \]

whose inverse is

\[ J^{-1} = e^{-i(\xi L + \xi L + \xi L + \cdots)} \]

\[ = 1 - \xi i L - \xi \left\{ i \left( \frac{1}{2} L^2 \right) \right\} - \xi^3 \left\{ i \left( \frac{1}{2} L^2 \right) \left( \frac{1}{2} L^2 + \frac{1}{2} \right) \left( \frac{1}{2} L^2 + \frac{1}{2} \right) \right\} + \cdots \quad (44) \]

Then, for

\[ H' = JHJ^{-1} = H_0 + \xi H_1 + \xi^2 H_2 + \xi^3 H_3 + \cdots \]

\[ H_0' = H_0 \]
\[ H_1' = H_1 + i[H_1, H_0] \]
\[ H_2' = H_2 + i[H_2, H_1] - \frac{1}{2} [H_1, [H_1, H_0]] + i[H_2, H_0] \]
\[ H_3' = H_3 + i[H_3, H_2] - \frac{1}{2} [H_1, [H_1, H_2]] - \frac{1}{3} [H_1, [H_1, H_1]] \]
\[ + i[H_3, H_1] - \frac{1}{2} [H_2, [H_2, H_0]] + [H_1, [H_2, H_0]] \]
\[ + i[H_3, H_0] \]

\[ \vdots \quad (45) \]

Since \( H_0' = H_0 \) as before,

\[ \psi_{1'} = \psi_{1}. \]

If \( H_1 \) is chosen so that \( H_1 \) equals zero or is diagonal (i.e. the zero order wave function matrix elements are diagonal);

\( H_2 \) is chosen so that \( H_2 \) equals zero or is diagonal;
\( s_3 \) is chosen so that \( H_3 \) equals zero; etc.,

then

\[
\psi' = \psi e^{i\gamma}
\]

and

\[
(\eta \gamma | \eta' \gamma') = (\eta \gamma | \eta' \gamma')
\]

where

\[
M'_\gamma = M_\gamma + \varepsilon_1 \langle s_1, M_\gamma \rangle
\]

\[
+ \varepsilon_2 \left\{ - \frac{1}{3} \langle s_1, [s_1, M_\gamma] \rangle + \frac{4}{3} \langle s_2, M_\gamma \rangle \right\}
\]

\[
+ \varepsilon_3 \left\{ - \frac{1}{3} \langle s_1, [s_1, [s_1, M_\gamma]] \rangle
\]

\[
- \frac{1}{3} \langle s_2, [s_1, M_\gamma] \rangle
\]

\[
+ \frac{1}{3} \langle s_3, M_\gamma \rangle
\]

\[
+ \varepsilon_4 \left\{ \ldots \right\}
\]

\( (46) \)

This scheme is practical, however, only when the appropriate

\( s_1, s_2, s_3, \ldots \) can be readily found.

Our work will deal only with the effect of the first order
correction terms in \( H \) on the line intensities. Additional dis­
cussion of the contact transformation method as applied to dipole
moment matrix element calculation is to be found in (14) and

(39).

The Expansion of the Electric Dipole Moment in Terms
of the Normal Vibrational Coordinates

Consider a set of point charges \( Q_j \), the locations of which are
given by the set of vectors \( L_j \). The electric dipole moment for such
a configuration is defined as

\[ \sum_j \mathcal{Q}_j \mathbf{e}_j \]  \hfill (47)

[See, for example, (40).]

For molecules whose bonds are primarily electrovalent in character, all charges may be considered in treatments such as ours to be localized to the extent that the atoms may be thought of as point charges. In such cases the \( \mathbf{r}_j \) are also the position vectors locating the "atoms" in the molecule. Let \( \{x_j, y_j, z_j\} \) be the components of the position vector locating the \( j \)-th atom in a reference frame the origin of which is located at the center of mass of the molecule and which is chosen so that the equilibrium configuration of the molecule does not rotate with respect to it. If \( \{x_{o_j}, y_{o_j}, z_{o_j}\} \) denotes the equilibrium position of the \( j \)-th atom in this frame and \( \{\delta x_j, \delta y_j, \delta z_j\} \) specifies its displacement from equilibrium (assumed to be very small), then

\[
\begin{pmatrix}
  x_j \\
y_j \\
z_j
\end{pmatrix}
= \begin{pmatrix}
x_{o_j} + \delta x_j \\
y_{o_j} + \delta y_j \\
z_{o_j} + \delta z_j
\end{pmatrix} \tag{48}
\]

and

\[
M_x = \sum_j \mathcal{Q}_j (x_{o_j} + \delta x_j) \\
M_y = \sum_j \mathcal{Q}_j (y_{o_j} + \delta y_j) \tag{49} \\
M_z = \sum_j \mathcal{Q}_j (z_{o_j} + \delta z_j)
\]
Now

\[ \delta x_j = \sum_k A_{jk} q_k \]

\[ \delta y_j = \sum_k B_{jk} q_k \]

\[ \delta z_j = \sum_k C_{jk} q_k , \]  

(50)

where the \( q_k \) are the normal vibrational coordinates. [See p. 276 of (41).] Hence, for our "electrovalent" molecule,

\[ M_x = M_{ox} + \sum_k \alpha_k q_k \]

\[ M_y = M_{oy} + \sum_k \beta_k q_k \]

\[ M_z = M_{oz} + \sum_k \gamma_k q_k \]  

(51)

where

\[ M_{ox} = \sum_j Q_j x_{0j} \]

\[ M_{oy} = \sum_j Q_j y_{0j} \]  

(52)

\[ M_{oz} = \sum_j Q_j z_{0j} \]

are the components of the permanent dipole moment and where the coefficients

\[ \alpha_k = \sum_j Q_j A_{jk} \]

\[ \beta_k = \sum_j Q_j B_{jk} \]  

(53)

\[ \gamma_k = \sum_j Q_j C_{jk} \]
characterize the linear dependence of the dipole moment on the normal coordinates. For molecules having symmetry, some of the sets

\[ \{ \alpha_i, \beta_i, \gamma_i \} \text{ may be } \{0, 0, 0\} \]. In such cases it is seen that the respective normal coordinates \( q_i \) do not appear in the dipole moment component expressions. Vibrations associated with such coordinates will be "infrared inactive" (they do not give rise to infrared spectra), while vibrations associated with normal coordinates appearing in one or more of the dipole moment component expressions are "infrared active".

[See p. 239f. of (25).]

Now the molecular model for which all charges are localized to the extent that the atoms may be considered as point charges is unrealistic, particularly if any or all of the bonds in the actual molecule are largely covalent in character. In a covalent bond, electrons are shared by the two atoms involved, and there is effectively a continuous charge distribution over the space surrounding the nuclei and non-bonding inner electron shells of these atoms. [See, for instance, (41).] For the entire molecule, the charge distribution (and hence the electric dipole moment) is obtainable from the electronic wave function for the bonding electrons and the net charges of the nuclei plus inner shell non-bonding electrons. This rather complicated procedure will not be carried out here. Instead, it will be assumed that the electric dipole moment components can be expanded in a power series in the normal coordinates and that \( q_k \) which are not present in the \( \{ M_x, M_y, M_z \} \) for the corresponding point charge atom model will be present only in products involving the \( q_i \) which do occur in the simplified model. [See (13); p. 41 of (41); p. 241 of (25).]
These series will be formally represented here as

\[
\begin{align*}
M_x &= a_x + \sum_i \beta_i q_i + \sum_i \sum_j \alpha_{ij} q_i q_j + \sum_i \sum_j \sum_k \omega_{ijk} q_i q_j q_k + \ldots \nonumber \\
M_y &= a_y + \sum_i \beta_i q_i + \sum_i \sum_j \alpha_{ij} q_i q_j + \sum_i \sum_j \sum_k \omega_{ijk} q_i q_j q_k + \ldots \nonumber \\
M_z &= a_z + \sum_i \beta_i q_i + \sum_i \sum_j \alpha_{ij} q_i q_j + \sum_i \sum_j \sum_k \omega_{ijk} q_i q_j q_k + \ldots 
\end{align*}
\]

The non-zero coefficients in these expansions are left in symbolic form in the results of our work. Their values are left to be determined from the electronic wave function or to be inferred from experimental data.

The Projections of the Electric Dipole Moment in a "Space Fixed" Reference Frame

\[ \{ M_x, M_y, M_z \} \] are the components of the electric dipole moment in a reference frame the origin of which is located at the center of mass of the molecule and whose orientation is so chosen that the equilibrium configuration does not rotate with respect to it. In the case of a molecule whose equilibrium configuration is linear, an infinite number of such frames can be set up having as a common axis the line joining the atoms. (The atoms are regarded here as point masses.)

If the molecule is not distorted from its linearity, the dipole moment, if it exists, will lie along this common axis. (Strictly speaking, the molecule will not remain completely linear due to zero point vibration.) If the molecule becomes distorted from its linearity, as is the case when a perpendicular mode of vibration is excited, all of the \( x y z \) axes can be set up with a definite orientation with respect to
the configuration. There may be a dipole moment component along each of these axes which "rotate with the molecule".

In order to obtain the line intensities, we need the components of $\mathbf{M}$ in the reference system of the spectrometer, namely our "space fixed" frame. We will take the components of $\mathbf{M}$ in an $X'Y'Z'$ frame whose axes remain parallel to those of the spectrometer fixed frame but whose origin is coincident with that of the moving $xyz$ frame. It is readily seen that the projections of $\mathbf{M}$ in the $X'Y'Z'$ frame are the same as those in the non-translating spectrometer fixed frame.

The $xyz$ and $X'Y'Z'$ reference frames can be related to each other by means of Eulerian angles $\varphi, \theta, \psi$ as indicated in Fig. 2.

\[ \begin{align*}
\text{Eulerian Angles} \\
\text{Fig. 2}
\end{align*} \]
Our choice of these angles, which can be set up in more than one way, is that of Whittaker (43). With this choice, the components of $\mathbf{M}$ in the $XYZ$ frame are given in terms of $M_x, M_y, M_z$ by the relation

$$
\begin{pmatrix}
M_x \\
M_y \\
M_z
\end{pmatrix} =
\begin{pmatrix}
\cos\phi\cos\theta\cos\psi - \sin\phi\sin\psi & -\cos\phi\cos\theta\sin\psi - \sin\phi\cos\psi & \cos\phi \sin\theta \\
\sin\phi\cos\theta\cos\psi + \cos\phi\sin\psi & -\sin\phi\cos\theta\sin\psi + \cos\phi\cos\psi & \sin\phi \sin\theta \\
-\sin\theta \cos\psi & \sin\theta \sin\psi & \cos\theta
\end{pmatrix}
\begin{pmatrix}
M_x \\
M_y \\
M_z
\end{pmatrix}
$$

[See (43); p. 231 of (22); the components of $\mathbf{M}$, being projections of a vector along the various axes, transform like rectangular coordinates.]

As was mentioned on p. 28, it will be more convenient to deal with the quantities

$$
\begin{align*}
M_+ &= (\frac{1}{2})^{\frac{3}{2}} (M_X + iM_Y) \\
M_- &= (\frac{1}{2})^{\frac{3}{2}} (M_X - iM_Y) \\
M_Z &= M_Z
\end{align*}
$$

than with $M_X, M_Y, M_Z$. One reason for this is the simpler functional dependence of the transformation matrix for the $+$ and $-$ combinations on the Eulerian angles. Direct operation yields the relation

$$
\begin{pmatrix}
M_+ \\
M_- \\
M_Z
\end{pmatrix} =
\begin{pmatrix}
\frac{1}{2} (1+\cos\phi) e^{i(\phi+\theta)} & -\frac{1}{2} (1-\cos\phi) e^{-i(\phi-\theta)} & \frac{1}{2} \sin\phi e^{i\theta} \\
\frac{1}{2} (1-\cos\phi) e^{-i(\phi-\theta)} & \frac{1}{2} (1+\cos\phi) e^{i(\phi+\theta)} & -\frac{1}{2} \sin\phi e^{-i\theta} \\
-\frac{1}{2} \sin\phi e^{-i\theta} & -\frac{1}{2} \sin\phi e^{i\theta} & \cos\theta
\end{pmatrix}
\begin{pmatrix}
M_x \\
M_y \\
M_z
\end{pmatrix}
$$

From this expression and from the dependence of $M_x, M_y, M_z$ on the
normal coordinates given in Equation (54) on p. 34, one obtains the explicit dependence of the $M_x$, $M_y$, $M_z$ on the normal coordinates and the Eulerian angles.

It happens that the elements of the transformation matrix in Equation (57) are representation coefficients of the three dimensional rotation group. Use will be made of certain properties of these quantities to greatly simplify the evaluation of our

$$
\Pi_{\gamma}^{\gamma'} = \sum_{\gamma} \sum_{\gamma'} \sum_{\eta} |C_{\gamma \gamma'}^{\eta} M_{\eta} | \gamma' \rangle \langle \gamma |^2
$$

$$
= \sum_{\gamma} \sum_{\gamma'} \sum_{\eta} |C_{\gamma \gamma'}^{\eta} M_{\eta} | \gamma' \rangle \langle \gamma |^2
$$

(58)

(See p. 100; Appendix VI.)

The representation coefficients will be depicted here by the symbol $D_{km}^j$. The $D_{km}^j$ for $j = 1$ are given below in Table 5. (See p. 176.)

**Table 5**

Representation Coefficients $D_{km}^j$ for $j = 1$

<table>
<thead>
<tr>
<th>$m$</th>
<th>$k$</th>
<th>1</th>
<th>0</th>
<th>-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>$(1/2)(1+\cos \phi) e^{-i(\gamma+j)}$</td>
<td>$(1/2) \sin e^{-i \gamma}$</td>
<td>$(1/2) \sin e^{i(\gamma-\gamma)}$</td>
</tr>
<tr>
<td>0</td>
<td>-1</td>
<td>$-(1/2) \sin e^{-i \gamma}$</td>
<td>$\cos \phi$</td>
<td>$-(1/2) \sin e^{i \gamma}$</td>
</tr>
<tr>
<td>-1</td>
<td>1</td>
<td>$\frac{1}{2} (1-\cos \phi) e^{-i(\gamma-j)}$</td>
<td>$-(1/2) \sin e^{i \gamma}$</td>
<td>$\frac{1}{2} (1+\cos \phi) e^{i(\gamma+j)}$</td>
</tr>
</tbody>
</table>
CHAPTER III
THE LINE INTENSITIES FOR THE LINEAR
SYMMETRIC X-Y-X MOLECULE

Definition of Coordinates

Consider the motion of the linear symmetric X-Y-X molecule when it is rotating and undergoing its degenerate perpendicular mode of vibration. We will let the masses of X and Y atoms be \( m \) and \( M \) respectively. Our choice of \( x, y, z, \gamma, \theta, \) and \( \gamma' \), and our labelling of the atoms are shown in Fig. 3.

Reference Frames for Describing the Motion of a Linear "Symmetric" X-Y-X Molecule

Fig. 3
The paths of the three atoms have been greatly enlarged relative to the interatomic distances for clarity. When the molecule is not undergoing its degenerate mode of vibration, the angle \( \gamma \) is meaningless, while \( \varphi \) and \( \varepsilon \) give the orientation of the internuclear axis. \( \varphi \) and \( \varepsilon \) also locate an \( x' \) and a \( y' \) axis, the latter being the line of nodes for our choice of Eulerian angles. It is with respect to the \( x' y' z' \) system that we will define our vibrational coordinates. This is a satisfactory procedure since the \( x' y' z' \) system can be seen to have its origin at the center of mass of the molecule and is such that the equilibrium configuration doesn't rotate with respect to it. (See Appendix II.) Note that these conditions also hold for the \( x y z \) system when it can be uniquely defined.

If \( \{ \delta x'_i, \delta y'_i, \delta z'_i \} \) are the components of the small displacement from equilibrium of the \( i \)-th "atom" referred to the \( x' y' z' \) reference frame, our normal vibrational coordinates in their final dimensionless form can be expressed as

\[
q_1 = 2\pi (2\omega_i m/\hbar)^{1/2} \left\{ \frac{1}{2} (\delta z'_1 - \delta z'_3) \right\}
\]

\[
q_{2a} = 2\pi (\mu' c \omega_2/\hbar)^{1/2} \left\{ \delta x'_2 - \frac{1}{3} (\delta x'_1 + \delta x'_3) \right\}
\]

\[
q_{2b} = 2\pi (\mu' c \omega_2/\hbar)^{1/2} \left\{ \delta y'_2 - \frac{1}{3} (\delta y'_1 + \delta y'_3) \right\}
\]

\[
q_3 = 2\pi (\mu' c \omega_3/\hbar)^{1/2} \left\{ \delta z'_2 - \frac{1}{3} (\delta z'_1 + \delta z'_3) \right\}
\]

where \( \mu' = (2mM)/(2m+M) \)

\( c \) = the velocity of light,

\( h \) = Planck's constant, and
\( \omega_1 \) = the fundamental frequency \((\text{cm}^{-1})\) associated with
normal coordinate \(q_1\). (The values of the \(\omega_n\) are
obtained in the process of finding the normal co-
ordinates.)

See Appendix I; p. 292 of (44) and p. 184 of (45). The inverse rela-
tions to (59)–(62), which will be useful, are

\[
\delta x_1^i = \delta x_3^i = -\left(\frac{\mu_i}{\omega_{\text{cm}_2}}\right)^{\frac{3}{2}} \frac{1}{(1/4\pi^2)^{\frac{1}{2}}} q_{a_1} \\
\delta x_2^i = \left(\frac{\mu_i}{\omega_{\text{cm}_2}}\right)^{\frac{3}{2}} \frac{1}{(1/2\pi^2)^{\frac{1}{2}}} q_{a_2} \\
\delta y_1^i = \delta y_3^i = -\left(\frac{\mu_i}{\omega_{\text{cm}_2}}\right)^{\frac{3}{2}} \frac{1}{(1/4\pi^2)^{\frac{1}{2}}} q_{a_2} \\
\delta y_2^i = \left(\frac{\mu_i}{\omega_{\text{cm}_2}}\right)^{\frac{3}{2}} \frac{1}{(1/2\pi^2)^{\frac{1}{2}}} q_{a_2} \\
\delta z_1^i = \left(\frac{\mu_i}{2\text{mcw}_1}\right)^{\frac{3}{2}} \frac{1}{(1/2\pi^2)^{\frac{1}{2}}} q_{a_1} - \left(\frac{\mu_i}{\omega_{\text{cm}_2}}\right)^{\frac{3}{2}} \frac{1}{(1/4\pi^2)^{\frac{1}{2}}} q_{a_2} \\
\delta z_3^i = -\left(\frac{\mu_i}{2\text{mcw}_1}\right)^{\frac{3}{2}} \frac{1}{(1/2\pi^2)^{\frac{1}{2}}} q_{a_1} - \left(\frac{\mu_i}{\omega_{\text{cm}_2}}\right)^{\frac{3}{2}} \frac{1}{(1/4\pi^2)^{\frac{1}{2}}} q_{a_2} \\
\delta z_2^i = \left(\frac{\mu_i}{\omega_{\text{cm}_2}}\right)^{\frac{3}{2}} \frac{1}{(1/2\pi^2)^{\frac{1}{2}}} q_{a_2}
\]

The motion associated with each of the normal coordinates is
represented in Fig. 4.

Motion of the Individual Atoms Associated with
Each of the Normal Coordinates

Fig. 4
It will be convenient at times to express quantities in terms of

\[ r = (q_{2a}^2 + q_{2b}^2)^{\frac{1}{2}}, \text{ and} \]

\[ \gamma = \arctan \left( \frac{q_{2b}}{q_{2a}} \right) \]  

rather than \( q_{2a} \) and \( q_{2b} \). Equation (72) may be considered to constitute the definition of the angle \( \gamma \) of Fig. 3.

The Electric Dipole Moment Components in Terms of
the Normal Coordinates and the Eulerian Angles

Let us first consider the "point charge atom" model of our linear symmetric X-Y-X molecule, where atoms 1 and 3 have charge \( Q \), and atom 2 has charge \( Q_L \). Since \( x_{01}^i = y_{01}^i = 0 \) for all \( i \) due to the linearity of the equilibrium configuration and since \( z_{01}^i = -z_{03} \) and \( z_{02}^i = 0 \) due to symmetry,

\[ M_{0x} = M_{0y} = M_{0z} = 0, \]  

i.e., our molecule has no permanent electric dipole moment. (See p. 31f.) From (53) and (64)-(70) we obtain the coefficients \( \{ \alpha_k, \beta_k, \gamma_k \} \) characterizing the linear dependence of the dipole moment on the normal coordinates. They are:

\[ \alpha_1 = \alpha_{2b} = \alpha_3 = 0 \]  

(74)

\[ \alpha_{2a} = \left( \frac{1}{2\pi} \right) \left( \mu \right. \left. \frac{h}{cm} \right)^\frac{3}{2} \left( -\frac{Q_1}{m} + \frac{Q_L}{m} \right) \]  

(75)

\[ \beta_1 = \beta_{2a} = \beta_3 = 0 \]  

(76)

\[ \beta_{2b} = \left( \frac{1}{2\pi} \right) \left( \mu \right. \left. \frac{h}{cm} \right)^\frac{3}{2} \left( -\frac{Q_1}{m} + \frac{Q_L}{m} \right) \]  

(77)
\[ \gamma_1 = \gamma_{2a} = \gamma_{2b} = 0 \quad (78) \]
\[ \gamma_3 = (1/2\pi) (\mu' h/\omega_c)^{3/2} \left( -\frac{Q}{m} + \frac{Q_x}{K} \right) \quad (79) \]

Thus, from Equation (51) on p. 32,
\[ M_{x'} = (1/2\pi) (\mu' h/\omega_c)^{3/2} \left( -\frac{Q}{m} + \frac{Q_x}{K} \right) q_{3a} \quad (80) \]
\[ M_{y'} = (1/2\pi) (\mu' h/\omega_c)^{3/2} \left( -\frac{Q}{m} + \frac{Q_x}{K} \right) q_{3b} \quad (81) \]
\[ M_{z'} = (1/2\pi) (\mu' h/\omega_c)^{3/2} \left( -\frac{Q}{m} + \frac{Q_x}{K} \right) q_3 \quad (82) \]

Note that these equations demonstrate the infrared inactivity of normal coordinate \( q_1 \).

Since
\[ M_x = M_{x'} \cos \gamma + M_{y'} \sin \gamma \quad (83) \]
\[ M_y = -M_{x'} \sin \gamma + M_{y'} \cos \gamma \quad (84) \]
\[ M_z = M_{z'} \quad (85) \]

and since the inverse of (71)-(72) is
\[ q_{3a} = r \cos \gamma \quad (86) \]
\[ q_{3b} = r \sin \gamma \quad (87) \]
\[ M_{x'} = (1/2\pi) (\mu' h/\omega_c)^{3/2} \left( -\frac{Q}{m} + \frac{Q_x}{K} \right) r \quad (88) \]
\[ M_{y'} = 0 \quad (89) \]
\[ M_{z'} = (1/2\pi) (\mu' h/\omega_c)^{3/2} \left( -\frac{Q}{m} + \frac{Q_x}{K} \right) q_3 \quad (90) \]
Expressions (88-90) were derived for the point charge atom model of our molecule. In accordance with the discussion on pp. 33 and 34 regarding molecules with covalent bonds, we expand our $x\ y\ z$ dipole moment components in the following series:

$$M_x = M^z(q_1q_3r)$$
$$= B_{2r} + C_{22}q^2 + C_{12}q_1r + C_{32}q_3r$$
$$+ D_{222}q^3 + D_{122}q_1r^2 + D_{112}q_1^2r + D_{322}q_3r^2$$
$$+ D_{332}q_3^2r + D_{132}q_1q_3r$$
$$+ \ldots \ldots \quad \text{(91)}$$

$$M_y = 0$$

$$M_z = M^y(q_1q_3r)$$
$$= B_{3q_3} + C_{33}q^3 + C_{13}q_1q_3 + C_{23}q_3r$$
$$+ D_{333}q^4 + D_{133}q_1q^3 + D_{113}q_1^2q_3 + D_{233}q_3^2r$$
$$+ D_{223}q_3^2r + D_{123}q_1q_3r$$
$$+ \ldots \ldots \quad \text{(92)}$$

It should be noted that if this more general form of $M$ is to have a symmetry identical to that the $M$ of the corresponding point charge atom model, $M_x$ should include only terms involving $r$ to odd powers and $q_3$ to even powers (including 0); $M_z$ should include only terms involving $q_3$ to odd powers and $r$ to even powers. Of course, any power of the totally symmetric coordinate $q_1$ (see Table 18 on p. 158) can be multiplied into a $q_3^2r^{2m+1}$ to form an acceptable $M_x$ term, or
multiplied into $q_3^{2n+1}r^{2m}$ to form an acceptable $M_z$ term. (n and m are non-negative integers.) Additional terms are included in our expansion because the charge distribution of a covalently bonded linear molecule need not have quite the same symmetry as the corresponding point charge model, due to the presence of "\$-type" bonds. [See pp. 76f. of (42).]

While it is expected that these additional terms will contribute relatively little, we have retained them in order to find out what sort of terms they give rise to. In this treatment, cubic and higher powered terms in these expansions will be neglected. As was mentioned previously, the coefficients will be left in symbolic form in our results.

From Equations (91) and (92), and Equation (57) on p. 36, it follows that the combinations $M_{\gamma}$ of the space fixed frame components of $M$ are given by

$$M_{\gamma} = m^{L_1(q_3)}(q_3^2r^2)X + m^{L_2(q_3^2r^2)}\lambda_{\gamma}$$

(93)

where the subscript $\gamma$ is $\pm$, $\pm$, or $Z$; and

$$\lambda_+ = (\frac{3}{2})^{\frac{1}{3}}\left\{\frac{3}{2}(1+\cos\theta)e^{i(\varphi+\gamma)} - \frac{3}{2}(1-\cos\theta)e^{i(\varphi-\gamma)}\right\}$$

(94)

$$\lambda_- = (\frac{3}{2})^{\frac{1}{3}}\left\{-\frac{3}{2}(1-\cos\theta)e^{-i(\varphi-\gamma)} + \frac{3}{2}(1+\cos\theta)e^{-i(\varphi+\gamma)}\right\} = \lambda^*_+$$

(95)

$$\lambda_Z = (\frac{3}{2})^{\frac{1}{3}}\left\{-(\frac{3}{2})^{\frac{1}{3}}\sin\theta e^{i\gamma} - (\frac{3}{2})^{\frac{1}{3}}\sin\theta e^{-i\gamma}\right\}$$

(96)

$$\lambda_+ = (\frac{3}{2})^{\frac{1}{3}}\sin\theta e^{i\gamma}$$

(97)

$$\lambda_- = (\frac{3}{2})^{\frac{1}{3}}\sin\theta e^{-i\gamma} = \lambda^*_+$$

(98)

$$\lambda_Z = \cos\theta$$

(100)
In terms of the representation coefficients $D_{km}^j$, these are

\[ a_+ = \left( \frac{1}{2} \right) \left( D_{11} - D_{1-1} \right) \tag{101} \]

\[ a_- = \left( \frac{1}{2} \right) \left( -D_{-11} + D_{11} \right) \tag{102} \]

\[ a_z = \left( \frac{1}{2} \right) \left( D_{10} - D_{-10} \right) \tag{103} \]

\[ \lambda_+ = D_{0-1} \tag{104} \]

\[ \lambda_- = -D_{01} \tag{105} \]

\[ \lambda_z = D_{00} \tag{106} \]

The Quantum Mechanical Hamiltonian

The wave functions and the contact transformation needed in our intensity calculations are characteristic of the quantum mechanical Hamiltonian for our molecular system. The Hamiltonian for the linear symmetric X-Y-X molecule, derived in Appendix II by the Wilson and Howard method \(^{(46)}\) modified for linear molecules \(^{(47)}\) is

\[ H = \hbar c \varepsilon (1 + 2\varepsilon q_1 + 3\varepsilon^2 q_1^2 + 4\varepsilon^3 q_1^3 + \ldots) (1/\hbar^2) \left\{ (P_x - P_x')^2 \right. \]

\[ + \left( P_{y'} - P_{y} \right)^2 \right\} + \frac{\hbar c}{2} \left\{ w_1 \left[ (p_1/\hbar)^2 + q_1^2 \right] + w_2 \left[ (p_{2a}/\hbar)^2 \right. \]

\[ + (p_{3b}/\hbar)^2 + q_{2a}^2 + q_{2b}^2 \bigg] + w_3 \left[ (p_3/\hbar)^2 + q_3^2 \right] \bigg] - \hbar c w_1 (1 + \varepsilon q_1 \]

\[ + \varepsilon^2 q_1^2 + \varepsilon^3 q_1^3 + \ldots) (p_1/\hbar) + \varepsilon \hbar c \left\{ k_{111} q_1^2 + k_{12} q_2^2 (q_{2a} + q_{2b}) \]

\[ + k_{133} q_3^2 \right\} + \varepsilon^2 \hbar c \left\{ k_{1111} q_1 + k_{112} q_2 (q_{2a} + q_{2b}) + k_{1133} q_3^2 \right\} \]
\[ + K_{3333}q_3 + K_{3322}q_2^2 + K_{2222}(q_{2a}^2 + q_{2b}^2) + K_{2222}(q_{2a}^2 + q_{2b}^2) \]

\[ + \ldots \quad (107) \]

where \( B_e = \frac{\hbar}{2m^2c_i_0} \); \( I_o \) = the non-vanishing moment of inertia of the linear equilibrium configuration

\[ = 2ma^2, \text{ where } a \text{ is the equilibrium X-Y distance.} \]

\[ = \left( \frac{2B_e}{p_1} \right)^{\frac{1}{2}} \]

\( P_{X'}, \ P_{Y'} \) are the operators associated with the projections of the total (rotation-vibration) angular momentum vector along \( x' \) and \( y' \) respectively;

\[ \mathcal{P}_{X'} = - \sqrt{\frac{m}{w_3}} q_3 P_{2b} + \sqrt{\frac{m}{w_2}} q_2 P_3 \quad (108) \]

\[ \mathcal{P}_{Y'} = \sqrt{\frac{w_3}{w_2}} q_3 P_{2a} - \sqrt{\frac{w_3}{w_2}} q_2 P_3 \quad (109) \]

(\( \mathcal{P}_{X'} \) and \( \mathcal{P}_{Y'} \) are operators associated with internal angular momentum.)

\[ p_j = - \hbar \frac{2}{\partial q_j} \quad = \text{the operator associated with the momentum conjugate to normal coordinate } q_j \quad (j = 1, 2a, 2b, \ 3); \]

\[ \hbar = \hbar / 2\pi \quad \text{; and} \]

\( K_{ijkl} \) and \( K_{ijkl} \) are cubic and quartic anharmonic vibrational potential function constants, respectively.
Now
\[(P_x^1 - P_x^1)^2 + (P_y^1 - P_y^1)^2\]
\[= P_x^2 + P_y^2 - (P_x^1 P_x^1 + P_y^1 P_y^1 + P_x^1 P_x^1 + P_y^1 P_y^1)\]
\[+ \phi_x^2 + \phi_y^2\]  \hspace{1cm} (110)

(The \(\phi^1\)'s and the \(P^1\)'s do not commute.) We know the eigenvalues of the dot product of total angular momentum with itself and of the component of total angular momentum along one of the body fixed axes.

\[\text{See Chapter III of } (25)\] Hence we write

\[P_x^2 + P_y^2 = P^2 - P_z^2,\]  \hspace{1cm} (111)

where \(P^2\) is the operator associated with the dot product of the total angular momentum vector with itself, and \(P_z^1\) is the operator associated with the projection of the total angular momentum vector along the \(z^1\) axis. Since the \(z\) and \(z^1\) axes coincide, and since we are dealing with projections,

\[P_z^1 = P_z.\]  \hspace{1cm} (112)

Also, \(P_z^1 = -i\hbar \frac{\partial}{\partial \gamma}\) is equal to \(\phi_z^1 = q_{2a}p_{2b} - q_{2b}p_{2a}\), where \(\phi_z^1\) is the operator associated with the \(z^1\) component of vibrational angular momentum. (See Appendixes II and III.)

We break our Hamiltonian up for a perturbation treatment as follows: \[\text{See (45)}\]

\[H = H_0 + \varepsilon H_1 + \varepsilon^2 H_2 + ...\]  \hspace{1cm} (113)
where

\[
H_0 = \hbar c B_0 \left( \frac{1}{\hbar^2} \right) (P^2 - P_{z1}^2)
+ \frac{\hbar c}{2} \left( w_1 \left( \frac{p_{1x}^2}{\hbar^2} + q_{1x}^2 \right) + w_2 \left( \frac{p_{2a}^2 + p_{2b}^2}{\hbar^2} + q_{2a}^2 + q_{2b}^2 \right) \right)
+ w_3 \left( \frac{p_3^2}{\hbar^2} + q_{3x}^2 \right)
\]

(114)

\[
H_1 = 2\hbar c B_0 q_3 \left( \frac{1}{\hbar^2} \right) (P^2 - P_{z1}^2)
+ \frac{\hbar c}{2} \left\{ K_{111}q_{13}^3 + K_{122}q_1(q_{2a}^2 + q_{2b}^2) + K_{133}q_1q_{3x}^2 \right\}
+ \frac{\epsilon}{2} \frac{\hbar c w_1}{\hbar^2} \left( \rho_{x1} p_{x1} + \rho_{y1} p_{y1} + p_{x1} \rho_{x1} + p_{y1} \rho_{y1} \right)
- \frac{\hbar c w_1}{\hbar^2} \frac{P_{1x}}{\hbar^2}
\]

(115)

\[
H_2 = 3\hbar c B_0 q_3 \left( \frac{1}{\hbar^2} \right) (P^2 - P_{z1}^2)
+ \frac{\hbar c}{2} \left\{ K_{1111}q_{14}^4 + K_{1122}q_1(q_{2a}^2 + q_{2b}^2) + K_{1133}q_1q_{3x}^2 \right\}
+ K_{2222}(q_{2a}^2 + q_{2b}^2)^2 + K_{3333}q_3^4 + K_{3332}q_3(q_{2a}^2 + q_{2b}^2)
+ \frac{\hbar c w_1 \epsilon q_1}{\hbar^2} \left( \rho_{x1} p_{x1} + \rho_{y1} p_{y1} + p_{x1} \rho_{x1} + p_{y1} \rho_{y1} \right)
- \frac{\hbar c w_1 q_1}{\hbar^2} \frac{P_{1x}}{\hbar^2} + \frac{\hbar c w_1}{\hbar^2} \frac{1}{\hbar^2} \left( \rho_{x1}^2 + \rho_{y1}^2 \right)
\]

(116)

[Cf. p. 96 of (37); (48: - 52)]

In this treatment, only the terms in $E_1$ will be studied as to

their effects on the zero order intensities.
The Contact Transformation

$H_1$ can be expressed as

$$H_1 = \sum_k H_{1k}$$  \hfill (117)

where

$$H_{11} = 2\hbar c B_1 \frac{1}{\hat{\lambda}^2} (\hat{p}_1^2 - \hat{p}_0^2)$$  \hfill (118)

$$H_{12} = \hbar c K_{11} q_1$$  \hfill (119)

$$H_{13} = \hbar c K_{123} q_2$$  \hfill (120)

$$H_{14} = \hbar c K_{123} q_3$$  \hfill (121)

$$H_{15} = \hbar c K_{133} q_3$$  \hfill (122)

$$H_{16} + \ldots + H_{1,13} = - \frac{\hbar c}{\lambda} \left( P_x P_x + P_y P_y + \frac{\hbar c}{\lambda} P_x P_y \right)$$  \hfill (123)

i.e., $H_{16} = \varepsilon \frac{1}{2} \hbar c \omega_1 \frac{1}{\hat{\lambda}^2} \sqrt{\frac{\omega_2}{\omega_3}} \Delta_{q_2 b} P_{x1}$ (See p. 46)  \hfill (124)

$$H_{17} = - \varepsilon \frac{1}{2} \hbar c \omega_1 \frac{1}{\hat{\lambda}^2} \sqrt{\frac{\omega_3}{\omega_2}} \Delta_{q_2 b} P_{y1}$$  \hfill (125)

$$H_{18} = - \varepsilon \frac{1}{2} \hbar c \omega_1 \frac{1}{\hat{\lambda}^2} \sqrt{\frac{\omega_2}{\omega_3}} \Delta_{q_2 a} P_{y1}$$  \hfill (126)

$$H_{19} = \varepsilon \frac{1}{2} \hbar c \omega_1 \frac{1}{\hat{\lambda}^2} \sqrt{\frac{\omega_3}{\omega_2}} \Delta_{q_2 a} P_{y1}$$  \hfill (127)

$$H_{1,10} = \varepsilon \frac{1}{2} \hbar c \omega_1 \frac{1}{\hat{\lambda}^2} \sqrt{\frac{\omega_2}{\omega_3}} P_{x1} \Delta_{q_2 b}$$  \hfill (128)

$$H_{1,11} = - \varepsilon \frac{1}{2} \hbar c \omega_1 \frac{1}{\hat{\lambda}^2} \sqrt{\frac{\omega_3}{\omega_2}} P_{x1} \Delta_{q_2 b}$$  \hfill (129)
Recall that the $S$-function of the contact transformation

\[ T = e^{iLS} \]

can be expressed as

\[ S = \sum_k S_k \]

so that

\[ H_1^k = \sum_k H_1^k = \sum_k \left\{ H_1^k + i \left[ S_k, H_0 \right] \right\} \]

(See p. 25.)

For each $H_{1k}$, we wish to find $S_k$ so that

\[ H_{1k} + i \hbar \Sigma_k \frac{1}{n^2} \left[ S_{k^*} (\mathbf{p}^2 - P_{k^*}^2) \right] + i \hbar \Sigma_k \frac{1}{n^2} \left[ S_{k^*} \left( \frac{P_1}{n^2} + q_f \right) \right] + i \hbar \Sigma_k \frac{1}{n^2} \left[ S_{k^*} \left( \frac{P_2}{n^2} + q_b \right) \right] + i \hbar \Sigma_k \frac{1}{n^2} \left[ S_{k^*} \left( \frac{P_3}{n^2} + q_3 \right) \right] \]

= 0 or has only diagonal zero order wave function matrix elements.

(135)

In verifying our $S_k$-functions, use will be made of the readily derived relation...
where \(\alpha, \beta, \gamma\) are operators.

Let us consider the \(H_{1k}\) in turn, and, with the aid of Table 4 on p. 27, find the appropriate \(S_{k}\)-functions.

\[
H_{11} = 2\hbar c \varepsilon q_{1} \frac{1}{\hbar^{2}} (p^{2} - p_{z}^{2}) .
\]

Table 4 indicates that we try

\[
S_{1} = -\varepsilon^{2} \frac{1}{\hbar^{2}} (p^{2} - p_{z}^{2}) \frac{P_{1}}{\hbar} ,
\]

for which

\[
\frac{i\hbar}{2} \text{hom}_{1} \left[ S_{1}, \left( \frac{P_{1}^{2}}{\hbar^{2}} + q_{1}^{2} \right) \right] = -H_{11} .
\]

From Equation (136),

\[
\left[ S_{1}, (p^{2} - p_{z}^{2}) \right] = -\varepsilon^{2} \frac{1}{\hbar^{2}} \left\{ (p^{2} - p_{z}^{2}) \left[ p_{1}, (p^{2} - p_{z}^{2}) \right] + \left[ (p^{2} - p_{z}^{2}), (p^{2} - p_{z}^{2}) \right] p_{1} \right\} = 0 .
\]

Also,

\[
\left[ S_{1}, \left( \frac{p_{2a}^{2} + p_{2b}^{2}}{\hbar^{2}} + q_{2a}^{2} + q_{2b}^{2} \right) \right]
\]

\[
= -\varepsilon^{2} \frac{1}{\hbar^{4}} \frac{1}{r} \left[ \left( \frac{2}{d/d\gamma} \frac{1}{d/d\gamma} \right), \left( -\frac{2}{d/d\gamma} - \frac{1}{r} \frac{2}{d/d\gamma} - \frac{2}{d/d\gamma} \frac{1}{r} + r^{2} \right) \right] = 0 ,
\]

since

\[
(p^{2} - p_{z}^{2}) = -\varepsilon^{2} \left( \frac{2}{d/d\gamma} \frac{1}{d/d\gamma} + \frac{2}{d/d\gamma} \frac{1}{d/d\gamma} - \frac{2}{d/d\gamma} \frac{1}{d/d\gamma} \right) . \quad (138)
\]

(See Appendix III.) The remaining commutators in Equation (135) for \(k = 1\) are readily seen to be zero due to the mutual independence of the normal coordinates. Hence, the \(S_{1}\) given by Equation (137) is satisfactory.
\[ E_{12} = \hbar c E_{111} q_1^2 \]

for which, from Table 4, the readily verifiable \( S_2 \) is

\[
S_2 = -\frac{2K_{111}}{\omega_1} \left\{ \frac{1}{\mathfrak{m}^3} P_1^3 + \frac{1}{\mathfrak{m}^4} q_1 P_1 q_1 \right\} \quad \text{(139)}
\]

\[ E_{13} + E_{14} = \hbar c E_{122} q_1 (\sigma_2 a + \sigma_2 b) \]

so Table 4 indicates that we try

\[
S_3 + S_4 = -\frac{K_{122}}{\omega_1 (4\omega_2^2 - \omega_1^2)} \left\{ \frac{(2\omega_2^2 - \omega_1^2)(\sigma_2 a + \sigma_2 b) P_1}{\mathfrak{m}^4} \right. \\
+ \omega_2\omega_1 \frac{1}{\mathfrak{m}^3} (P_3 a q_2 a + q_2 a P_3 a + P_3 b q_2 b + q_2 b P_3 b) q_1 \\
\left. + 2\omega_2 \frac{1}{\mathfrak{m}^2} (P_3 a + P_3 b) q_1 \right\} \quad \text{(140)}
\]

If this \( S_3 + S_4 \), which is readily seen to commute with

\[ \frac{P_3^2}{\mathfrak{m}^2} + \sigma_3^2 \]

also commutes with \( P^2 - P_z^2 \) given by Equation (138), it will be satisfactory. \( (\sigma_2 a + \sigma_2 b) = r^2 \) is not a function of \( \mathfrak{m} \) and thus commutes with \( P^2 - P_z^2 \).

\[
(P_3 a q_2 a + q_2 a P_3 a + P_3 b q_2 b + q_2 b P_3 b) = -2i\mathfrak{m} (1 + r \frac{2}{\mathfrak{m}r}) \quad \text{(141)}
\]

not a function of \( \mathfrak{m} \), certainly commutes with \( P^2 - P_z^2 \).

\[
(P_3 a + P_3 b) = -r^2 \left( \frac{2}{\mathfrak{m}r^3} + \frac{i}{\mathfrak{m}} \frac{2}{\mathfrak{m}r} + \frac{1}{\mathfrak{m} r^3} \frac{2}{\mathfrak{m} r^3} \right) \quad \text{(142)}
\]

is also seen to commute with \( P^2 - P_z^2 \). Hence, \( S_3 + S_4 \) given by Equation (140) is satisfactory, as it makes

\[
\frac{E_1^1}{13} + \frac{E_1^1}{14} = 0.
\]
\[ H_{15} = \hbar \omega_{3} q_{1} q_{3} \]

No difficulty is experienced by having

\[
S_5 = - \frac{K_{133}}{w_1(w_3 - w_2)} \left\{ (2w_3^2 - w_1^2)q_3^2 p_1 \right. \\
\left. + w_3 w_1 \frac{1}{n} (p_3 q_3 + q_3 p_3) q_1 + 2w_2 \frac{1}{n^2} p_3^2 p_1 \right\} . \tag{143}
\]

\[ H_{16} + \ldots + H_{113} = - \frac{1}{2} \hbar \omega_1 \frac{1}{n^2} \left( \partial_x \partial_x^* + \partial_y \partial_y^* + P_x \partial_x^* + P_y \partial_y^* \right) \]

\[
= - \frac{\hbar \omega_1}{2n^2} \left\{ \left( \sqrt{\frac{w_3}{w_2}} q_3 p_2 a + \sqrt{\frac{w_3}{w_2}} q_3 p_3 b \right) P_x^* \\
+ \left( \sqrt{\frac{w_3}{w_2}} q_3 p_2 a + \sqrt{\frac{w_3}{w_2}} q_3 p_3 b \right) P_y^* \\
+ P_x^* \left( \sqrt{\frac{w_3}{w_2}} q_3 p_2 a - \sqrt{\frac{w_3}{w_2}} q_3 p_3 b \right) \\
+ P_y^* \left( \sqrt{\frac{w_3}{w_2}} q_3 p_2 a - \sqrt{\frac{w_3}{w_2}} q_3 p_3 b \right) \right\} . \tag{144}
\]

We are tempted, after looking at Table 4, to try the S-function,

\[
S_6 + \ldots + S_{13} = - \frac{1}{2} \hbar \omega_1 \frac{w_1}{(w_3 - w_2)^2} \left\{ \left( \frac{w_3}{w_2} + \frac{w_3}{w_2} \right) \right. \\
\left. \left( \frac{w_3}{w_2} + \frac{w_3}{w_2} \right) q_3 p_3 b + 2 \sqrt{\frac{w_3}{w_2}} \frac{p_3 p_3 b}{n^2} \right) P_x^* \frac{p_x^*}{n} \\
- \left( \frac{w_3}{w_2} + \frac{w_3}{w_2} \right) q_3 p_3 b + 2 \sqrt{\frac{w_3}{w_2}} \frac{p_3 p_3 b}{n^2} \right) P_y^* \frac{p_y^*}{n} \\
+ P_x^* \left( \frac{w_3}{w_2} + \frac{w_3}{w_2} \right) q_3 p_3 b + 2 \sqrt{\frac{w_3}{w_2}} \frac{p_3 p_3 b}{n^2} \right) \\
- P_y^* \left( \frac{w_3}{w_2} + \frac{w_3}{w_2} \right) q_3 p_3 b + 2 \sqrt{\frac{w_3}{w_2}} \frac{p_3 p_3 b}{n^2} \right) \right\} . \tag{144}
\]
However, this $S$-function does not commute with $P^2 - P^2_{z_1}$, the commutator
\[
\left[ S_6 + \ldots + S_{13} , P^2 - P^2_{z_1} \right]
\]
giving rise to such complication in $H'_{16} + \ldots + H'_{1,13}$ that it is better to retain $H_{16} + \ldots + H_{1,13}$ in its
original form in $H'_{1}$. Later it will be shown that, for our linear
molecule, these terms have no non-vanishing off diagonal zero order
wave function matrix elements. (See p. 66.)

\[
H_{1,14} = - \hbar \omega_1 \frac{P_1}{M},
\]

and the respective $S$-function is

\[
S_{14} = - i q_1 .
\]  \hspace{1cm} (145)

Summarizing,

\[
S = \sum_k S_k
\]  \hspace{1cm} (133)

where

\[
S_1 = - \varepsilon^2 \frac{1}{m^2} \left( \frac{P^2 - P^2_{z_1}}{P_1} \right)
\]  \hspace{1cm} (137)

\[
S_2 = - \frac{2K_{111}}{\omega_1} \left( \frac{1}{m^3} P_1^3 + \frac{1}{2m} q_1 P_1 q_1 \right)
\]  \hspace{1cm} (139)

\[
S_3 + S_4 = - \frac{K_{122}}{\omega_1 (4\omega_2^2 - \omega_1^2)} \left\{ (2\omega_2^2 - \omega_1^2) (q_{za}^2 + q_{zb}^2) \frac{P_1}{\hbar} \right. 
\]

\[
\left. + \omega_2^2 \frac{1}{m^3} (p_{za} q_{za} + q_{za} p_{za} + p_{zb} q_{zb} + q_{zb} p_{zb}) q_1 
\]

\[
\left. + 2\omega_2^2 \frac{1}{m^3} (p_{za}^2 + p_{zb}^2) P_1 \right\}
\]  \hspace{1cm} (140)

\[
S_5 = - \frac{K_{133}}{\omega_1 (4\omega_2^2 - \omega_1^2)} \left\{ (2\omega_3^2 - \omega_1^2) q_3^2 \frac{P_1}{\hbar} \right. 
\]
\[ + \omega_3 \omega_1 \frac{1}{\hbar^2} (p_3 q_3 + q_3 p_3)q_1 + 2\omega_3 \frac{1}{\hbar^2} p_3 p_1 \]  \hspace{1cm} (143)

\[ S_6 + \ldots + S_{13} = 0 \]  \hspace{1cm} (146)

\[ S_{14} = -i q_1 \]  \hspace{1cm} (145)

so that

\[ H'_0 = H_0 \]  \hspace{1cm} (147)

\[ H'_1 = H_1 + \ldots + H_{1,13} \]  \hspace{1cm} (148)

**The Zero Order Wave Functions**

The zero order Hamiltonian is

\[ H_0 = H_{0_{\text{Rot.}}} + H_{0_{\text{Vib.}}} \]  \hspace{1cm} (149)

where

\[ H_{0_{\text{Rot.}}} = \hbar^2 \varepsilon_1 \frac{1}{\hbar^2} (p^2 - p_z^2) \]  \hspace{1cm} (150)

\[ H_{0_{\text{Vib.}}} = \frac{3}{2} \hbar c \left\{ \omega_1 \left( \frac{p_1^2}{\hbar^2} + q_1^2 \right) + \omega_3 \left( \frac{p_3^2}{\hbar^2} + q_3^2 \right) - \omega_2 \left( \frac{2}{r^2} + \frac{1}{r^2} + \frac{1}{r^2} \frac{2}{r^2} - \frac{5}{r^2} \right) \right\} \]  \hspace{1cm} (151)

The eigenfunctions of \( H_{0_{\text{Rot.}}} \) are of the same functional form as those for the rigid symmetric rotator whose Hamiltonian is

\[ \hbar^2 \varepsilon_1 \frac{1}{\hbar^2} (p^2 - p_z^2) + \hbar^2 \varepsilon_2 \frac{1}{\hbar^2} p_z^2 \]  .
since

\[ P_z = -i \hbar \frac{d}{dy} = P_z, \text{ and} \]

\[ P_z \text{ commutes with } P^2. \]

The Schrödinger Equation for the symmetric rotator has been treated by Dennison (53), Reiche and Rademacher (54), and Kronig and Rabi (55). (See also p. 100 of (37).) The solutions involve hypergeometric functions. W. H. Shaffer, using raising and lowering operators, has found that the normalized rigid symmetric rotator wave functions can be expressed as

\[ \psi_{0 \text{ Rot.}} = \frac{1}{2\pi} e^{iM\varphi} e^{iK\varphi} \int \frac{(J+M)!(J+K)!(2J+1)}{(J-M)!(J-K)!} \frac{1}{2^{2J-2K-2}} \frac{2J-K-M}{(2J)\Gamma} \]

\[ \times \left\{ \begin{array}{c}
\left( \sin \varphi \right)^{M-K} \left( \cos \varphi \right)^{K-M} \\
\left( \sin \varphi \right)^{M-K} \left( \cos \varphi \right)^{K-M} \end{array} \right\} (152) \]

where

\[ J = 0, 1, 2, \ldots ; \]

\[ M = J, J-1, J-2, \ldots, -J ; \]

\[ K = J, J-1, J-2, \ldots, -J. \]

(The derivation of this was given by Prof. Shaffer in the course of his presentation of Physics 351 at the Ohio State University.) We will use the notation

\[ \psi_{0 \text{ Rot.}} = F_{JKM} (\varphi) e^{iK\varphi} \sqrt{\frac{1}{2\pi}} \]

(153)
where

\[
f_{JKM}(\psi) = \frac{e^{iM\phi}}{\sqrt{2\pi}} \left( -1 \right)^J \frac{J!}{(J+K)!} \frac{1}{2^{(J+K)!}} \frac{1}{(J-K)!} \frac{1}{(2J+1)}
\]

\[
\cdot \frac{1}{(2J)!} \frac{2^{2J-K-M}}{(\sin \frac{\theta}{2})^M \left( \frac{\cos \frac{\theta}{2}}{2} \right)^{-K-M}}
\]

\[\cdot \frac{\hat{A}^{JK}}{\hat{A}(\cos \theta)^{J-K}} \left\{ \frac{\sin \frac{\theta}{2}}{(\sin \frac{\theta}{2})^J \left( \frac{\cos \frac{\theta}{2}}{2} \right)^{-M}} \right\}^{1/2}
\]

The normalized eigenfunctions of \( H_{0Vib} \) are

\[
\psi_{\text{Vib}} = \phi_{\nu_1}(q_1) \phi_{\nu_2}(q_2) R_{\nu_2} \left( r \right) \frac{1}{\sqrt{2\pi}}
\]

(155)

where

\[
\phi_{\nu_j}(q_j) = \sqrt{\frac{1}{\nu_j}} \frac{1}{\sqrt{\pi}} e^{-\frac{q_j^2}{2}} H_{\nu_j}(q_j)
\]

(156)

where \( H_{\nu_j}(q_j) \) is the \( \nu \)-th degree Hermite polynomial, which can be expressed as

\[
H_{\nu_j}(q_j) = (-1)^{\nu_j} e^{q_j^2} \frac{d^{\nu_j}}{dq_j^{\nu_j}} \left( e^{-q_j^2} \right)
\]

(157)

and \( \nu_j = 0, 1, 2, \ldots ; \)

[See Schrödinger (56); sec. 11 of (15)].

\[
R_{\nu_2} \left( r \right) = \sqrt{\frac{\lambda \left( \nu_2 - \frac{1}{2} \right)}{(\nu_2 + \nu_2 + 1/2)^2}} e^{-\frac{r^2}{2}} r^{\nu_2 + \nu_2} L_{\nu_2 + \nu_2} \left( \frac{r^2}{2} \right)
\]

(158)

where the \( L_{\frac{\nu_2 + 1/2}{2}} \) are associated Laguerre polynomials.
given by

\[ L_{\frac{k+l}{2}}^{l}(r^1) = \frac{d}{d(r^1)} L_{\frac{k+l}{2}}^{l} \left\{ e^{r^1} \frac{d}{d(r^1)} \left( r^1 \frac{d^{l}}{d(r^1)^{l}} e^{-r^1} \right) \right\} \tag{160} \]

and \( V_2 = 0, 1, 2, \ldots \); \( l_2 = V_2, V_2 - 2, V_2 - 4, \ldots, 0 \) or 1.

\[ \text{See Shaffer (57); p. 114 of Condon and Shortley (28).} \]

We will use the notation

\[ \psi_{0, \text{Vib.}} = a_{V_1 V_2 V_3, 12} \left( q_{1q3r} \right) \frac{\pm i l_2 \mathcal{Y}}{2\pi} \]

(161)

where

\[ a_{V_1 V_2 V_3, 12} \left( q_{1q3r} \right) = \phi_{V_1} \left( q_{1} \right) \phi_{V_3} \left( q_{3} \right) R_{V_2 V_3} \left( r \right) \]

(162)

One might be tempted to say that since

\[ H_0 = H_{0, \text{Rot.}} + H_{0, \text{Vib.}} \]

the zero order wave functions are

\[ \psi_0 = \psi_{0, \text{Rot.}} \psi_{0, \text{Vib.}} = \frac{\mathcal{K}(\psi_0)}{2\pi} e^{iKX} a_{V_1 V_2 V_3, 12} \left( q_{1q3r} \right) \frac{\pm i l_2 \mathcal{Y}}{2\pi} \]

However, both \( H_{0, \text{Rot.}} \) and \( H_{0, \text{Vib.}} \) are \( \frac{2}{\mathcal{Y}} \) dependent, and if this assumed solution is substituted into

\[ H_0 \psi_0 = E_0 \psi_0 = \left( E_{0, \text{Rot.}} + E_{0, \text{Vib.}} \right) \psi_0 \]
one obtains, upon dividing both sides by $\frac{G \, \v_{1v_3v_{21}2}}{\sqrt{2\pi}}$

$$\frac{1}{\frac{F}{\text{Rot.}} J K M (\psi)} (H_0 - E_0) \frac{F}{\text{Rot.}} J K M (\psi) e^{i(K+1)\gamma}$$

$$\frac{1}{\frac{F}{\text{Rot.}} J K M (\psi)} (H_0 - E_0) \frac{F}{\text{Vib.}} J K M (\psi) e^{i(K+1)\gamma}$$

$$= -\frac{1}{\frac{G_{v_1v_3v_{21}2}(q_1q_3r)}{\text{Vib.}} \frac{F}{\text{Vib.}} J K M (\psi)} (H_0 - E_0) \frac{G_{v_1v_3v_{21}2}(q_1q_3r)}{\text{Vib.}} e^{i(K+1)\gamma}$$

We are assured that the assumed solution $\psi_0$ is good only if $K + 1 = K$ and $K + 1 = 1$, i.e., $K + 1 = 0$. This is the case of no $\gamma$ angular momentum, or no bending of the molecule from its linear equilibrium configuration.

However, the functions

$$\psi_0 = \frac{G_{v_1v_3v_{21}2}(q_1q_3r)}{\text{Vib.}} e^{i(K+1)\gamma} \frac{\text{J.}}{\text{Sup.}} J K M (\psi)$$

(163)

(which are not the products $\psi_0$) are, for certain sets of values of $\{v_1, v_3, v_2, l_2, J, K\}$, eigenfunctions of our $H_0$. C.f. p. 334 of Dennison (44). Substitution of (163) into

$$H_0 \psi_0 = E_0 \psi_0 = (E_0 \text{Rot.} + E_0 \text{Vib.}) \psi_0$$

and division by $\frac{F}{\text{J.}} J K M (\psi) J K M (v_1v_3v_{21}2)$ yields
\[ \frac{1}{\mathcal{F}_{j_{1/2}M}(\Phi e)} e^{\pm i l_2 \gamma} \]

\[ \mathcal{F}_{j_{1/2}M}(\Phi e) = \mathcal{F}_{j_{1/2}}(\Phi e) \]

\[ = - \frac{1}{G_{v_1v_3v_2l_2} G_{v_1v_3v_2l_2} (q_{1q_3r})} e^{\pm i l_2 \gamma} \]

\[ \sqrt{2 \pi} \]

\begin{equation}
(164)
\end{equation}

Comparison of this expression with Equations (153) and (161) shows that the function given in Equation (163) is a good eigenfunction of \( H_0 \) for

\[ v_1 = 0, 1, 2, \ldots; \]
\[ v_3 = 0, 1, 2, \ldots; \]
\[ V_2 = 0, 1, 2, \ldots; \]
\[ J = 0, 1, 2, \ldots; \]
\[ M = J, J-1, J-2, \ldots, -J \]
\[ l_2 = \text{values consistent with both of} \]
\[ \left\{ \begin{array}{l}
(1) \ J, J-1, J-2, \ldots, -J \ 	ext{and} \\
(2) \ V_2, V_2-2, \ldots, 0 \ 	ext{or} \ 1.
\end{array} \right. \]

Thus, if the molecule is in a state with a given value of \( l_2 \), \( J \) cannot be smaller than this value, as stands to reason since \( J \) characterizes total angular momentum and \( l_2 \) the \( z \) component of internal angular momentum. The \( J, V_2, l_2 \) conditions can therefore be restated as

\[ l_2 = 0, 1, 2, \ldots \]
\[ V_2 = l_2, l_2+2, l_2+4, \ldots \]
\[ J = l_2, l_2+1, l_2+2, \ldots \]
Note also that the part
\[
G_{v_1v_3V_2}(q_1q_3r) \frac{e^{i l_2 \lambda}}{\sqrt{2\pi}}
\]
is the same as the wave function of a "non-rotating" vibrator (with vibrational internal angular momentum), except that the quantum number \( l_2 \) can never be greater than \( J \). Also note that the remaining function \( F_{Jl_2M}(\phi) \) is a symmetric rotator wave function for the rigid dumbbell rotator. \( \sqrt{3} \) See Appendix B of (20) \( \) When \( l_2 = 0 \), the molecule is distorted from linearity and is neither symmetric nor linear. The fact that our wave functions satisfy the zero order Schrödinger Equation for our problem is an ample criterion for their validity, and the form of \( F_{Jl_2M} \) for \( l_2 \neq 0 \) may be considered to be a manifestation of nonlinearity.

In our evaluation of matrix elements, the factor \( \frac{e^{i l_2 \lambda}}{\sqrt{2\pi}} \) will be kept with \( F_{Jl_2M}(\phi) \) to enable us to make use of certain properties of the symmetric rotator wave functions. Hence, in dealing with functions of \( q_1 \), \( q_3 \), and \( r \), we will need to calculate matrix elements whose wave functions are the \( G_{v_1v_3V_2l_2}(q_1q_3r) \). From the orthonormality of the set of functions
\[
\left\{ G_{v_1v_3V_2l_2}(q_1q_3r) \frac{e^{i l_2 \lambda}}{\sqrt{2\pi}} \right\}
\]
the useful relation
\[
\int G^*_{v_1v_3V_2l_2}(q_1q_3r) G_{v_1v_4V_2l_3}(q_1q_3r) d^3r = \delta_{v_1v_4} \delta_{v_3v_4} \delta_{l_2l_3} \tag{165}
\]
is readily seen. It turns out that the values of

$$G_{v_1 v_3 v_2 l_2}^* G_{v_1 v_3 v_2 l_2} \, dl_{q_1 q_2 r}$$

for $l_2 \neq l_2$

will not be needed. From Equation (165) and the orthonormality of the symmetric rotator wave functions,

$$F_{J l_2 M}(\psi) \frac{\epsilon^{i l_{12} J}}{\sqrt{2\pi}},$$

the orthonormality of the $\psi_0$ is confirmed.

For brevity throughout this work we will denote particular sets of quantum numbers as indicated below.

$$\Gamma \equiv \{ v_1 v_3 v_2 l_2 J M \}$$

(166)

$$\Gamma_1 \equiv \{ v_1 v_3 v_2 l_2 \}$$

(167)

$$\Gamma_2 \equiv \{ v_1 v_3 v_2 l_2 J \}$$

(168)

$$\Gamma_3 \equiv \{ v_1 v_3 v_2 \}$$

(169)

In summary, our zero order wave functions are

$$\psi'_{\Gamma} = G_{v_1 v_3 v_2 l_2} (q_1 q_2 r) \frac{\epsilon^{i l_{12} J}}{\sqrt{2\pi}} F_{J l_2 M}(\psi)$$

(170)

where

$$\Gamma \equiv \{ v_1 v_3 v_2 l_2 J M \} ;$$

$$v_1 = 0, 1, 2, \ldots ;$$

$$v_3 = 0, 1, 2, \ldots ;$$

$$l_2 = 0, 1, 2, 3, \ldots ;$$

$$v_2 = l_2, l_2+2, l_2+4, \ldots ;$$
\[ J = l_2, l_2 + 1, l_2 + 2, \ldots; \]
\[ M = J, J-1, J-2, \ldots, -J \]

\[ G_{v_1v_2v_3}^{212}(q_1q_3r) = \phi_{v_1}^{1}(q_1)\phi_{v_2}^{2}(q_3)R_{v_212}^{212}(r) \tag{171} \]

where

\[ \phi_{v_j}^{j}(q_j) = \left\{ \frac{1}{2^{v_j}v_j!} \right\}^{\frac{1}{2}} \frac{-q_j^2}{2} R_{v_j}^{j}(q_j) \tag{172} \]

\[ R_{v_j}^{j}(r) = \left\{ \frac{2^{v_j}v_j^2}{(v_j + l_j)!} \right\}^{\frac{1}{2}} e^{-r^2/2} r^l_j L_{v_j + l_j}^{l_j}(r^2) \tag{173} \]

where \( R_{v_j}^{j}(q_j) \) and \( L_{v_j}^{l_j}(r) \) are Hermite and associated Legendre polynomials respectively:

and

\[ F_{Jl_2M}^{Jl_2M}(\phi) = \frac{4^M}{2^M}\frac{(-1)^{J-l_2}}{(2J-1)!} \left\{ \frac{(J+1)(J+2)l_2}{2J} \right\}^{\frac{1}{2}} \frac{1}{(2J)!} \]
\[ \cdot 2^{J-l_2-M}(\sin \frac{\phi}{2})^{M-l_2}(\cos \frac{\phi}{2})^{-l_2-M} \]
\[ \cdot \frac{\mathcal{A}^{J-l_2}}{\mathcal{A}(\cos \frac{\phi}{2})^{J-l_2}} \left\{ \frac{(\sin \frac{\phi}{2})^{2J-M}}{(\cos \frac{\phi}{2})^{J-M}} \mathcal{A}^{J-M}(\cos \frac{\phi}{2})^{4J} \right\} \tag{174} \]

Various possible combinations of \( \{ J, V_2, l_2 \} \) are listed in Table 6 below. It is readily seen that (a) if \( V_2 \leq J \), then \( l_2 = 0 \) or \( 1 \) and (b) if \( V_2 > J \), then

\[ l_2 = \begin{cases} 
J, J-2, \ldots, 0 \text{ or } 1 \text{ if } V_2 - J \text{ is even;} \\
J-1, J-3, \ldots, 0 \text{ or } 1 \text{ if } V_2 - J \text{ is odd.}
\end{cases} \]
### TABLE 6
Various Possible Combinations of $l_2$, $v_2$, $J$

<table>
<thead>
<tr>
<th>$l_2$</th>
<th>$v_2$</th>
<th>$J$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0, 1, 2, 3, 4, ...</td>
</tr>
<tr>
<td>2</td>
<td>0, 1, 2, 3, 4, ...</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0, 1, 2, 3, 4, ...</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0, 1, 2, 3, 4, ...</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>...</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1, 2, 3, 4, ...</td>
</tr>
<tr>
<td>3</td>
<td>1, 2, 3, 4, ...</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1, 2, 3, 4, ...</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>1, 2, 3, 4, ...</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>...</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>2, 3, 4, 5, ...</td>
</tr>
<tr>
<td>4</td>
<td>2, 3, 4, 5, ...</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>2, 3, 4, 5, ...</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>2, 3, 4, 5, ...</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>...</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>3, 4, 5, 6, ...</td>
</tr>
<tr>
<td>5</td>
<td>3, 4, 5, 6, ...</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>3, 4, 5, 6, ...</td>
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</tr>
<tr>
<td>9</td>
<td>3, 4, 5, 6, ...</td>
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<td></td>
<td>...</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>4, 5, 6, 7, ...</td>
</tr>
<tr>
<td>6</td>
<td>4, 5, 6, 7, ...</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>4, 5, 6, 7, ...</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>4, 5, 6, 7, ...</td>
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<tr>
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<td></td>
<td>...</td>
</tr>
</tbody>
</table>
The zero order energy eigenvalues are

$$E_{0_2} = E_{0_{\text{Vib.}}} (v_1, v_3, v_2) + E_{0_{\text{Rot.}}} (J, l_2),$$

(175)

where

$$E_{0_{\text{Vib.}}} = \hbar \sigma \left\{ \omega_1 (v_1 + \frac{1}{2}) + \omega_3 (v_3 + \frac{1}{2}) + \omega_2 (v_2 + 1) \right\}$$

(176)

$$E_{0_{\text{Rot.}}} = \hbar \sigma \sigma \left\{ J(J + 1) - l_2^2 \right\}$$

(177)

See Sec. 11 of (16); (57); (44). For each $E_{0_{2}}$, it is seen that there are $2J + 1$ different values, $J, J-1, J-2, \ldots, -J$, of $M$ which specify distinct zero order wave functions.

The Transformed Wave Functions

The eigenfunctions of our transformed Hamiltonian,

$$H' = H'_{0} + H'_{1} + \ldots$$

with

$$H'_{0} = H_{0}$$

$$H'_{1} = H_{1} + \ldots + H_{1,13}$$

See p. 55 are, according to Equation (19) on p. 22.
\[ \psi^i = \psi_0^i \Gamma_2^i M + \epsilon \psi_1^i \Gamma_2^i M + \ldots \quad , \quad (178) \]

where

\[
\psi^i_{\Gamma_2^i M} = \sum_{\Gamma_2} \sum_{\Gamma_2^i M^i} \left\{ \Gamma_2^i M^i \right\}_2 \psi_{\Gamma_2^i M^i} + \sum_{\Gamma_2^i M^i} \left\{ \Gamma_2^i M^i \right\}_2 \psi_{\Gamma_2^i M^i} \quad , \quad (179) \]

where

\[
\left\{ \Gamma_2^i M^i \right\}_2 \equiv \frac{\left( \Gamma_2^i M^i \right\}_1 | H^i | \Gamma_2^i M^i \right\} \left( E_{\Gamma_2^i M^i} - E_{\Gamma_2^i M^i} \right) \quad (180) \]

\[
\left\{ \Gamma_2^i M^i \right\}_2 \equiv \sum_{\Gamma_2^i M^i} \sum_{\Gamma_2^i M^i} \frac{\left( \Gamma_2^i M^i \right\}_1 | H^i | \Gamma_2^i M^i \right\} \left( E_{\Gamma_2^i M^i} - E_{\Gamma_2^i M^i} \right) \quad (181) \]

where

\[
\mathbb{H} = H^i + \epsilon H^i + \ldots \quad (182) \]

(Recall that)

\[
\Gamma = \left\{ v \Gamma \right\}_2 \right\}_{2 J 2 M}^2 \right\} \quad , \quad \Gamma = \left\{ v \Gamma \right\}_2 \right\}_{2 J 2 M}^2 \right\} \quad , \quad (183) \]

Now

\[
\left( \Gamma_2^i M^i \right\}_1 | H^i | \Gamma_2^i M^i \right\} = \sum_{J = 6}^{13} \left( \Gamma_2^i M^i \right\}_1 | H_1 J | \Gamma_2^i M^i \right\} \quad . \quad (184) \]

All the \( H_1 J \) in the expression involve \( P_x \) or \( P_y \). (See p. 49.) In the case of \( H_{16} \),

\[
\left( \Gamma_2^i M^i \right\}_1 | H_{16} | \Gamma_2^i M^i \right\} = \epsilon \frac{\hbar c m_1}{a_0^2} \left( \frac{m_2}{a_0^2} \right)^{\frac{1}{2}} \left( \Gamma_2^i M^i \right\}_1 | q_3 p x | \Gamma_2^i M^i \right\} \quad (185) \]
\[
\mathcal{E} \sum_{\frac{1}{2}} \omega \frac{1}{2} \sum_{r} \sum_{M} (P_{r} M | q_{2} p_{ab} | P_{r} M) (P_{r} M | P_{x}^{'1} | P_{x} M')
\]

Now

\[
P_{x}^{1} = \cos \gamma P_{x} - \sin \gamma P_{y} \tag{183}
\]

(and \(P_{y}^{1} = \sin \gamma P_{x} + \cos \gamma P_{y}\)) \tag{184}

(See Appendix III.) The matrix elements of \(P_{x}^{1}\) (and \(P_{y}^{1}\)) can be obtained from those of \(P_{x}, P_{y}, \cos \gamma, \sin \gamma\) by means of the product rule. Recall that the \(\gamma\) portion of our wave functions are of the same functional form as symmetric rotator wave functions, with the usual quantum number \(K\) being replaced by our \(L_{z}\). The non-vanishing symmetric rotator wave function matrix elements of \(P_{x}\) and \(P_{y}\), which depend only on \(\gamma, \epsilon, \) and \(\gamma\) are well known to be given by

\[
(J \delta M | P_{x} | J \delta K, M) = \pm \frac{1}{2} \frac{1}{h} \left[(J + 1, M, K) \right].
\]

(See, for example, p. 101 of Nielsen, (37).) The non-vanishing matrix elements of \(P_{x}\) and \(P_{y}\) in our case then appear to be

\[
(J \delta K | P_{x} | J \delta L_{z}, \pm 1) = \pm \frac{1}{2} \frac{1}{h} \left[(J + 1, L_{z}, J) \right].
\]

However, our wave functions are such that

\[
L_{z} = \text{values consistent with both of}
\]

\[
\begin{cases}
(1) & J, J-1, \ldots, -J \\
(2) & V, V-2, \ldots, 0 \text{ or } 1.
\end{cases}
\]

If state \((L_{z}, L_{z})\) exists, then states \((L_{z}, L_{z} \pm 1)\) cannot exist, and vice versa. This leads to there being no non-vanishing matrix
elements of \( P_x \) and \( P_y \), and hence of \( H_1' \). \( \sqrt{\psi_0} \) f. p. 104 of (37).

If \( H_1' \) has no off diagonal matrix elements, the off diagonal \( \{ \gamma_2M | \gamma_2M' \} \) and \( \{ \gamma_2M || \gamma_2M' \} \) are zero, and from Equation (179) on page 66, \( \psi_1'_{\gamma_2M} = 0 \). Our transformed wave functions then become \( \psi_0'_{\gamma_2M} \) for first order calculations.

**The Transformed Electric Dipole Moment**

According to the theory of the third section of Chapter II, one can obtain the \( \langle \Gamma | M'_{\nu'} | \gamma' \rangle \) to first order by calculating the zero order wave function matrix elements of the transformed electric dipole moment component combinations

\[
M'_{\nu'} = e^{-iS} M_{\nu'} e^{iS},
\]

providing the transformed wave functions are the zero order wave functions to first order. Recall that \( M'_{\nu'} \) can be represented to first order as

\[
M'_{\nu'} = M_{\nu'} + \epsilon i \left[ S, M_{\nu'} \right]
\]

(see p. 28), and that our \( S \) can be expressed as the sum

\[
S = \sum_j S_j
\]

where the respective \( S_j \) are given on pp. 54–55. Therefore
\[ M'_{\gamma} = M_{\gamma} + \epsilon i \sum_j [S_j, M_{\gamma}] \]

Also,
\[ M_{\gamma} = \mathcal{M}_{(q_{1q3})} A_{\gamma}(q \cdot \lambda) + \mathcal{M}^{(q_{1q3})} A_{\gamma}(q \cdot \lambda) \]

where \( \mathcal{M}_{(q_{1q3})}, \mathcal{M}^{(q_{1q3})}, A_{\gamma}(q \cdot \lambda) \),

and \( A_{\gamma}(q \cdot \lambda) \) are given on pages 43 to 45. Hence,
\[ M'_{\gamma} = \mathcal{M}_{(q_{1q3})} A_{\gamma}(q \cdot \lambda) \]
\[ + \epsilon i \sum_j [S_j, \mathcal{M}_{(q_{1q3})} A_{\gamma}(q \cdot \lambda)] + \ldots \]
\[ + \mathcal{M}^{(q_{1q3})} A_{\gamma}(q \cdot \lambda) \]
\[ + \epsilon i \sum_j [S_j, \mathcal{M}^{(q_{1q3})} A_{\gamma}(q \cdot \lambda)] + \ldots \quad (185) \]

In obtaining the \([S_j, \mathcal{M}_{\gamma}^{(q_{1q3})}]\) and \([S_j, \mathcal{M}^{(q_{1q3})}_{\gamma}]\), use was made of

the fact that if \( \alpha, \beta, A, \) and \( B \) are operators such that
\[ [\alpha, B] = 0 \] and \[ [\beta, A] = 0, \]

then
\[ [\alpha A, \beta B] = \alpha \beta [A, B] + \alpha [\beta, A] B A \quad (186) \]
\[ = \beta \alpha [A, B] + \beta [\alpha, B] A B \quad (187) \]

For the \( S_j \) given on pages 54 and 55, the \([S_j, \mathcal{M}_{\gamma}^{(q_{1q3})}]\) and \([S_j, \mathcal{M}^{(q_{1q3})}_{\gamma}]\) were found to be the following:
\[ [S_1, \mathcal{M}_{\gamma}^{(q_{1q3})}] = -\epsilon^2 \left( \frac{\mathcal{M}_{(q_{1q3})}}{m} \frac{1}{r} \right) \left[ p^2 - p_z^2, A_{\gamma} \right] \]
\[ s_2, m^\perp / \gamma \] = - \frac{2a_1}{\omega_1} \left\{ \frac{1}{3\hbar^3} \left[ \frac{p_3^2}{\hbar^2} - \frac{\partial^2}{\partial r^2} \right], m^\perp / \gamma \right\} (189) \\
\left[ s_3 + s_4, m^\perp / \gamma \right] = \frac{a_2}{\omega_1(4\omega_3^2 - \omega_2^2)} \left\{ (2w_3^2 - w_1^2) \right. \\
\left. + \frac{1}{\hbar^2} \left[ p_1, m^\perp / \gamma \right] - 2im_1\omega_2 q_1 \left[ \frac{\partial}{\partial r}, m^\perp / \gamma \right] \right\} (190) \\
\text{Making use of relation (141) on p. 52} \\
\left[ s_5, m^\perp / \gamma \right] = \frac{a_3}{\omega_1(4\omega_3^2 - \omega_2^2)} \left\{ (2w_3^2 - w_1^2) \right. \\
\left. + \frac{1}{\hbar^2} \left[ p_1, m^\perp / \gamma \right] + \omega_1\omega_3 q_1 \frac{1}{\hbar^2} \left[ p_3 q_3 + q_3 p_3, m^\perp / \gamma \right] \right\} (191) \\
\left[ s_6 + \ldots + s_{13}, m^\perp / \gamma \right] = 0 (192) \\
\left[ s_{14}, m^\perp / \gamma \right] = 0 (193) \\
\left[ s_1, m^\parallel / \gamma \right] = - \varepsilon^2 \left\{ m^\parallel \frac{p_1}{\hbar^2} \frac{1}{\hbar^2} \left[ \frac{p_3^2}{\hbar^2} - \frac{\partial^2}{\partial z^2}, \lambda / \gamma \right] \right. \\
\left. + \frac{1}{\hbar^2} \left[ p_1, m^\parallel \right] \frac{1}{\hbar^2} \left( \frac{p^2}{\hbar^2} - \frac{\partial^2}{\partial z^2} \right) / \gamma \right\} (194) \\
\left[ s_2, m^\parallel / \gamma \right] = - \frac{2a_1}{\omega_1} \left\{ \frac{1}{3\hbar^3} \left[ \frac{p_3^2}{\hbar^2}, m^\parallel / \gamma \right] \lambda / \gamma \right. \\
\left. + \frac{1}{\hbar^2} \left[ p_1, m^\parallel \right] \frac{1}{\hbar^2} \left( \frac{p^2}{\hbar^2} - \frac{\partial^2}{\partial z^2} \right) / \gamma \right\} (194) \\
\left[ s_3 + s_4, m^\parallel / \gamma \right] = \frac{a_2}{\omega_1(4\omega_3^2 - \omega_2^2)} \left\{ (2w_3^2 - w_1^2) \right. \\
\left. + \frac{1}{\hbar^2} \left[ p_1, m^\parallel / \gamma \right] - 2im_1\omega_2 q_1 \left[ \frac{\partial}{\partial r}, m^\parallel / \gamma \right] \right\} (190) \\
\text{Making use of relation (141) on p. 52}
\[
\begin{align*}
\left[ s_3 + s_{14}, m^H \lambda_\gamma \right] &= -\frac{a_2}{w_1(\lambda w_3 - w_2^2)} \left\{ (2w_3^2 - w_2^2) \\
& \cdot r \frac{1}{2} \left[ p_1, m^H \right] \lambda_\gamma - 2w_2 w_3 q_1 \left[ r \frac{1}{2}, m^H \right] \lambda_\gamma \\
& + 2w_2 \frac{1}{2} \left[ p_1 (p_{2a} + p_{2b}), m^H \right] \lambda_\gamma \right\} \\
\left[ s_6 + \ldots + s_{13}, m^H \lambda_\gamma \right] &= 0 \\
\left[ s_{14}, m^H \lambda_\gamma \right] &= 0
\end{align*}
\]

Hence, the transformed electric dipole moment component combinations \( M^{1'}_\gamma \) can be expressed as follows:

\[
M^{1'}_\gamma = \mu_1 (q_{1s2r} p_{1s2} \frac{2}{2r}) \lambda_\gamma (\phi \phi) + \mu_2 (q_{1s2r} p_1) \frac{1}{2} \left[ p^2 - \frac{p_z^2}{2}, \lambda_\gamma (\phi \phi) \right] + \mu_3 (q_{1s2r} p_1) \frac{1}{2} \left[ p^2 - \frac{p_z^2}{2}, \lambda_\gamma (\phi \phi) \right] + \mu_4 \frac{1}{2} \left[ p_1 (p_{2a} + p_{2b}), m^H (q_{1s2r}) \lambda_\gamma (\phi \phi) \right] + \ldots
\]

\[
+ \mu_1 (q_{1s2r} p_{1s2} \frac{2}{2r}) \lambda_\gamma (\phi \phi)
\]
\[
+ \mu_1' (q_1 g_3 r P_1) \frac{1}{h^2} (p_1 - p_2^2) I H (\gamma \otimes \gamma) \\
+ \mu_1 (q_1 g_3 r P_1) \frac{1}{h^2} \left[ p_1^2 - p_2^2, \langle \gamma \otimes \gamma \rangle \right] \\
+ \mu_4 \frac{1}{h^2} \left[ p_1^2 (p_1^2 + p_2^2), \langle q_1 g_3 \rangle \langle \gamma \otimes \gamma \rangle \right] + \ldots \quad (200)
\]

where

\[
\mu_1 (q_1 g_3 r P_1 P_3 \frac{n}{r}) = m_H (q_1 g_3 r) - \epsilon i \left\{ A_{11} \frac{1}{h^2} [p_1^2, m] \\
+ A_{12} \frac{1}{h^2} [q_1 P_1 q_1, m] + A_{13 r^2} \frac{1}{h^2} [p_1, m] \\
+ A_{14} \frac{1}{h^2} [p_1, m] - A_{15 q_1} [r \frac{\partial q_1}{\partial r}, m] \\
+ A_{16 q_1} \frac{1}{h^2} [p_1 q_3 + q_3 P_3, m] \\
+ A_{17} \frac{1}{h^2} [p_1 p_3, m] \right\} \quad (201)
\]

\[
\mu_2 (q_1 g_3 r P_1) = -i \epsilon^3 \frac{1}{h^2} [p_1, m] \quad (202)
\]

\[
\mu_3 (q_1 g_3 r P_1) = -i \epsilon^3 m^H \frac{p_1}{h} \quad (203)
\]

\[
\mu_4 = -i \epsilon A_{11} \quad (204)
\]

\[
\mu_1' (q_1 g_3 r P_1 P_3 \frac{n}{r}) = m^H (q_1 g_3 r) - \epsilon i \left\{ A_{11} \frac{1}{h^2} [p_1^2, m^H] \\
+ A_{12} \frac{1}{h^2} [q_1 P_1 q_1, m^H] + A_{13 r^2} \frac{1}{h^2} [p_1, m^H] \\
+ A_{14} \frac{1}{h^2} [p_1, m^H] - A_{15 q_1} [r \frac{\partial q_1}{\partial r}, m^H] \\
+ A_{16 q_1} \frac{1}{h^2} [p_1 q_3 + q_3 P_3, m^H] \right\}
\]
\[ + A_{17} \frac{1}{\hbar^3} \left[ p_1 p_2^3, m_{\perp L} \right] \]  

(205)

\[ \mu_2(q_1 q_2 p_1) = -i \varepsilon^3 \frac{1}{\hbar} \left[ p_1, m_{\perp L} \right] \]  

(206)

\[ \mu_3(q_1 q_2 p_1) = -i \varepsilon^3 m \frac{p_1}{\hbar} \]  

(207)

\[ \mu_4 = -i \varepsilon A_{41} \]  

(208)

where

\[ A_{11} = \frac{2k_{111}}{3w_1} \quad A_{15} = \frac{2k_{122}w_2}{(4w_2^2 - w_1^2)} \]

\[ A_{12} = \frac{k_{111}}{w_1} \quad A_{16} = \frac{k_{133}w_3}{(4w_3^2 - w_1^2)} \]

\[ A_{13} = \frac{k_{122}(2w_2^2 - w_1^2)}{w_1 (4w_2^2 - w_1^2)} \quad A_{17} = \frac{2k_{133}w_3^2}{w_1 (4w_3^2 - w_1^2)} \]

\[ A_{14} = \frac{k_{133}(2w_3^2 - w_1^2)}{w_1 (4w_3^2 - w_1^2)} \quad A_{41} = \frac{2k_{122}w_2^2}{w_1 (4w_2^2 - w_1^2)} \]

(209)

where, it is to be recalled, \( k_{111}, k_{122}, \) and \( k_{133} \) are cubic anharmonic potential function constants going with \( q_1^3, q_1 q_2^2 a \) or \( q_1 q_2^2 b, \) and \( q_1 q_3^2 \) respectively. We retain \( \mu_2, \mu_3, \mu_4, \) and \( \mu_4^* \) involving \( \varepsilon^3 \) to note their effect.

We see that \( \mu_4 \lambda_{\gamma} \) and \( \mu_4^* \lambda_{\gamma} \) contain, in addition to the original untransformed dipole moment component combinations \( m \lambda_{\gamma}^* \)}
and $M_{\perp}\Lambda_\gamma$, terms resulting from commutators involving $S_2$, $S_3 + S_4$, and $S_5$, which go with the cubic anharmonic terms $H_{12}$, $H_{13} + H_{14}$, and $H_{15}$ in the first order Hamiltonian.

$$\mu_2 \frac{1}{\hbar^2} (p^2 - z^2) \Lambda_\gamma$$

$$\mu_2 \frac{1}{\hbar^2} (p^2 - z^2) \Lambda_\gamma$$

$H_{11} = 2\hbar c B_e q_1 (p^2 - z^2) / \hbar^2$

in $H_1$. (Recall that $p_z = p_z$.)

The terms

$$\mu_1 \frac{1}{\hbar^3} \left[ p_1 (p_2^2 + p_3^2), M_{\parallel} \Lambda_\gamma \right]$$

and

$$\mu_1 \frac{1}{\hbar^3} \left[ p_1 (p_2^2 + p_3^2), M_{\perp} \Lambda_\gamma \right]$$

are seen to enter due to the cubic anharmonic terms

$$H_{13} + H_{14} = \hbar c K_{12a} q_1 (q_{2a}^2 + q_{2b}^2) = \hbar c K_{12a} q_1 r.$$  

$M_{\parallel}$ and $M_{\perp}$ are expanded in terms of the normal coordinates as indicated by Equations (91) and (92) on page 43. If cubic and higher terms are neglected, 

$$M_{\parallel} = \Theta_{3a} q_3 + C_{3a} q_3^2 + C_{1a} q_3 + C_{2a} q_3^2,$$  

(210)
and

\[ m^\perp = \Theta_2 r + C_{22} r^2 + C_{12} q_1 + C_{32} q_3 \]  

(211)

In finding the commutators involving \( m^\parallel \) and \( m^\perp \), use is made of the commutation properties of the normal coordinates and associated momenta. (See Appendix IV.) For the \( m^\parallel \) and \( m^\perp \) given in Equations (210) and (211) these commutators become

\[
\frac{1}{\hbar^2} \left[ p_1^2, m^\parallel \right] = -3i C_{13} \frac{1}{\hbar^2} p_1^2 q_3
\]

\[
\frac{1}{\hbar} \left[ q_1 p_1, m^\parallel \right] = -i C_{13} q_2 q_3
\]

\[
\frac{1}{\hbar} \left[ p_1, m^\parallel \right] = -i C_{13} q_3
\]

\[
\left[ r \frac{d}{dr}, m^\parallel \right] = C_{23} r q_3
\]

\[
\frac{1}{\hbar} \left[ p_3 q_3 + q_3 p_3, m^\parallel \right] = -2i (\Theta_3 q_3 + 2C_{33} q_3^2 + C_{13} q_1 q_3 + C_{23} r q_3)
\]

\[
\frac{1}{\hbar^2} \left[ p_1 p_3, m^\parallel \right] = -2i (\Theta_3 \frac{1}{\hbar^2} p_1 p_3 + C_{33} \frac{1}{\hbar^2} p_1 \{ p_3 q_3 + q_3 p_3 \}
\]

\[
+ C_{13} \frac{1}{\hbar^2} p_1 q_1 p_3 + \frac{i}{2} C_{13} \frac{1}{\hbar^2} q_3 p_3^2
\]

\[
+ C_{23} r p_1 p_3)
\]

\[
\frac{1}{\hbar^2} \left[ p_1^2, m^\perp \right] = -3i C_{13} \frac{1}{\hbar^2} p_1^2
\]

\[
\frac{1}{\hbar} \left[ q_1 p_1, m^\perp \right] = -i C_{13} q_2^2
\]
\[
\frac{1}{\hbar} \left[ p_1, m^\perp \right] = -i C_{12r}
\]
\[
\frac{1}{\hbar} \left[ \frac{\partial}{\partial r}, m^\perp \right] = B_{2r} + 2 C_{23q^2} + C_{12r} q_1 + C_{23r} q_3
\]
\[
\frac{1}{\hbar} \left[ p_{3q^3} + q_{3p}, m^\perp \right] = -2i C_{32r} q_3
\]
\[
\frac{1}{\hbar} \left[ p_{1p^2}, m^\perp \right] = -i C_{12r} \frac{1}{\hbar^2} p_3^2 - 2i C_{32r} \frac{1}{\hbar^2} p_{1p^3}
\]

Thus, from the definitions of the \( \mu_1 \)'s and \( \mu_1^\perp \)'s,

\[
\mu_1 = B_{3q^3} + C_{33q^3} + C_{13q_1q_3} + C_{23r} q_3
\]

\[
= -\varepsilon \left\{ 3A_{11} C_{13} \frac{1}{\hbar^2} p_3^2 q_3 + A_{13} C_{13} q_3^2 + A_{13} C_{13} r^2 q_3
\]

\[
+ A_{14} C_{13} q_3^2 - A_{15} C_{23} r q_3 + 2 A_{16} \left[ B_{3} q_3 q_3
\]

\[
+ 2 C_{33q_1q_3} + C_{13q_1q_3} + C_{23r} q_3 \right] \right. \left. + 2 A_{17} \left[ B_{3} \frac{1}{\hbar^2} p_{1p^3} + C_{33} \frac{1}{\hbar^2} p_1 (p_{3q^3} + q_{3p})
\]

\[
+ C_{13} \frac{1}{\hbar^2} p_{1p^3} + \frac{1}{2} C_{13} \frac{1}{\hbar^2} q_{3p^3}
\]

\[
+ C_{23r} p_{1p^3} \right) \right\} \right\}
\]

\[
\mu_2 = -\varepsilon \frac{3}{4} C_{13q_3}
\]

\[
\mu_3 = -\varepsilon \frac{3}{4} \left\{ (B_{3q_3} + C_{33q^3} + C_{23r} q_3) \frac{1}{\hbar} p_1
\]

\[
+ C_{13} \frac{1}{\hbar} q_{1p^3} q_3 \right\} \right\}
\]
\[ \mu_1 = -\varepsilon i A_{41} \] (215)

\[ \mu_1' = 3A_{11} C_{12} r + 6A_{12} C_{12} r^2 + A_{13} C_{12} r^3 + A_{14} C_{12} r_3^2 \]

\[ + A_{15} q_1 (3A_{11} C_{22} r + 6A_{12} C_{22} r^2 + A_{13} C_{22} r^3 + A_{14} C_{22} r_3^2) + A_{15} C_{12} r_3^2 \]

\[ + 2A_{16} C_{32} r_1 q_3 \]

\[ + A_{17} (C_{12} (C_{32} r + 2C_{32} r^2 + C_{32} r_3^2) + 2C_{32} r_1 q_1) \] (216)

\[ \mu_2 = -\varepsilon^3 C_{12} r \]

\[ \mu_3 = -\varepsilon^3 \left\{ (3A_{11} C_{22} r + 6A_{12} C_{22} r^2 + A_{13} C_{22} r^3 + A_{14} C_{22} r_3^2) \frac{1}{\hbar} \right\} P_1 \]

\[ + C_{12} r \frac{1}{\hbar} q_1 P_1 \} \] (217)

\[ \mu_4 = -\varepsilon i A_{41} \] (218)

Recall from Equation (200) that the transformed dipole moment combinations are given by

\[ M_{11} = \mu_1 \lambda \gamma + \mu_2 \frac{1}{\hbar^2} (P^2 - P_z^2) \lambda \gamma + \mu_3 \frac{1}{\hbar^2} \left[ P^2 - P_z^2, \lambda \gamma \right] \]

\[ + \mu_4 \frac{1}{\hbar^3} \left[ P_1 (P_{2a} - P_{2b}), \gamma \lambda \gamma \right] + ... \]

\[ + \mu_1 \lambda \gamma + \mu_2 \frac{1}{\hbar^2} (P^2 - P_z^2) \lambda \gamma + \mu_3 \frac{1}{\hbar^2} \left[ P^2 - P_z^2, \lambda \gamma \right] \]
$+ \mu_4 \frac{1}{3s} \left[ \mathbf{p}_1 (\mathbf{p}_{2a}^2 + \mathbf{p}_{2b}^2), \mathbf{M} \right] + \cdots$ 

The Matrix Elements of the Dipole Moment Combinations $\mathbf{M}$

Breakdown of the Problem

Recall that in our approximation,

$$\langle r | M_\gamma | r' \rangle = \langle r | M_\gamma | r' \rangle$$

(219)

where the integral on the left involves corrected wave functions and the integral on the right involves zero order wave functions.

(See p. 21 f.)

From the expression for $M_\gamma$ on page 71, and separation of the $q_1 q_3 r$ parts of the integrals from the $\varphi \cdot \mathbf{J}$ parts, one obtains

$$\langle r | M_\gamma | r' \rangle = \langle r_1 | \mu_1 | r_1 \rangle \langle J_{1sM} | \lambda_\gamma | J_{1sM} \rangle$$

$$+ \langle r_1 | \mu_2 | r_1 \rangle \frac{1}{n_2} \langle J_{1sM} | (P^2 - \mathbf{p}_{2}^2) \lambda_\gamma | J_{1sM} \rangle$$

$$+ \langle r_1 | \mu_3 | r_1 \rangle$$

$$\frac{1}{n_3} \langle J_{1sM} | \left[ P^2 - \mathbf{p}_{2}^2, \lambda_\gamma \right] | J_{1sM} \rangle$$

$$+ \mu_4 \frac{1}{3s} \left[ \mathbf{p}_1 (\mathbf{p}_{2a}^2 + \mathbf{p}_{2b}^2), \mathbf{M} \lambda_\gamma \right] | r' \rangle$$

$$+ \langle r_1 | \mu_1 | r_1 \rangle \langle J_{1sM} | \lambda_\gamma | J_{1sM} \rangle$$
\[ + \langle \Gamma_1 | \mu_2 | \Gamma_1 \rangle \frac{1}{n^2} \langle Jl_2M | (P^2 - \frac{P_z^2}{2}) \lambda \gamma | J'1l_2M' \rangle \\
+ \langle \Gamma_1 | \mu_3 | \Gamma_1 \rangle \frac{1}{n^2} \langle Jl_2M | [P^2 - \frac{P_z^2}{2}, \lambda \gamma] | J'1l_2M' \rangle \\
+ \mu_4 \\
\frac{1}{n^2} \langle \Gamma_1 | \left[ \mu_1 (p_{2a}^2 + p_{2b}^2), \mathcal{M}_{\lambda \gamma} \right] | \Gamma_1 \rangle + \ldots \tag{220} \]

where

\[ \Gamma = \{ v_1 v_3 v_2 l_2 j m \} \quad \text{and} \quad \Gamma_1 = \{ v_1 v_3 v_2 l_2 \} . \]

Now the non-vanishing matrix elements of \( \frac{1}{n^2} (P^2 - \frac{P_z^2}{2}) \) are the diagonal ones,

\[ \frac{1}{n^2} \langle Jl_2M | P^2 - \frac{P_z^2}{2} | Jl_2M \rangle = J(J + 1) - \frac{1}{2} \tag{221} \]

(See, for example, p. 101 of (37).) This relation and the product rule yield the non-vanishing matrix elements of the \( (P^2 - \frac{P_z^2}{2}), \lambda \gamma, \) and \( \lambda / \gamma \) combinations:

\[ \frac{1}{n^2} \langle Jl_2M | (P^2 - \frac{P_z^2}{2}) \lambda \gamma | J'1l_2M' \rangle \]

\[ = \left\{ J(J+1) - \frac{1}{2} \right\} \langle Jl_2M | \lambda \gamma | J'1l_2M' \rangle \tag{222} \]

\[ \frac{1}{n^2} \langle Jl_2M | [P^2 - \frac{P_z^2}{2}, \lambda \gamma] | J'1l_2M' \rangle \]

\[ = \left\{ J(J + 1) - \frac{1}{2} \right\} \langle Jl_2M | \lambda \gamma | J'1l_2M' \rangle \tag{223} \]
\[
\left\{ J(J + 1) - \frac{1}{2} \right\} - \left\{ J'(J' + 1) - \frac{1}{2} \right\} \left( J'_{1/2} M_{1/2} | J_{1/2} M_{1/2} \right)
\]

\[
\cdots \quad (224)
\]

\[
\frac{1}{\Xi^2} \left( J_{1/2} M \left| \begin{array}{cc}
F_2 & F_2 \\
\Lambda_{\gamma} & J_{1/2} M \end{array} \right| J_{1/2} M \right)
\]

\[
= \left\{ J(J + 1) - \frac{1}{2} \right\} - \left\{ J'(J' + 1) - \frac{1}{2} \right\} \left( J_{1/2} M | \Lambda_{\gamma} | J_{1/2} M \right)
\]

\[
\cdots \quad (225)
\]

The \( \mu_{\gamma} \) and \( \mu_{\gamma}' \) terms, which involve \( p_1, p_2 a + p_3 b, m^\|, m^\perp \).

\( \Lambda_{\gamma} \) and \( \Lambda_{\gamma}' \) are somewhat more cumbersome to deal with. From the product rule,

\[
\frac{1}{\Xi^2} \left( \Gamma_{\mu} \left| \frac{1}{F_{2a} + F_{2b}} \right| , m^\| \Lambda_{\gamma} \right) \Gamma_{\Gamma'}
\]

\[
= \sum \sum \frac{1}{\Xi} \left( \frac{\Gamma_{\mu} \Gamma_{p} \Gamma_{\Gamma''}}{\Xi} \right) \frac{1}{\Xi} \left( \frac{\Gamma_{\Gamma''} \Lambda_{\gamma} \Gamma_{\Gamma'}}{\Xi} \right) \left( \frac{\Gamma_{p} \Gamma_{m}}{\Xi} \right)
\]

\[
- \sum \sum \left( \frac{\Gamma_{\mu} \Lambda_{\gamma} \Gamma_{p} \Gamma_{m}}{\Xi} \right) \frac{1}{\Xi} \left( \frac{\Gamma_{\Gamma''} \Lambda_{\gamma} \Gamma_{\Gamma'}}{\Xi} \right) \left( \frac{\Gamma_{p} \Lambda_{\gamma} \Gamma_{\Gamma'}}{\Xi} \right)
\]

\[
= \sum \sum \left( \frac{\Gamma_{\mu} \Lambda_{\gamma} \Gamma_{p} \Gamma_{m}}{\Xi} \right) \frac{1}{\Xi} \left( \frac{\Gamma_{\Gamma''} \Lambda_{\gamma} \Gamma_{\Gamma'}}{\Xi} \right) \left( \frac{\Gamma_{p} \Lambda_{\gamma} \Gamma_{\Gamma'}}{\Xi} \right)
\]

\[
= \sum \sum \left( \frac{\Gamma_{\mu} \Lambda_{\gamma} \Gamma_{p} \Gamma_{m}}{\Xi} \right) \frac{1}{\Xi} \left( \frac{\Gamma_{\Gamma''} \Lambda_{\gamma} \Gamma_{\Gamma'}}{\Xi} \right) \left( \frac{\Gamma_{p} \Lambda_{\gamma} \Gamma_{\Gamma'}}{\Xi} \right)
\]

\[
(226)
\]

The non-vanishing \( \frac{1}{\Xi} \left( \Gamma_{\mu} | p_1 | \Gamma_{\Gamma'} \right) \) are readily seen to be

\[
\frac{1}{\Xi} \left( v_1 v_2 v_3 J M | p_1 | v_1 - 1, v_3 J_2 J M \right) = \frac{\sqrt{v_1}}{2}
\]

\[
(227)
\]

\[
\frac{1}{\Xi} \left( v_1 v_2 v_3 J M | p_1 | v_1 + 1, v_3 J_2 J M \right) = -i \frac{\sqrt{v_1 + 1}}{2}
\]

\[
(228)
\]

(See p. 172 in Appendix V.) The non-vanishing \( \frac{1}{\Xi} \left( \Gamma_{\mu} | p_2 a + p_3 b | \Gamma_{\Gamma'} \right) \) are
\[
\frac{1}{n^3} \left( v_1 v_3 V_2 V_2 JM \right| p_{2a}^2 + p_{2b}^2 \left| v_1 v_3 V_2 - 2,1_2 JM \right) = \frac{1}{2} \sqrt{(V_2 - 1_2)(V_2 + 1_2)}
\]
(229)

\[
\frac{1}{n^3} \left( v_1 v_3 V_2 V_2 JM \right| p_{2a}^2 + p_{2b}^2 \left| v_1 v_3 V_2,1_2 JM \right) = V_2 + 1
\]
(230)

\[
\frac{1}{n^3} \left( v_1 v_3 V_2 V_2 JM \right| p_{2a}^2 + p_{2b}^2 \left| v_1 v_3 V_2 + 2,1_2 JM \right) = \frac{1}{2} \sqrt{(V_2 - 1_2 + 2)(V_2 + 1_2 + 2)}
\]
(231)

(See p. 174 in Appendix V.) Also,

\[
(r \left| \mathcal{M}^H_\gamma \gamma \right| r') = (v_1 v_3 V_2 V_2 \left| \mathcal{M}^H \left| v_1 v_3 V_2 V_2 \right) \right.
\]

\[
\cdot (J_{12}^M \left| \lambda_\gamma \right| j'^{12}M')
\]
(232)

\[
(r \left| \mathcal{M}_\gamma^\perp \gamma \right| r') = (v_1 v_3 V_2 V_2 \left| \mathcal{M}_\gamma^\perp \left| v_1 v_3 V_2 V_2 \right) \right.
\]

\[
\cdot (J_{12}^M \left| \lambda_\gamma \right| j'^{12}M')
\]
(233)

where the \( \mathcal{M}^H \) and \( \mathcal{M}^\perp \) integrals involve \( q_1, q_2, \) and \( r \), and the \( \lambda_\gamma \) and \( \lambda_\gamma \) integrals involve \( \gamma, \epsilon, \) and \( \gamma' \). From Equations (226 - 233), we obtain

\[
\frac{1}{n^3} \left( r \left| \left[ p_1 (p_{2a}^2 + p_{2b}^2), \mathcal{M}^H_\gamma \gamma \right] \right. \left. r' \right) = i \left\{ \frac{\sqrt{V_1}}{2} \left[ \frac{1}{2} \sqrt{(V_2 - 1_2)(V_2 + 1_2)(V_1 - 1_2)(V_3 - 2_2,1_2)} \left| v_1 v_3 V_2 V_2 \right) \mathcal{M}^H \left| v_1 v_3 V_2 V_2 \right) \right.ight.
\]

\[
+ (V_2 + 1)(V_2 - 1_2 V_3,1_2) \mathcal{M}^H \left. \left| v_1 v_3 V_2 V_2 \right) \right.
\]

\[ + \frac{1}{2} \sqrt{(V_2 - l_2 + 2)(V_2 + l_2 + 2)} \]

\[ \cdot \langle v_1 - 1, v_3, v_2 + 2, l_2 \mid \gamma^H \mid v_1 v_3 v_2^{\dagger} \rangle \]

\[ - \sqrt{\frac{v_1 + 1}{2}} \left[ \frac{1}{2} \sqrt{(V_2 - l_2)(V_2 + l_2)} \right] \]

\[ \cdot \langle v_1 + 1, v_3, v_2 - 2, l_2 \mid \gamma^H \mid v_1 v_3 v_2^{\dagger} \rangle \]

\[ + (V_2 + 1) \langle v_1 + 1, v_3, v_2, l_2 \mid \gamma^H \mid v_1 v_3 v_2^{\dagger} \rangle \]

\[ + \frac{1}{2} \sqrt{(V_2 - l_2 + 2)(V_2 + l_2 + 2)} \]

\[ \cdot \langle v_1 + 1, v_3, v_2 + 2, l_2 \mid \gamma^H \mid v_1 v_3 v_2^{\dagger} \rangle \]
\[ \langle v_1 v_3 v_2^{1,2} \mid \gamma \mid v_1 v_3 v_2^{1,2} \rangle \]

\[ \langle J_{12} \mid J \rangle \langle J^\dagger \rangle \]

(234)

Similarly,

\[ \frac{1}{2^3} \left( \prod_{i=1}^{\ell} \left[ p_i (p_{i-1} + p_i) \right], \gamma_{1}^{\dagger} \right) \]

\[ = \frac{1}{2} \left( \sqrt{\frac{v_1}{2}} \left[ \frac{1}{2} \sqrt{(v_2 - 1) (v_2 + 1)} \right] \right) \]

\[ \left( v_1 - 1, v_3, v_2 - 2, l_2 \mid \gamma_{1}^{\dagger} \right) \left( v_1 v_3 v_2^{1,2} \rangle \right) \]

\[ + (v_2 + 1) (v_1 - 1, v_3, v_2, l_2 \mid \gamma_{1}^{\dagger} \right) \left( v_1 v_3 v_2^{1,2} \rangle \right) \]

\[ + \frac{1}{2} \sqrt{(v_2 - 1 + 2) (v_2 + 1 + 2)} \]

\[ \left( v_1 - 1, v_3, v_2 - 2, l_2 \mid \gamma_{1}^{\dagger} \right) \left( v_1 v_3 v_2^{1,2} \rangle \right) \]

\[ - \sqrt{\frac{v_1 + 1}{2}} \left[ \frac{1}{2} \sqrt{(v_2 - 1) (v_2 + 1)} \right] \]

\[ \left( v_1 + 1, v_3, v_2 - 2, l_2 \mid \gamma_{1}^{\dagger} \right) \left( v_1 v_3 v_2^{1,2} \rangle \right) \]

\[ + (v_2 + 1) (v_1 + 1, v_3, v_2, l_2 \mid \gamma_{1}^{\dagger} \right) \left( v_1 v_3 v_2^{1,2} \rangle \right) \]

\[ + \frac{1}{2} \sqrt{(v_2 - 1 + 2) (v_2 + 1 + 2)} \]

\[ \left( v_1 + 1, v_3, v_2 - 2, l_2 \mid \gamma_{1}^{\dagger} \right) \left( v_1 v_3 v_2^{1,2} \rangle \right) \]

\[ - \sqrt{\frac{v_1 + 1}{2}} \left[ \frac{1}{2} \sqrt{(v_2^i - 1) (v_2^i + 1)} \right] \]

\[ \left( v_1 v_3 v_2^{1,2} \mid \gamma_{1}^{\dagger} \right) \left( v_1 - 1, v_3, v_2 - 2, l_2 \rangle \right) \]
\begin{align*}
+ (v_3^i + 1)(v_1 v_3 v_2 | m_{\downarrow} \downarrow | v_1^i - 1, v_3 v_2, l_2^i) \\
+ \frac{1}{2} \sqrt{(v_1^i - l_2^i + 2)(v_1^i + l_2^i + 2)} \\
\cdot (v_1 v_3 v_2 | m_{\downarrow} \downarrow | v_1^i + 1, v_3 v_2 + 2, l_2^i) \\
+ \frac{\sqrt{v_1^i + 1}}{2} \left[ \frac{1}{2} \sqrt{(v_2^i - l_2^i)(v_2^i + l_2^i)} \\
\cdot (v_1 v_3 v_2 | m_{\downarrow} \downarrow | v_1^i + 1, v_3 v_2 - 2, l_2^i) \\
+ (v_2^i + 1)(v_1 v_3 v_2 | m_{\downarrow} \downarrow | v_1^i + 1, v_3 v_2, l_2^i) \\
+ \frac{1}{2} \sqrt{(v_2^i - l_2^i + 2)(v_2^i + l_2^i + 2)} \\
\cdot (v_1 v_3 v_2 | m_{\downarrow} \downarrow | v_1^i + 1, v_3 v_2 + 2, l_2^i) \right] \\
\cdot (j_{l_2^i} | \lambda \gamma | j_{l_2^i}^{1'}) \tag{235}
\end{align*}

Now \( m_{\downarrow} = \beta_{3 q_3} + c_{3 s q_3} + c_{1 a q_3} + c_{23 r q_3} \), and

\( m_{\downarrow} = \beta_{2 r} + c_{22 r^2} + c_{12 q_1 r} + c_{32 q_3 r} \).

Substitution of the first of these relations into Equation (234), separation of portions of integrals involving different normal coordinates, use of the orthonormality of the \( q_1 \) portion of the zero order wave functions, and rearrangement of terms yield

\begin{align*}
\mu_4 \frac{1}{23} (\Gamma | [ v_1 (p_{\beta a} + p_{\beta b}), m_{\downarrow} \downarrow | \lambda \gamma ] | \Gamma^i) \\
= \mu_4 (\Gamma_{1 i}) (j_{l_2^i} | \lambda \gamma | j_{l_2^i}^{1'}) \tag{236}
\end{align*}
\[ x(T_{\Delta}|T|T_{\Delta}) = \frac{x(T_{\Delta}|T_{\Delta})}{x(T_{\Delta}|T_{\Delta})} \]
\[ + (V_2 + 1)(V_{2} | 1) \left( V_{2}^{1} \left| r \right. \right) \]
\[ + \frac{1}{2} \sqrt{(V_2 - 1_2 + 2)(V_2 + 1_2 + 2)(V_2 + 2, 1_2 | r | V_{2}^{1})} \]
\[ \cdot \left[ \delta \alpha_{-1} \alpha_{i} \left( \frac{\alpha_{i}}{2} - \delta \alpha_{i+1} \alpha_{i} \left( \frac{\alpha_{i+1}}{2} \right) \right) C_{\lambda_{3}} \left( \alpha_{3} \left| q_{3} \right| \alpha_{3} \right) \right] \]
\[ + \mu_{4} \left[ \frac{1}{2} \sqrt{(V_2 - 1_2 + 1_2)(V_2 + 1_2 + 1_2)(V_{2}^{1} | r | V_2 + 2, 1_2) \right] \]
\[ + \frac{1}{2} \sqrt{(V_2 - 1_2 + 2)(V_2 + 1_2 + 2)(V_2 + 2, 1_2 | r | V_{2}^{1})} \]
\[ \cdot \left[ \delta \alpha_{i} \alpha_{i-1} \left( \frac{\alpha_{i}}{2} + \delta \alpha_{i+1} \alpha_{i} \left( \frac{\alpha_{i+1}}{2} \right) \right) C_{\lambda_{3}} \left( \alpha_{3} \left| q_{3} \right| \alpha_{3} \right) \right] \] (237)

Similarly,
\[ \mu_{4} \left[ r \left| p_3 \alpha_3 + \alpha_3 \right| M \left| \gamma \right| \right] \gamma \]
\[ = \mu_{4} \left( \gamma_1, \gamma_1 \right) \left( M_2 \left| \gamma \right| \right) \gamma^{1} \left| M_1 \right| \] (238)

where
\[ \mu_{4} \left( \gamma_1, \gamma_1 \right) \]
\[ = \mu_{4} \left[ \frac{1}{2} \sqrt{(V_2 - 1_2 + 2)(V_2 + 1_2 + 2)(V_2 + 2, 1_2 | r | V_{2}^{1})} \right] \]
\[ + \frac{1}{2} \sqrt{(V_2 - 1_2 + 2)(V_2 + 1_2 + 2)(V_2 + 2, 1_2 | r | V_{2}^{1})} \]
\[ + \frac{1}{2} \sqrt{(V_2 - 1_2 + 2)(V_2 + 1_2 + 2)(V_2 + 2, 1_2 | r | V_{2}^{1})} \]

(continued on next page)
(continued)

\[
\begin{align*}
\frac{\tau (\varphi_{1,2} - \varphi_0) \varphi_{i_1} - \tau i_1 + \varphi_{i_2} + \varphi_0) \varphi_{i_2} + \varphi_1}{\left( \frac{\varphi_i}{i_1 + \varphi_0} \left( \frac{1 + \varphi_0}{1 + i_1} \right) \varphi_{i_2} + \frac{\varphi_i}{i_1 + \varphi_0} \left( \frac{1 + \varphi_0}{1 + i_1} \right) \varphi_{i_2} \right) \tau_0}.
\end{align*}
\]

\[
\begin{align*}
\left[ \frac{\tau (\varphi_{1,2} - \varphi_0) \varphi_{i_1} - \tau i_1 + \varphi_{i_2} + \varphi_0) \varphi_{i_2} + \varphi_1}{\left( \frac{\varphi_i}{i_1 + \varphi_0} \left( \frac{1 + \varphi_0}{1 + i_1} \right) \varphi_{i_2} + \frac{\varphi_i}{i_1 + \varphi_0} \left( \frac{1 + \varphi_0}{1 + i_1} \right) \varphi_{i_2} \right) \tau_0}.
\end{align*}
\]
The subscript \( r \) in the expressions \( (V_{21}^\dagger \mid r \mid V_{21}^1)^r \), 
\( (V_{21}^\dagger \mid r \mid V_{21}^1)^r \), etc., indicates that only the \( r \) dependent parts of
the twofold degenerate simple harmonic oscillator wave functions are
included.

Thus, from Equations (220), (222)-(225), (236), and (238),

\[
(M^r \mid \eta \mid n') = \frac{\mu}{1} (\eta_i, \eta_i') (J \lambda_1 | \lambda_i') - \mu (\eta_i, \eta_i') (J \lambda_1 | \lambda_i'),
\]

where

\[
\mathcal{M}(r_2, r_2') = (r_1 \mid \lambda_1 | r_1')_{q_1q_3}, \quad + \left[ J(J + 1) - \frac{2}{3} \right] (r_1 | \mu_2 | r_1')_{q_1q_3r} + \left\{ \left[ J(J + 1) - \frac{2}{3} \right] - \left[ J'(J' + 1) - \frac{2}{3} \right] \right\} (r_1 | \mu_3 | r_1')_{q_1q_3r} + \mathcal{M}_4 (r_1, r_1'),
\]

and

\[
\mathcal{M}(r_2, r_2') = (r_1 | \mu_1 | r_1')_{q_1q_3r} + \left[ J(J + 1) - \frac{2}{3} \right] (r_1 | \mu_2 | r_1')_{q_1q_3r},
\]

\[
+ \left\{ \left[ J(J + 1) - \frac{2}{3} \right] - \left[ J'(J' + 1) - \frac{2}{3} \right] \right\} (r_1 | \mu_3 | r_1')_{q_1q_3r}.
\]
where

\[ r_1 = \left\{ v_1 v_3 v_2 1_2 \right\} \]

\[ r_2 = \left\{ v_1 v_3 v_2 2_2 \right\} , \]

and subscript \( q_{1q_{3}} r \) indicates that only coordinates \( q_{1q_{3}} \) and \( r \) are involved. \( \mu_1, \mu_2, \mu_3, \mu_1, \mu_2, \) and \( \mu_3 \) are given on pp. 76 and 77, and \( \mu_1 \) and \( \mu_2 \) are given on pages 85 - 88. From these relations and the orthonormality of the \( q_1 \) and \( q_3 \) portions of the zero order wave functions, we obtain

\[
(r_1 | \mu_1 | r_1')_{q_{1q_{3}} r} = \]

\[
(v_{21 2} | 1 | v_{21 2}') \left\{ \delta_{v_1 v_1} \left[ 0\left(v_3 | q_3 | v_3' \right) + c_{33}(v_3 | q_3 | v_3') \right] \right\} \]

\[
+ c_{13}(v_1 | q_1 | v_1')(v_3 | q_3 | v_3') \]

\[
- \varepsilon \left\{ c_{13}(v_3 | q_3 | v_3') \left[ 3A_{11} \frac{1}{n^2} (v_1 | p_1 | v_1') \right] \right\} \]

\[
+ (A_{12} + 2A_{16})(v_1 | q_1 | v_1') \]

\[
+ 2A_{16}(v_1 | q_1 | v_1') \left[ 0\left(v_3 | q_3 | v_3' \right) \right] \]

\[
+ 2c_{33}(v_3 | q_3 | v_3') + A_{14} C_{13} r_{v_1 v_1'}(v_3 | q_3 | v_3') \]

\[
+ 2A_{17} \frac{1}{n} (v_1 | p_1 | v_1') \left[ 0\left(v_3 | p_3 | v_3' \right) \right] \]
\[ + C_{33} \frac{1}{4} (v_3 | p_3 q_3 + q_3 p_3 | v_3^i) \]

\[ + A_{17} C_{33} \left[ 2 \frac{1}{4} (v_1 | p_1 q_1 | v_1^i) \frac{1}{4} (v_3 | p_3 | v_3^i) \right] \]

\[ + \delta_{v_1 v_1^i} \frac{1}{4} (v_3 | q_3 p_3^2 | v_3^i) \]

\[ + (v_{32} | r | v_{32}^i) \right] \delta_{v_1 v_1^i} C_{33} (v_3 | q_3 | v_3^i) \]

\[ - \varepsilon \left\{ (A_{15} + 2A_{16}) C_{33} (v_1 | q_1 | v_1^i) (v_3 | q_3 | v_3^i) \right\} \]

\[ + 2A_{17} C_{33} \frac{1}{4} (v_1 | p_1 | v_1^i) \frac{1}{4} (v_3 | p_3 | v_3^i) \]}

\[ + (v_{32} | r^2 | v_{32}^i) \]

\[ \cdot \left\{ - \varepsilon A_{13} \delta_{v_1 v_1^i} (v_3 | q_3 | v_3^i) \right\} \] \hspace{1cm} (243)

\[ (r_1 \mid \mu_3 \mid r_1^i) \]

\[ = (v_{32} | l | v_{32}^i) \]

\[ \cdot \left\{ - \varepsilon \delta_{v_1 v_1^i} \right\} \] \hspace{1cm} (244)

\[ (r_1 \mid \mu_3 \mid r_1^i) \]

\[ = (v_{32} | l | v_{32}^i) \]

\[ \cdot \left\{ - \varepsilon \left\{ \frac{1}{4} (v_1 | p_1 | v_1^i) \right\} \right\} \]

\[ \cdot \left[ B_3 (v_3 | q_3 | v_3^i) + C_{33} (v_3 | q_3 | v_3^i) \right] \]

\[ + C_{13} \frac{1}{4} (v_1 | q_1 p_1 | v_1^i) (v_3 | q_3 | v_3^i) \]}

\[ + (v_{32} | r | v_{32}^i) \]

\[ \cdot \left\{ - \varepsilon \left\{ C_{23} \frac{1}{4} (v_1 | p_1 | v_1^i) \right\} \right\} \] \hspace{1cm} (245)

\[ (\mu_4 (r_1, r_1^i) \text{ is given by Equation (237) on pages 85 and 86.}) \]
\[(r_1 | \mu_1 | r')_{q_1 q_3 r} =
\]
\[
(v_{312} | r | v_{312}') \left\{ \delta_{v_1 v_1} \delta_{v_3 v_3} \Theta_2 + C_{12} \delta_{v_3 v_3} (v_1 | q_1 | v_1) + C_{32} \delta_{v_1 v_1} (v_3 | q_3 | v_3) \right\}
\]
\[
- \varepsilon \left\{ \delta_{v_3 v_3} C_{12} \left[ 3A_{11} \frac{1}{n^2} (v_1 | p_1 | v_1) + (A_{12} + A_{15}) (v_1 | q_1^2 | v_1) \right] + (v_1 | q_1 | v_1) \left[ A_{15} \delta_{v_3 v_3} + C_{32} (A_{15} + 2A_{16}) (v_3 | q_3 | v_3) \right] + \delta_{v_1 v_1} C_{12} \left[ A_{14} (v_3 | q_2 | v_3) + A_{17} \frac{1}{n^2} (v_3 | q_3 | v_3) \right] + 2A_{17} C_{32} \frac{1}{n} (v_1 | p_1 | v_1) \frac{1}{n} (v_3 | p_3 | v_3) \right\}
\]
\[
+ (v_{312} | r^2 | v_{312}') \delta_{v_3 v_3} C_{22} \left\{ \delta_{v_1 v_1} - \varepsilon 2A_{15} (v_1 | q_1 | v_1) \right\}
\]
\[
+ (v_{312} | r^3 | v_{312}') \left\{ - \varepsilon \delta_{v_1 v_1} \delta_{v_3 v_3} A_{13} C_{12} \right\} \quad (246)
\]
\[
(r_1 | \mu_3 | r')_{q_1 q_3 r} = (v_{312} | r | v_{312}') \left\{ - \varepsilon 3 \delta_{v_1 v_1} \delta_{v_3 v_3} C_{12} \right\} \quad (247)
\]
\[
(r_1 | \mu_3 | r')_{q_1 q_3 r} =
\]
\[
(v_{312} | r | v_{312}') \left\{ - 3 \varepsilon \delta_{v_1 v_1} \left[ \Theta_2 \delta_{v_3 v_3} + \delta_{v_3 v_3} \left( v_1 | q_1 p_1 | v_1 \right) \right] \right\}
\]
\[
+ C_{32} (v_3 | q_3 | v_3) + C_{12} \delta_{v_3 v_3} \left[ v_1 | q_1 p_1 | v_1 \right] \right\}
\]
\[
+ (v_{312} | r^2 | v_{312}') \left\{ - 3 \varepsilon \delta_{v_1 v_1} \delta_{v_3 v_3} \left[ v_1 | p_1 | v_1 \right] \right\} \quad (248)
\]
\[
\mu_4 (r_1, r') \text{ is given by Equation (239) on pages 87-88. It is to be}
\]
recalled from page 73 that

\[ A_{11} = \frac{2K_{111}}{3w_1} \quad A_{15} = \frac{2K_{122\omega_2}}{(4w_2^2 - \omega_2^2)} \]

\[ A_{12} = \frac{K_{111}}{w_1} \quad A_{16} = \frac{K_{133\omega_2}}{(4w_2^2 - \omega_2^2)} \]

\[ A_{13} = \frac{K_{122(2w_2^2 - \omega_1^2)}}{w_1(4w_2^2 - \omega_1^2)} \quad A_{17} = \frac{2K_{133\omega_3}}{w_1(4w_2^2 - \omega_1^2)} \]

\[ A_{14} = \frac{K_{133(2w_2^2 - \omega_1^2)}}{w_1(4w_2^2 - \omega_1^2)} \quad \left( A_{14} = \frac{2K_{122\omega_2}}{w_1(4w_2^2 - \omega_1^2)} \right) \]

where the \( K_{ijk} \) are cubic anharmonic potential function constants.

Recall also that \( B_a, B_b, C_{22}, \) etc., are coefficients in the expansions of the body fixed frame components of the dipole moment. (See p. 43.)

**Evaluation of \( \mathcal{M}(r_2, r_2') \) and \( \mathcal{N}(r_2, r_2') \)**

Values of the matrix elements \( (v_1 | q_1 | v_1^1), (v_1 | q_2^1 | v_1^1), \)

\( \frac{1}{2} (v_1 | r_1 | v_1^1), \ldots, \) contained in the expressions for

\( (r_1 | \mu_1 | r_1^1), \ldots, \mathcal{M}_{ij} \) are well known and are given in Appendix V.

Hence, for specific transitions, the quantities

\[ \mathcal{M}(r_2, r_2') = (r_1 | \mu_1 | r_1^1) + \left[ J(J + 1) - l_2^2 \right] (r_1 | \mu_2 | r_1^1) \]

(continued on next page)
and

\[ \mathcal{M}(r_2, r'_2) = (r_1 | \mu_3 | r'_1) + \left[ \{ J(J + 1) - \frac{1}{2} \} - \{ J'(J' + 1) - \frac{1}{2} \} \right](r_1 | \mu_1 | r'_1) + \mu_4 \]

are readily obtainable. We postpone obtaining them until we find in the next two sections some limitations in the values \( l_2 \) can assume.

**Evaluation of \( (Jl_2M | J'1'2'M') \) and \( (Jl_2M | J'y(\psi) | J'1'2'M') \)**

Recall that the quantities \( J'y(\psi) \) and \( J'V_\gamma(\psi) \) are given in terms of the representation coefficients \( D_{km}^j \) of the three-dimensional rotation group, i.e.,

\[ \lambda_+ = \frac{1}{\sqrt{2}} (D_{-1-1}^1 - D_{1-1}^1) \]

(250)

\[ \lambda_- = \frac{1}{\sqrt{2}} (-D_{-11}^1 + D_{11}^1) \]

\[ \lambda_2 = D_{00}^1 \]

\[ \lambda_- = \frac{1}{\sqrt{2}} (D_{-10}^1 - D_{10}^1) \]

(See p. 45.) Tsao and Curnutte, making use of E. Wigner's work (58) on the properties of the representation coefficients and symmetric rotator wave functions, have shown that
\[
\int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} T * \Psi_{J,k} \Psi_{J',k'} \Psi_{J,K_1M_1} \sin \theta \, d\varphi \, dy
\]
\[
= \frac{1}{2\pi} \sqrt{\frac{\ell (\ell+1)(2\ell+1)}{2 \ell (2\ell+1)}} \langle J_1K_1k \mid J_2K_2 \rangle \langle J_1J_1 \ell m_1 \mid J_2M_2 \rangle
\]

where

\[
\psi_{JKM} = \psi_{JKM}(\theta, \varphi)
\]

are rigid symmetric rotator wave functions, and

\[
\langle j_1j_2m_1m_2 \mid Jm \rangle =
\]

\[
\delta_{m,m_1m_2} \left[ \frac{(j+j_1-j_2)!!(j-j_1+j_2)!!(j_1+j_2-j)!j+m)!j-(j+m)!!(2j+1)!}{(j+j_1+j_2+1)!!(j_1-m_1)!!(j_1+m_1)!!(j_2-m_2)!!(j_2+m_2)!!} \right]
\]

\[
\sum_K (-1)^{K+j_2+j_1} \frac{(j_2+j_1-k)!j_1-k)!j_1+m-k)!j+m-k)!}{(j-j_1-j_2-k)!j_1+k)!j_1+k+j_2-k)!}
\]

(\text{all } K \text{ giving no factorials of negative numbers})

are the so-called "vector addition coefficients", some of which are tabulated on pages 76, 77 of Condon and Shortley (28). See Appendix VI., p. 206 of Wigner (58); Tseu's and Curmutte's discussion is to be found in Appendices A and B of (20). Very important is the fact derived by Wigner (58) that the symmetric rotator wave functions and the representation coefficients are proportional to each other.

\* \( (j^i j^k \mid j^m_k \rangle \) is often denoted by \( (jj^1k^1 \mid jj^2k^2 \rangle \).
More specifically,

\[
\psi_{jm}(\phi \gamma) = (-1)^{-k-m} \frac{1}{2\pi} \sqrt{\frac{2j + 1}{2}} \ D_j^{(j \gamma)}(\phi \gamma)
\]  

(253)

Hence,

\[
\iint \iint \psi^* \ D_j^{(j \gamma)} \psi \ \sin \theta \ d\theta 
\]

\[
= (-1)^{-k-m} \sqrt{\frac{2j + 1}{2j + 1}} \ (J_{1j}k \ | \ J_{2K_2}) (J_{1j}1 \ | \ J_{2K_2})(254)
\]

or

\[
\iint \iint \psi^* \ D_j^{(j \gamma)} \psi \ \sin \theta \ d\theta 
\]

\[
= (-1)^{k+m} \sqrt{\frac{2j + 1}{2j + 1}} \ (J_{1j}1 \ | \ J_{2K_2}) (J_{1j}1 \ | \ J_{2K_2})(255)
\]

The eigenfunctions involved in our \((J_{12}M \ | \ J_\gamma \ | \ J'_{12}M')\) and

\((J_{12}M \ | \ J_\gamma \ | \ J'_{12}M')\) are rigid symmetric rotator wave functions.

Hence

\[
(J_{12}M \ | \ D_{km}^{(j \gamma)} \ | \ J'_{12}M') = \int_0^{2\pi} \int_0^{2\pi} \int_0^{2\pi} \psi^* \ D_{km}^{(j \gamma)} \psi' \ J_{12}M \ J_{12}M' \sin \theta \ d\theta \ d\gamma 
\]

\[
= (-1)^{k+m} \sqrt{\frac{2j + 1}{2j + 1}} \ (J_{1j}1 \ | \ J_{2K_2})(J_{1j}1 \ | \ J_{2K_2})(256)
\]

This equation together with Equation (250) relating the \(J_\gamma\) and

the \(J_\gamma\) with the \(D_{km}^{(j \gamma)}\) lead to
\[(J_{12}M | \lambda_+ | J_{12}'M') = - \sqrt{\frac{2J' + 1}{2J + 1}} (J'1120 | J_{12}) (J'1M'1 | JM) \]
\[(J_{12}M | \lambda_- | J_{12}'M') = \sqrt{\frac{2J' + 1}{2J + 1}} (J'1120 | J_{12}) (J'1M' -1 | JM) \]
\[(J_{12}M | \lambda_2 | J_{12}'M') = \sqrt{\frac{2J' + 1}{2J + 1}} (J'1120 | J_{12}) (J'1M'0 | JM) \]
\[(J_{12}M | \lambda_+ | J_{12}'M') = \]
\[
\frac{1}{\sqrt{2}} \left[ \frac{2J' + 1}{2J + 1} \right] \left\{ (J'1121 | J_{12}) - (J'112 -1 | J_{12}) \right\} (J'1M'1 | JM) \]
\[(J_{12}M | \lambda_- | J_{12}'M') = - \frac{1}{\sqrt{2}} \left[ \frac{2J' + 1}{2J + 1} \right] \left\{ (J'1121 | J_{12}) - (J'112 -1 | J_{12}) \right\} (J'1M' -1 | JM) \]
\[(J_{12}M | \lambda_2 | J_{12}'M') = - \frac{1}{\sqrt{2}} \left[ \frac{2J' + 1}{2J + 1} \right] \left\{ (J'1121 | J_{12}) - (J'112 -1 | J_{12}) \right\} (J'1M'0 | JM) \]

All of the vector addition coefficients \((j_{12} j_{12}' m_{12} | j_{12}' m_{12}')\) in the above relations have \(J_2 = 1\). The non-vanishing \((j_{12} j_{12}' m_{12} | j_{12}' m_{12}')\) are given in Table 2 on page 76 of Condon and Shortley (28). They are reproduced here in Table 7. In order to obtain the absorption coefficients, we will need to calculate the quantities

\[
\sum M \sum M' \sum \gamma (J'1M' | \lambda_\gamma | J_{12}M)^2
\]
TABLE 7

The Non-vanishing \((j_1 m_1 m_2 | j m)\)

\((m \text{ must equal } m_1 + m_2)\)

<table>
<thead>
<tr>
<th>(m_2)</th>
<th>1</th>
<th>0</th>
<th>-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>(j_{1+1})</td>
<td>(\sqrt{\frac{(j_1 + m)(j_1 + m + 1)}{(2j_1 + 1)(2j_1 + 2)}})</td>
<td>(\sqrt{\frac{(j_1 - m + 1)(j_1 + m + 1)}{(2j_1 + 1)(j_1 + 1)}})</td>
<td>(\sqrt{\frac{(j_1 - m)(j_1 - m + 1)}{(2j_1 + 1)(2j_1 + 2)}})</td>
</tr>
<tr>
<td>(j_1)</td>
<td>(-\sqrt{\frac{(j_1 + m)(j_1 - m + 1)}{2j_1(j_1 + 1)}})</td>
<td>(\frac{m}{\sqrt{j_1(j_1 + 1)}})</td>
<td>(\sqrt{\frac{(j_1 - m)(j_1 + m + 1)}{2j_1(j_1 + 1)}})</td>
</tr>
<tr>
<td>(j_{1-1})</td>
<td>(\sqrt{\frac{(j_1 - m)(j_1 - m + 1)}{2j_1(2j_1 + 1)}})</td>
<td>(-\sqrt{\frac{(j_1 - m)(j_1 + m)}{j_1(2j_1 + 1)}})</td>
<td>(\sqrt{\frac{(j_1 + m + 1)(j_1 + m)}{2j_1(2j_1 + 1)}})</td>
</tr>
</tbody>
</table>
\[
\sum_{M} \sum_{M'} \sum_{\gamma} (J'_{12} M' | \gamma | J_{12} M)^2 , \text{ and } \\
\sum_{M} \sum_{M'} \sum_{\gamma} (J'_{12} M' | \gamma | J_{12} M) (J'_{12} M' | \gamma | J_{12} M) .
\]

(See the next section.) These calculations are greatly simplified if the \((J'_{12} m_2 | \gamma | J_{12} M)\) and \((J'_{12} m_1 | \gamma | J_{12} M)\) are left in terms of the vector addition coefficients while the summations are being carried out and one of the properties of the \((j_{12} m_1 m_2 | j_m)\) is utilized. For future reference we list the non-vanishing vector addition coefficients which occur in our problem.

\[
\begin{align*}
(J_{12} 0 | J+1 l_2) &= \sqrt{\frac{(J-1^2+1)(J+1^2+1)}{(2J+1)(J+1)}} \\
(J_{12} 0 | J+1 l_2) &= \sqrt{\frac{J^2}{J(J+1)}} \\
(J_{12} 0 | J-1 l_2) &= -\sqrt{\frac{(J-1^2)(J+1^2)}{J(2J+1)}} \\
(J_{12} l_2 | J+1 l_2+1) &= \sqrt{\frac{(J+1^2+1)(J+1^2+2)}{(2J+1)(2J+2)}} \\
(J_{12} l_2 | J l_2+1) &= -\sqrt{\frac{(J+1^2+1)(J-1^2)}{2J(J+1)}} \\
(J_{12} l_2 | J-1 l_2+1) &= \sqrt{\frac{(J-1^2-1)(J-1^2)}{2J(2J+1)}} \\
(J_{12} -1 | J+1 l_2-1) &= \sqrt{\frac{(J-1^2+1)(J-1^2+2)}{(2J+1)(2J+2)}} 
\end{align*}
\]

(continued on next page)
\[
\begin{align*}
(J_{ll_2}|J_{l_2} &= -1) = \sqrt{\frac{(J_{l_2}+1)(J_{l_2}+2)}{2J(J+1)}} \quad (262) \\
(J_{ll_2}|-1|J_{l_2} &= -1) = \sqrt{\frac{(J_{l_2}+1)(J_{l_2}+2)}{2J(2J+1)}} \\
(J_{IM}|J+1 M) &= \sqrt{\frac{(J_{l_2}+1)(J_{l_2}+2)}{2J(2J+1)}} \quad (263) \\
(J_{IM}|J-1 M) &= -\sqrt{\frac{(J_{l_2}+1)(J_{l_2}+2)}{2J(J+1)}} \\
(J_{IM}|J+1 M+1) &= \sqrt{\frac{(J_{l_2}+1)(J_{l_2}+2)}{2J(2J+1)}} \\
(J_{IM}|J+1 M-1) &= \sqrt{\frac{(J_{l_2}+1)(J_{l_2}+2)}{2J(2J+1)}} \quad (264) \\
(J_{IM}|J-1 M+1) &= \sqrt{\frac{(J_{l_2}+1)(J_{l_2}+2)}{2J(2J+1)}} \\
(J_{IM}|J-1 M-1) &= \sqrt{\frac{(J_{l_2}+1)(J_{l_2}+2)}{2J(2J+1)}} \quad (265)
\end{align*}
\]

Note that since $J \geq M$ and $J \geq l_2$ and $J$ is non-negative, all these vector addition coefficients are real. Thus $(J_{l_2} M | J_{l_2} M)$ and
\((J'2M'1L \gamma |J2M)\) are real. [See Equations (257) and (258) on p. 26.]

The quantities

\[ \Pi_{\Gamma_2}^{\Gamma_1} = \sum_{M} \sum_{M'} \sum_{\gamma} |(\Gamma_2^{1M'}, M_\gamma | \Gamma_2^{1M})|^2 \]

From page 20 we see that the absorption coefficient for a vibration-rotation spectral line caused by all the possible transitions

\[ \psi_{\Gamma_2^2M} \rightarrow \psi_{\Gamma_2^1M'} \quad (\Gamma_2 = \{ v_1 v_2 v_3 \}) \]

from energy \(E_{\Gamma_2^2}\) to energy \(E_{\Gamma_2^1}\) is proportional to

\[ \Pi_{\Gamma_2}^{\Gamma_1'} = \sum_{M} \sum_{M'} \sum_{\beta} |(\Gamma_2^{1M'} | M_\beta | \Gamma_2^{1M})|^2 \]

Also, it was pointed out on page 23 that, by direct operation,

\[ \Pi_{\Gamma_2}^{\Gamma_1'} = \sum_{M} \sum_{M'} \sum_{\gamma} (\Gamma_{2M'}^{1M}|M_\gamma | \Gamma_{2M})^2 \quad \text{i.e.,} \]

\[ \Pi_{\Gamma_2}^{\Gamma_1'} = \sum_{M} \sum_{M'} \sum_{\gamma} (\Gamma_{2M'}^{1M}|M_\gamma | \Gamma_{2M})^2 (\Gamma_{2M'}^{1M}|M_\gamma | \Gamma_{2M}) \quad \text{(266)} \]

In our approximation,

\[ (\Gamma_{2M'}^{1M}|M_\gamma | \Gamma_{2M}) = (\Gamma_{2M'}^{1M}|M_\gamma | \Gamma_{2M}) \]

\[ = M(\Gamma_2^{1M'} | \Gamma_2^{1M}| M_\gamma | J_{12M}) + M(\Gamma_2^{1M'} | \Gamma_2^{1M}| M_\gamma | J_{12M}) \]

\[ \text{[See p. 21 f.; Equation (240) on p. 88.] Therefore, since the} \]

\[ \text{... (267)} \]
quantities \( \langle J' \frac{1}{2} M' | \gamma | J \frac{1}{2} M \rangle \) and \( \langle J' \frac{1}{2} M' | \gamma | J \frac{1}{2} M \rangle \) are real,\n
\[
\Pi_{\frac{1}{2} \frac{1}{2}} = \mu^* (r^1_{\frac{3}{2} \frac{1}{2}}) \mu (r^1_{\frac{3}{2} \frac{1}{2}}) \sum_{M} \sum_{M'} \sum_{\gamma} \langle J' \frac{1}{2} M' | \gamma | J \frac{1}{2} M \rangle^2
\]

\[+ \mu^* (r^1_{\frac{3}{2} \frac{1}{2}}) \mu (r^1_{\frac{3}{2} \frac{1}{2}}) \sum_{M} \sum_{M'} \sum_{\gamma} \langle J' \frac{1}{2} M' | \gamma | J \frac{1}{2} M \rangle^2
\]

\[+ \{ \mu^* (r^1_{\frac{3}{2} \frac{1}{2}}) \mu (r^1_{\frac{3}{2} \frac{1}{2}}) + \mu^* (r^1_{\frac{3}{2} \frac{1}{2}}) \mu (r^1_{\frac{3}{2} \frac{1}{2}}) \}
\]

\[\sum_{M} \sum_{M'} \sum_{\gamma} \langle J' \frac{1}{2} M' | \gamma | J \frac{1}{2} M \rangle \langle J \frac{1}{2} M | \gamma | J \frac{1}{2} M \rangle \]  

From Equations (257) and (258) on page 96,

\[
\sum_{M} \sum_{M'} \sum_{\gamma} \langle J' \frac{1}{2} M' | \gamma | J \frac{1}{2} M \rangle^2 = \frac{2J+1}{2J+1} \langle J \frac{1}{2} 0 | J' \frac{1}{2} 0 \rangle^2
\]

\[\cdot \sum_{M} \sum_{M'} \left\{ (JLM -1 | J'M')^2 + (JLMO | J'M')^2 + (JLMI | J'M')^2 \right\} \]  

\[
\sum_{M} \sum_{M'} \sum_{\gamma} \langle J' \frac{1}{2} M' | \gamma | J \frac{1}{2} M \rangle^2 = \frac{1}{2} \left( \frac{2J+1}{2J+1} \right) \left( \langle J \frac{1}{2} 0 | J' \frac{1}{2} 0 \rangle^2 - \langle J \frac{1}{2} -1 | J' \frac{1}{2} 1 \rangle^2 \right) \]  

\[\cdot \sum_{M} \sum_{M'} \left\{ (JLM -1 | J'M')^2 + (JLMO | J'M')^2 + (JLMI | J'M')^2 \right\} \]  

and

\[
\sum_{M} \sum_{M'} \sum_{\gamma} \langle J' \frac{1}{2} M' | \gamma | J \frac{1}{2} M \rangle \langle J \frac{1}{2} M | \gamma | J \frac{1}{2} M \rangle \]

\[= - \frac{1}{2} \left( \frac{2J+1}{2J+1} \right) \langle J \frac{1}{2} 0 | J' \frac{1}{2} 0 \rangle \left\{ (J \frac{1}{2} 0 | J' \frac{1}{2} 1) - (J \frac{1}{2} -1 | J' \frac{1}{2} 1) \right\} \]

\[\cdot \sum_{M} \sum_{M'} \left\{ (JLM -1 | J'M')^2 + (JLMO | J'M')^2 + (JLMI | J'M')^2 \right\} \]  

\[\ldots \hspace{1cm} (271)\]
Now the vector addition coefficients \((j_1j_2^m|jm)\) have the property

\[
\sum_{m_1} \sum_{m} (j_1j_2^m|jm)(j_1j_2^m|jm) = \delta_{j_2j_2} \frac{2j_2+1}{2j_2+1} \tag{272}
\]

where the summation is over all \(m\) and \(m_1\) giving non-zero terms (See Appendix VI.) Also, the \((j_1j_2^m|jm)\) are defined only for

\[
|m_1| \leq j_1 \quad \text{and} \quad j_1 + m_1 = \text{integer},
\]

\[
|m_2| \leq j_2 \quad \text{and} \quad j_2 + m_2 = \text{integer}, \quad \text{and}
\]

\[
|m| \leq j \quad \text{and} \quad j + m = \text{integer}.
\]

(See Section I of Simon (59)\textsuperscript{7} In our problem \(j_1 = J, j_2 = 1, \) and \(j = J'\) are all non-negative integers, \(m_1 = M\) and \(m = M'\). This verifies the fact that the summations in Equation (272) are over the usual \(M = -J, -J + 1, \ldots, J\) and \(M' = -J', -J' + 1, \ldots, J'\) in our problem. Equation (272) becomes, for \(j_2 = j'_2 = 1,\)

\[
\sum_{M} \sum_{M'} (JLM|J'M')^2 = \frac{2J'+1}{3}, \tag{273}
\]

where \(m_2 = -1, 0, 1\). Hence, from this and Equations (269)-(271),

\[
\sum_{M} \sum_{M'} \sum_{\gamma} (J'_{1}^{M'}|\lambda_{\gamma}|J_{12}M)^2 = (2J+1)(J_{1120}|J'_{12})^2, \tag{274}
\]

\[
\sum_{M} \sum_{M'} \sum_{\gamma} (J'_{1}^{M'}|\lambda_{\gamma}|J_{12}M)^2 \\
= \frac{1}{2} (2J+1) \left\{(J_{1121}|J'_{12}) - (J_{1121}|J'_{12}) \right\}^2. \tag{275}
\]
and

\[ \sum_{M} \sum_{M'} \sum_{\gamma} (J'_{12}M' | \lambda_{\gamma} | J_{12}M)(J'_{12}M' | \lambda_{\gamma} | J_{12}M) \]

\[ = \frac{-1}{\sqrt{2}} (2J+1)(J_{12}0 | J'_{12}1) \left\{ (J_{11}1 | J'_{12}1) - (J_{11}1 | J'_{12}1) \right\} \]

\[ = \frac{(J-1_{2})(J+1_{2})}{J} \equiv J(J_{12}J-1_{12}) \]  \hspace{1cm} (276)

Hence, from Equations (260 – 262), the non-vanishing

\[ \sum_{M} \sum_{M'} \sum_{\gamma} (J'_{12}M' | \lambda_{\gamma} | J_{12}M)^2 \] are:

\[ = \frac{(J-1_{2})(J+1_{2})}{J} \equiv J(J_{12}J-1_{12}) \]  \hspace{1cm} (277)

(There is no \( J = 0 \) case, since then \( J' = J-1 \) would be negative.)

\[ \sum_{M} \sum_{M'} \sum_{\gamma} (J_{12}M' | \lambda_{\gamma} | J_{12}M)^2 = \frac{(2J+1)_{12}}{J(J+1)} \equiv J(J_{2J12}) \]  \hspace{1cm} (278)

(If \( J = 0 \), L'Hospital's rule gives \( J(J_{12}J_{12}) = 2_{12} \).

From Table 6 on page 64 the only \( 1_{2} \) for \( J = 0 \) is \( 1_{2} = 0 \).

Hence \( J(J_{2J12}) \bigg| J = 0 = 0 \).

\[ \sum_{M} \sum_{M'} \sum_{\gamma} (J+1_{2}M' | \lambda_{\gamma} | J_{12}M)^2 \]

\[ = \frac{(J-1_{2}+1)(J+1_{2}+1)}{J+1} \equiv J(J_{2J+11_{2}}) \]  \hspace{1cm} (279)
Similarly, the non-vanishing \( \sum_{M} \sum_{M'} \sum_{\gamma} (J' l_{2} M' | \gamma | J l_{2} M)^{2} \) are

\[
\sum_{M} \sum_{M'} \sum_{\gamma} (J-1 l_{2}-1 M' | \gamma | J l_{2} M)^{2} = \frac{(J+1_2)(J+1_2-1)}{4J} \equiv f(J l_{2} J-1 l_{2}-1) \quad (280)
\]

(There is no \( J = 0 \) case, since then \( J' = J-1 \) would be negative.)

\[
\sum_{M} \sum_{M'} \sum_{\gamma} (J l_{2}-1 M' | \gamma | J l_{2} M)^{2} = \frac{(2J+1)(J-1_{2}+1)(J+1_{2})}{4J(J+1)} \equiv f(J l_{2} J 1_{2}-1) \quad (281)
\]

(There is no \( J = 0 \) case as only \( l_{2} \) for \( J = 0 \) is \( l_{2} = 0 \) making \( l'_{2} = l_{2}-1 \) negative. \( l_{2} \) may assume no negative values.)

\[
\sum_{M} \sum_{M'} \sum_{\gamma} (J+1 l_{2}-1 M' | \gamma | J l_{2} M)^{2} = \frac{(J-1_{2}+1)(J-1_{2}+2)}{4(J+1)} \equiv f(J l_{2} J+1 1_{2}-1) \quad (282)
\]

\[
\sum_{M} \sum_{M'} \sum_{\gamma} (J-1 l_{2}+1 M' | \gamma | J l_{2} M)^{2} = \frac{(J-1_{2}-1)(J-1_{2})}{4J} \equiv f(J l_{2} J-1 1_{2}+1) \quad (283)
\]

(There is no \( J = 0 \) case, since then \( J' = J-1 \) would be negative.)
\[ \sum_{M} \sum_{N} \sum_{\gamma} (J_{l_2+1} M_{l_2} | \lambda_{\gamma} | J_{l_2 M})^2 \]
\[ = \frac{(2J+1)(J+l_2+1)(J-l_2)}{4J(J+1)} \equiv \mathcal{F}(J_{l_2} J_{l_2+1}) \] (284)

(There is no \( J = 0 \) case, since the only \( l_2 \) for \( J = 0 \)
is \( l_2 = 0, l_2 = l_2 + 1 \) being nonexistent.)

\[ \sum_{M} \sum_{N} \sum_{\gamma} (J_{l_2+1} M_{l_2} | \lambda_{\gamma} | J_{l_2 M})^2 \]
\[ = \frac{(J+l_2+1)(J+l_2+2)}{4(J+1)} \equiv \mathcal{F}(J_{l_2} J_{l_2+1}) \] (285)

Also,

\[ \sum_{M} \sum_{N} \sum_{\gamma} (J'_{l_2+1} M'_{l_2} | \lambda_{\gamma} | J_{l_2 M})(J'_{l_2 M'} | \lambda_{\gamma} | J_{l_2 M}) = 0 \] (286)

for all values of the quantum numbers.

It is to be noted that the \( \mathcal{F} \)'s satisfy the relation

\[ \mathcal{F}(J_{l_2} J'_{l_2}) = \mathcal{F}(J'_{l_2} J_{l_2}) \] . (287)

Hence, in no transitions are both \( \lambda_{\gamma} \) and \( \lambda_{\gamma} \) involved.

(See p. \#\# for the definitions of \( \lambda_{\gamma} \) and \( \lambda_{\gamma} \).
\( \lambda_{\gamma} \), associated with XYZ projections of the component of the dipole moment parallel to the \( z \) axis (principal axis of greatest symmetry), is involved only in transitions where \( \Delta l_2 = l_2 - l_2 = 0 \), while \( \lambda_{\gamma} \), associated with XYZ projections of the component of the dipole moment perpendicular to the \( z \) axis is involved only in transitions where \( \Delta l_2 = \pm 1 \).
From Equations (268) and (277-286), the non-vanishing are, for

\[ \Gamma_3 \equiv \{ v_1 v_2 v_3 \} \quad \text{and} \quad \mathcal{M}^\ast \left( r_2^1 r_2^2 \right) / \mathcal{M}^\ast \left( r_2^1 r_2^2 \right) = \mathcal{M}^\ast \left( r_2^1 r_2^2 \right) : \\
\Pi \left( r_3^1 J_l^1 l_2, r_3^2 J_l^2 l_2 \right) \mathcal{F} \left( J_l^1 J_l^2 l_2 \right) \]

(288)

(289)

(290)

(The above expressions are for lines in "parallel bands;" since \( \lambda \) is the projection factor involved. The expressions below are for lines in "perpendicular bands").

\[ \Pi \left( r_3^1 J_l^1 l_2, r_3^2 J_l^2 l_2 \right) \mathcal{F} \left( J_l^1 J_l^2 l_2 \right) \]

(291)

(292)

(293)

The \( \mathcal{F} \left( J_l^1 J_l^2 l_2 \right) \) factors which occur in the above expressions and are given in Equations (277-285) are the so-called rigid symmetric top line strengths. These quantities were derived first by H"onel and London (60) on the basis of the old quantum theory, and later by Dennison (53) and Rademacher and Reiche (8). These line strengths also hold for the diatomic molecule with electronic angular momentum if \( l_2 \) is replaced by the quantum number \( \lambda \) associated with electronic angular momentum about the internuclear axis. [See
p. 208 of Herzberg, Volume I. Of prime interest here are the
details of the quick derivation of the $J(J\alpha J')$, how they arise
in the case of the vibrating rotating symmetric triatomic molecule,
and how vibration-rotation interaction and anharmonicity modify the
intensity expressions as manifested in the factors $\mu^*\mu (r'_2 r'_2)$ and
$\mu^*\mu' (r'_2 r'_2)$.

The $\mu^*\mu$ and $\mu^*\mu'$ which occur for non-zero $r'_2$
are readily obtainable from Equations (241 - 249) on pages 88 f.

From Equations (241) and (242),

$$
\mu(r'_2 r'_2) = (\mu_1 | r_1)_{q_1 q_2 r} + \mu_1(J'1_2)(r'_1 | \mu_2 | r_1)_{q_1 q_2 r} + \mu_2(J'1_2)(r'_1 | \mu_1 | r_1)_{q_1 q_2 r} + \mu_1(J'1_2)(r'_1 | \mu_2 | r_1)_{q_1 q_2 r} + \mu_2(J'1_2)(r'_1 | \mu_1 | r_1)_{q_1 q_2 r} + \mu_1(J'1_2)(r'_1 | \mu_2 | r_1)_{q_1 q_2 r} + \mu_2(J'1_2)(r'_1 | \mu_1 | r_1)_{q_1 q_2 r}
$$

where

$$
\mu_1(J'1_2) = J'(J'1_2) - 1_2^2
$$

and

$$
\mu_2(J'1_2) = \{J'(J'1_2) - 1_2^2\} - \{J(J1) - 1_2^2\}.
$$

The terms in $\mu(r'_2 r'_2)$ and $\mu'(r'_2 r'_2)$ involving $\mu_1(J'1_2)$ and
$\mu_2(J'1_2)$ are all due to the vibration-rotation interaction
term

$$
H_{11} = 2\hbar c\sigma_{\alpha} (P^2 - P_z^2) / \hbar^2.
$$
in the first order Hamiltonian, while the $\mu_1^1, \mu_1^2, \mu_1^3$, and
$\mu_1^4$ terms are due to zero order and cubic anharmonic terms in
$H$. (See p. 73 f.) The $F_1(J^1 l^1_2)$ and $F_2(Jl_2^1 J^1 l^1_2)$ which occur
in the non-vanishing $H_{\tilde{\Gamma}}^{\tilde{\Gamma}'}$ are:

\begin{align*}
F_1(J-1 l_2-1) &= (J-1)J-(l_2-1)^2 \\
F_1(J l_2-1) &= J(J+1)-(l_2-1)^2 \\
F_1(J+1 l_2-1) &= (J+1)(J+2)-(l_2-1)^2 \\
F_1(J-1 l_2+1) &= (J-1)J-(l_2+1)^2 \\
F_1(J l_2+1) &= J(J+1)-(l_2+1)^2 \\
F_1(J+1 l_2+1) &= (J+1)(J+2)-(l_2+1)^2 \\
F_1(J-1 l_2) &= (J-1)J-l_2^2 \\
F_1(J l_2) &= J(J+1)-l_2^2 \\
F_1(J+1 l_2) &= (J+1)(J+2)-l_2^2
\end{align*}

and

\begin{align*}
F_2(Jl_2 J-1 l_2-1) &= -2J+2l_2-1 \\
F_2(Jl_2 J l_2-1) &= 2l_2-1 \\
F_2(Jl_2 J+1 l_2-1) &= 2(J+1)+2l_2-1 \\
F_2(Jl_2 J-1 l_2+1) &= -2J-2l_2-1
\end{align*}

(continued on next page)
Due to the fact that the only non-vanishing \( P^7 \) are those for \( l_2 = l_2', l_2 \neq l_2', \) many terms in expressions (246 - 248) for the \( (r_1' | \mu_1 | r_1) \) and \( (r_1' | \mu_1 | r_1) \) vanish. This is brought about because \( r \) has non-vanishing radial matrix elements \( (V_{3l_2} | \rho | V_{3l_2}) \) for which \( l_2 = l_2', \) and \( r' \) has no non-vanishing radial matrix elements \( (V_{3l_2'} | \rho' | V_{3l_2'}) \) for which \( l_2' = l_2' \). [See p. 259 of Shaffer (57); Appendix V.]

The \( (r_1' | \mu_1 | r_1) \) and \( (r_1' | \mu_1 | r_1) \), which occur only for the case \( l_2 = l_2', \) are:

\[
(r_{3l_2} | \mu_1 | r_{3l_2}) = \delta_{v_2'v_2} \left[ \delta_{v_1'v_1} \left[ B_3(v_3' | q_3 | v_3) + C_{33}(v_3' | q_3 | v_3) \right] \\
+ C_{13}(v_1' | q_1 | v_1)(v_3' | q_3 | v_3) \\
- \varepsilon \left[ C_{13}(v_3' | q_3 | v_3) \left[ \frac{3}{4} \frac{A_{11}}{\ell_2} (v_1' | p_2' | v_1) \right] \right] \right]
\]
\[ + (A_{12} + 2A_{16})(v_1^1 | q_1^2 | v_1) \]
\[ + 2A_{16}(v_1^1 | q_1^1 | v_1) \left[ \Theta_3(v_3^1 | q_3^1 | v_3) + 2 C_{33}(v_3^3 | q_3^3 | v_3) \right] \]
\[ + \delta_{v_1^1 v_1^1} A_{14} C_{13}(v_3^3 | q_3^3 | v_3) \]
\[ + 2A_{17} \frac{1}{\hbar} (v_1^1 | p_1^1 | v_1) \left[ \Theta_3 \frac{1}{\hbar} (v_3^3 | p_3^1 | v_3) \right. \]
\[ \left. + C_{33} \frac{1}{\hbar} (v_3^3 | p_3^2 q_3^2 + q_3^2 p_3 | v_3) \right] \]
\[ + A_{17} C_{13} \left[ 2 \frac{1}{\hbar} (v_1^1 | q_1 q_1 | v_1) \frac{1}{\hbar} (v_3^3 | p_3^1 | v_3) \right. \]
\[ \left. + \delta_{v_1^1 v_1^1} \frac{1}{\hbar} (v_3^3 | q_3^2 q_3^2 | v_3) \right] \]
\[ - \epsilon A_{13} C_{13} (v_3^1 z_2 | r^2 | v_3^1 z_2) \delta_{v_1^1 v_1^1} (v_3^3 | q_3^3 | v_3) \quad (304) \]

\[ (n_{12}^1 | \mu_2 | \Gamma_{312})_{q_1 q_3 r} \]
\[ = - \epsilon \delta_{v_3 y_2} \delta_{v_1^1 v_1^1} (v_3^3 | q_3^3 | v_3) \quad (305) \]

\[ (n_{32}^1 | \mu_3 | \Gamma_{312})_{q_1 q_3 r} \]
\[ = - i \epsilon \delta_{v_3 y_2} \left\{ \frac{1}{\hbar} (v_1^1 | p_1^1 | v_1) \left[ \Theta_3(v_3^3 | q_3^1 | v_3) + C_{33}(v_3^3 | q_3^2 | v_3) \right] \right. \]
\[ \left. + C_{13} \frac{1}{\hbar} (v_1^1 | q_1 q_1 | v_1)(v_3^3 | q_3^3 | v_3) \right\} \quad (306) \]

\[ \mu_4(n_{32}^1, n_{312}^1) \]
\[ = \epsilon A_{41} \left[ \frac{1}{2} \sqrt{(v_{2-3}+2)(v_{2+3}+2)} \delta_{v_2^1 v_2^1} \right. \delta_{v_2^3 v_2^{3+2}} \left. \right] \]
\[ + (v_{2+1}) \delta_{v_2^1 v_2^1} \quad (continued \ on \ next \ page) \]
\[ + \frac{1}{2} \sqrt{(V_{2}^2-1)(V_{2}^2+1)} \delta_{V_{2}^2, V_{2}^2-2} \]

\[ \left\{ 2 \left( \delta_{V_{1}^2, V_{1}^2+1} \frac{\sqrt{V_{1}^2+1}}{2} - \delta_{V_{1}^2, V_{1}^2-1} \frac{\sqrt{V_{1}^2}}{2} \right) \left[ B_{3}(v_{3}^i | q_{3}^i | v_{3}) + C_{33}(v_{3}^i | q_{3}^i | v_{3}) \right] \]

\[ + \left[ (V_{1}^2-1) q_{1} | V_{1}^2 \right] \frac{\sqrt{V_{1}^2}}{2} - (V_{1}^2+1) q_{1} | V_{1}^2 \right] \frac{\sqrt{V_{1}^2+1}}{2} \]

\[ - (V_{1}^2-1) q_{1} | V_{1}^2-1 \right] \frac{\sqrt{V_{1}^2}}{2} + (V_{1}^2+1) q_{1} | V_{1}^2+1 \right] \frac{\sqrt{V_{1}^2+1}}{2} \right] C_{13}(v_{3}^i | q_{3}^i | v_{3}) \]

\[
\text{etc.} \]

In deriving Equation (307), use was made of the fact that

\[ \frac{1}{2} \sqrt{(V_{2}^2-1)(V_{2}^2+1)} \delta_{V_{2}^2, V_{2}^2+2} = \frac{1}{3} \sqrt{(V_{2}^2-1)(V_{2}^2+1)} \delta_{V_{2}^2, V_{2}^2+2} \]

etc.

The \((\Gamma_{1}^i, \mu_{1}^i, \Gamma_{1}^i)_{q_{1}^i q_{3}^i r}^{}\) and \(\mu_{1}^i(\Gamma_{1}^i, \Gamma_{1}^i)\), which occur only for the cases \(l_{2}^i = l_{2} \pm 1\), are:

\[
(\Gamma_{3}^i l_{3} \pm 1 | \mu_{1}^i | \Gamma_{3}^i l_{2})_{q_{1}^i q_{3}^i r}^{}
\]

\[
= (V_{2}^2 l_{2} \pm 1 | V_{2}^2 l_{2})_{r} \left\{ \delta_{V_{1}^2 V_{1}^2} \delta_{V_{3}^2 V_{3}^2} B_{2} + C_{123} \delta_{V_{3}^2 V_{3}^2} (v_{1}^i | q_{1}^i | v_{1}^i) \]

\[ + C_{323} \delta_{V_{1}^2 V_{1}^2} (v_{3}^i | q_{3}^i | v_{1}^i) \]

\[ - \varepsilon \left\{ \delta_{V_{3}^2 V_{3}^2} C_{123} \left[ A_{11} \frac{1}{m^2} (v_{1}^i | p_{1}^i | v_{1}^i) + (A_{12} + A_{15}) (v_{1}^i | q_{1}^i | v_{1}^i) \right] \right. \]

\[ + (v_{1}^i | q_{1}^i | v_{1}^i) \left[ A_{15} \delta_{V_{3}^2 V_{3}^2} + C_{32} (A_{15} + 2A_{16}) (v_{3}^i | q_{3}^i | v_{3}^i) \right] \]

\[ \left. + \delta_{V_{1}^2 V_{1}^2} C_{123} \left[ A_{14} (v_{3}^i | q_{3}^i | v_{3}^i) + A_{17} \frac{1}{m^2} (v_{3}^i | p_{3}^i | v_{3}^i) \right] \right\} \]

(continued on next page)
\[
+ 2A_{17} C_{32} \frac{1}{n} (v_1 | p_1 | v_1) \frac{1}{n} (v_3 | p_3 | v_3) \}
\]

\[
- \varepsilon (v_2^l 1_{\alpha^1 l} | r^3 | v_{2^l 3})_r \delta \frac{1}{v_1 v_1 v_3 v_3} A_{13} C_{12}
\]

(308)

\[
(r_2^l 1_{\alpha^1 l} | \mu_2^l | r_3^l 1) = - \varepsilon^3 (v_2^l 1_{\alpha^1 l} | r | v_{2^l 3})_r \frac{1}{v_1 v_1 v_3 v_3} C_{12}
\]

(309)

\[
\mu_{1h}^l (r_3^l 1_{\alpha^1 l} r_3^l 1) = \varepsilon A_{41} \frac{1}{2} \left[ \frac{1}{(v_2^l - 1_{\alpha^1 l})(v_{2^l + 1_{\alpha^1 l}}) (v_{2^l - 1_{\alpha^1 l}} | r | v_{2^l 3})_r + (v_2^l + 1_{\alpha^1 l})(v_{2^l - 1_{\alpha^1 l}} | r | v_{2^l 3})_r}
\]

\[
+ \frac{1}{2} \left[ \frac{1}{(v_{2^l - 1_{\alpha^1 l} + 2})(v_{2^l + 1_{\alpha^1 l} + 2})(v_{2^l + 2} | r | v_{2^l 3})_r} \right]
\]

\[
\left[ \begin{array}{c}
\delta v_1 v_1 + 1 \\
\sqrt{\frac{v_1 + 1}{2}} - \\
\delta v_1 v_1 - 1 \\
\sqrt{\frac{v_1}{2}} \end{array} \right] \left[ \begin{array}{c}
\varepsilon^2 \delta v_3 v_3 + C_{32}(v_3 | q_3 | v_3) \\
+ (v_1 - 1 | q_1 | v_1) \sqrt{\frac{v_1 + 1}{2}} \end{array} \right] C_{12} \delta v_3 v_3
\]

\[
+ \varepsilon A_{41} \frac{1}{2} \left[ \frac{1}{(v_2 - 2)(v_{2^l + 2})(v_{2^l - 1_{\alpha^1 l}} | r | v_{2^l 2})_r + (v_2^l + 1)(v_{2^l - 1_{\alpha^1 l}} | r | v_{2^l 2})_r}
\]

\[
+ \frac{1}{2} \left[ \frac{1}{(v_{2^l - 1_{\alpha^1 l} + 2})(v_{2^l + 1_{\alpha^1 l} + 2})(v_{2^l + 2} | r | v_{2^l 2})_r} \right]
\]

\[
\left[ \begin{array}{c}
\delta v_1 v_1 + 1 \\
\sqrt{\frac{v_1 + 1}{2}} - \\
\delta v_1 v_1 - 1 \\
\sqrt{\frac{v_1}{2}} \end{array} \right] \left[ \begin{array}{c}
\varepsilon^2 \delta v_3 v_3 + C_{32}(v_3 | q_3 | v_3) \\
+ (v_1 - 1 | q_1 | v_1) \sqrt{\frac{v_1 + 1}{2}} \end{array} \right] C_{12} \delta v_3 v_3
\]

(continued on next page)
\[ + \left\{ - (v_1 | q_1 | v_1 - 1) \right\} \frac{v_1}{2} + (v_1 | q_1 | v_1 + 1) \right\} \frac{v_1 + 1}{2} \right\} C_{128} v_1 v_2 \right\} \]

where

\[ A_{11} = \frac{2K_{111}}{3w_1} \]
\[ A_{15} = \frac{2K_{122}w_2}{(4w_2^2 - w_1^2)} \]
\[ A_{12} = \frac{K_{111}}{w_1} \]
\[ A_{16} = \frac{K_{133}w_3}{(4w_3^2 - w_1^2)} \]
\[ A_{13} = \frac{K_{133}(2w_2^2 - w_1^2)}{w_1(4w_2^2 - w_1^2)} \]
\[ A_{17} = \frac{2K_{133}w_3^2}{w_1(4w_3^2 - w_1^2)} \]
\[ A_{14} = \frac{K_{133}(2w_2^2 - w_1^2)}{w_1(4w_2^2 - w_1^2)} \]
\[ A_{18} = \frac{2K_{133}w_3^2}{w_1(4w_3^2 - w_1^2)} \]

and where \( \theta_2, \theta_3, C_{13}, \) etc., are coefficients in the expansions of the body-fixed frame components of the dipole moment. (See p. 43.) Recall that the \( K_{ijk} \) are cubic anharmonic potential function constants. (See p. 45 f.)

Table 8 summarizes the general results of this section, while Table 9, obtained with the help of the matrix elements in Appendix V, summarizes the possible vibrational transitions. Values of \( \Pi_{\mu_1, \mu_2, \mu_3}^{\prime, \prime} \) for some specific transitions are to be found in the next section.

All of the transitions listed in Table 9 do not give rise to absorption, the phenomenon responsible for most infrared spectral data. Some of these transitions, such as those involving only negative changes in any or all of the quantum numbers are immediately seen to correspond
### TABLE 8

The Non-vanishing $\Pi^{J'}_{J,J'}$ (for $r_{3} = \{v_{1}v_{2}\}$)

(1) Parallel Bands: $\Delta l_{2} = 0$

$$\Pi^{J'}_{J,J'} = \sum (r_{3}^{J} J_{12} J_{312}) \mathcal{F}(J_{12} J'_{12})$$

where

$$\mathcal{M}(r_{3}^{J} J_{12} J_{312}) = (r_{3}^{J} J_{12} | \mu_{1} | r_{3}^{J} Q_{1} Q_{2} r_{3}^{J} J_{312}) q_{1} q_{3} r$$

| Cases | $\mathcal{F}(J_{12} J'_{12})$ | $\mathcal{F}_{1}(J'_{12})$ | $\mathcal{F}_{2}(J_{12} J'_{12})$ | $(r_{3}^{J} J_{12} | \mu_{1} | r_{3}^{J} Q_{1} Q_{2} r_{3}^{J} J_{312})$; $\mathcal{M}_{q}(r_{3}^{J} J_{12} J_{312})$ |
|-------|-----------------|-----------------|-----------------|-----------------|
| $J' = J$ | $\frac{(2J+1) J_{12}}{J(J+1)}$ | $J(J+1) - l_{2}^{2}$ | 0 | See Equations (304) - (307) on pp. 110-111; Table 9 on p. 116. |
| (Q Branches) | | | | |
| $J' = J-1$ | $\frac{(J-l_{2})(J+1)}{J}$ | $(J-1)J - l_{2}^{2}$ | $-2J$ | |
| (P Branches) | | | | |
| $J' = J+1$ | $\frac{(J-l_{2}+1)(J+1)}{J}$ | $(J+1)(J+2) - l_{2}^{2}$ | $2(J+1)$ | |
| (R Branches) | | | | |

Cases in which $\mathcal{F}(J_{12} J'_{12}) = \infty$ do not occur; see p. 103.

(Continued on next page)
TABLE 8 (Continued)

(2) Perpendicular Bands: \( \Delta l_2 = l_2^1 - l_2 = \pm 1 \)

\[
\Pi \frac{\mu'}{g_1 J_1} = \mu'(r_1 l_1 J_1) \mathcal{F}^{(11)}(J_1 l_1)
\]

where \( \mu'(r_1 l_1 J_1) = (r_1 l_1 J_1)_{\mu_1}^{q_1 q_3 r} + F_1(J_1 l_1)_{\mu_1}^{q_1 q_3 r} + F_2(J_1 l_1)_{\mu_1}^{q_1 q_3 r} \)

<table>
<thead>
<tr>
<th>Cases</th>
<th>( J' )</th>
<th>( \mathcal{F}(J_1 l_1 J_1) )</th>
<th>( F_1(J_1 l_1) )</th>
<th>( F_2(J_1 l_1 J_1) )</th>
<th>( (r_1 l_1 J_1)_{\mu_1}^{q_1 q_3 r} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( l_2^-1 )</td>
<td>( J ) (Q Branch)</td>
<td>( \frac{(2J+1)(J-1+1)(J-1)}{4J(J+1)} )</td>
<td>( J(J+1) - (l_2^-1)^2 )</td>
<td>( 2l_2^-1 )</td>
<td>( \mu'(r_1 l_1 J_1) )</td>
</tr>
<tr>
<td></td>
<td>( J-1 ) (P Branch)</td>
<td>( \frac{(J+1)(J+2)}{4J} )</td>
<td>( (J-1)J - (l_2^-1)^2 )</td>
<td>( -2J+2l_2^-1 )</td>
<td>( \mu'(r_1 l_1 J_1) )</td>
</tr>
<tr>
<td></td>
<td>( J+1 ) (R Branch)</td>
<td>( \frac{(J-1+1)(J+2+1)}{4(J+1)} )</td>
<td>( (J+1)(J+2) - (l_2^-1)^2 )</td>
<td>( 2(J+1)+2l_2^-1 )</td>
<td>( \mu'(r_1 l_1 J_1) )</td>
</tr>
</tbody>
</table>

| \( l_2^+1 \) | \( J \) (Q Branch) | \( \frac{(2J+1)(J+1+1)(J-2)}{4J(J+1)} \) | \( J(J+1) - (l_2^+1)^2 \) | \( -2l_2^+1 \) | \( \mu'(r_1 l_1 J_1) \) |
|       | \( J-1 \) (P Branch) | \( \frac{(J-1-1)(J-2)}{4J} \) | \( (J-1)J - (l_2^+1)^2 \) | \( -2J-2l_2^+1 \) | \( \mu'(r_1 l_1 J_1) \) |
|       | \( J+1 \) (R Branch) | \( \frac{(J+1-1)(J+2+1)}{4(J+1)} \) | \( (J+1)(J+2) - (l_2^+1)^2 \) | \( 2(J+1)-2l_2^+1 \) | \( \mu'(r_1 l_1 J_1) \) |

See Equations (308) - (311) on pp. 111-113.

Table 9, p. 117.
TABLE 9
Vibrational Transitions for Which $\Pi_{i,j,k}^{3}$ Does Not Vanish

(i) Parallel Bands: $\Delta l_2 = 0$

<table>
<thead>
<tr>
<th>$\Delta l_2$</th>
<th>$\Delta \nu_1$</th>
<th>$\Delta \nu_3$</th>
<th>Coefficients of Non-vanishing Terms in the Various Parts of $\mu(\Gamma_{3,1,2})$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>in $(\Gamma_{3,1,2}</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$C_{33}$ none none none</td>
</tr>
<tr>
<td>$\pm 1$</td>
<td>$\theta_3; \varepsilon C_3(A_{1u}, A_{1u}, A_{1u}, A_{1u}, A_{1u}, A_{1u})$</td>
<td>$\varepsilon^3 C_{13}$</td>
<td></td>
</tr>
<tr>
<td>$\pm 2$</td>
<td>$C_{33}$ none none</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\pm 3$</td>
<td>$\varepsilon C_{13}(A_{14}, A_{17})$</td>
<td>none</td>
<td></td>
</tr>
<tr>
<td>$\pm 1$</td>
<td>0</td>
<td>0</td>
<td>$\varepsilon C_{33} A_{1u}$</td>
</tr>
<tr>
<td>$\pm 1$</td>
<td>$C_{13}; \varepsilon \theta_3(A_{1u}, A_{17})$</td>
<td>none</td>
<td>$\varepsilon^3 \theta_3$</td>
</tr>
<tr>
<td>$\pm 2$</td>
<td>$\varepsilon C_{33}(A_{1u}, A_{17})$</td>
<td>none</td>
<td>$\varepsilon^3 C_{33}$</td>
</tr>
<tr>
<td>$\pm 2$</td>
<td>$\varepsilon C_{13}(A_{1u}, A_{1u}, A_{16}, A_{17})$</td>
<td>none</td>
<td>$\varepsilon^3 C_{13}$</td>
</tr>
<tr>
<td>$\pm 2$</td>
<td>0</td>
<td>$\pm 1$</td>
<td>$\varepsilon C_{33} A_{13}$</td>
</tr>
<tr>
<td>$\pm 1$</td>
<td>none</td>
<td>none</td>
<td></td>
</tr>
<tr>
<td>$\pm 1$</td>
<td>$\varepsilon C_{33} A_{41}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\pm 1$</td>
<td>$\varepsilon \theta_3 A_{41}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\pm 2$</td>
<td>$\varepsilon C_{33} A_{41}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE 9 (Continued)

(2) Perpendicular Bands: \( \Delta l_2 = l_2^1 - l_2 = \pm 1 \)

<table>
<thead>
<tr>
<th>( \Delta v_2 )</th>
<th>( \Delta v_1 )</th>
<th>( \Delta v_3 )</th>
<th>Coefficients of Non-vanishing Terms in the Various Parts of ( \mathcal{A}(r^1_3 \Gamma^{11}_1 \Gamma^2_3 \Gamma^3_1) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \pm 1 )</td>
<td>0</td>
<td>0</td>
<td>( \Theta_1; \varepsilon C_{12}(A_n, A_{13}, A_{14}, A_{17}) )</td>
</tr>
<tr>
<td>( \pm 1 )</td>
<td>0</td>
<td>0</td>
<td>( \varepsilon C_{12} )</td>
</tr>
<tr>
<td>( \pm 2 )</td>
<td>0</td>
<td>0</td>
<td>none</td>
</tr>
<tr>
<td>( \pm 1 )</td>
<td>0</td>
<td>0</td>
<td>( \varepsilon C_{12} )</td>
</tr>
<tr>
<td>( \pm 1 )</td>
<td>0</td>
<td>0</td>
<td>( \varepsilon C_{32} )</td>
</tr>
<tr>
<td>( \pm 2 )</td>
<td>0</td>
<td>0</td>
<td>( \varepsilon C_{32} )</td>
</tr>
<tr>
<td>( \pm 3 )</td>
<td>0</td>
<td>0</td>
<td>( \varepsilon C_{12} )</td>
</tr>
<tr>
<td>( \pm 1 )</td>
<td>0</td>
<td>0</td>
<td>none</td>
</tr>
<tr>
<td>( \pm 1 )</td>
<td>0</td>
<td>0</td>
<td>none</td>
</tr>
<tr>
<td>( \pm 2 )</td>
<td>0</td>
<td>0</td>
<td>none</td>
</tr>
</tbody>
</table>
to emission. (See Equation 176 on p. 65.) In cases where both positive and negative changes occur in the set \( \{ \Delta V_2, \Delta V_1, \Delta V_3 \} \), knowledge of the values of the energies is necessary to determine whether the combination transition goes with absorption or emission. We will consider the case of CO\(_2\) whose equilibrium configuration in the ground electronic state is linear and symmetric, and whose energies are well known.
The Case of CO$_2$ in Its Ground Electronic State

The term values and wave function symmetry species classifications for the lowest vibrational energies of CO$_2$ can be obtained from Table 56 on page 274 of Herzberg, Vol. 2 (25). The results in this table are mostly the work of Adel and Dennison (48) and Dennison (45). The term energies have the form

\[ \psi = \frac{1}{\hbar C} v_1 v_2 l_2 v_3 \]

\[ = w_1 (v_1 + \frac{1}{2}) + w_2 (v_2 + 1) + w_3 (v_3 + \frac{1}{2}) + x_{11} (v_1 + \frac{1}{2})^2 \]

\[ + x_{22} (v_2 + 1)^2 + g_{22} l_2^2 + x_{33} (v_3 + \frac{1}{2}) + x_{12} (v_1 + \frac{1}{2})(v_2 + 1) \]

\[ + x_{13} (v_1 + \frac{1}{2})(v_2 + 1) + x_{23} (v_2 + 1)(v_3 + \frac{1}{2}) + \ldots \]

where the $x_{ij}$ and $g_{22}$ are given by the above authors in terms of the cubic and quartic vibrational constants, the $w_i$ and the moment of inertia. \[See also p. 211 of (25)\]

The resultant statistics for linear symmetric CO$_2$

12 16 12 18 13 16 (C O$_2$, C O$_2$, C O$_2$) is Bose since we do not have an odd number of nuclei with half integer spin on each side of the central C atom. This rests on the assumption that the spins of the oxygen nuclei, I(0), are all zero. The statistical weights $g(1)$ and $g(2)$ of energy levels going with $\psi$ complete obtained from Equations (14) and (15) on page 15 are given in Table 10 for some cases involving
different isotopes of carbon and oxygen. Table 2 on page 16 indicates which of these two factors is applicable for a given energy level.

**TABLE 10**

**Statistical Weight Factors** $g(1)$ and $g(2)$ for Linear Symmetric $C$-$C$-$O$ Vibration-Rotation Energy Levels

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$I(0)$</th>
<th>$I(1)$</th>
<th>Resultant Statistics</th>
<th>$g(1)$</th>
<th>$g(2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{12}O_2$</td>
<td>$0$</td>
<td>$0$</td>
<td>Bose (2J+1)</td>
<td>$0$</td>
<td></td>
</tr>
<tr>
<td>$^{12}O_2$</td>
<td>$\frac{3}{2}$</td>
<td>$0$</td>
<td>Bose 2(2J+1)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

These results, along with the statistical weights for the levels of other linear molecules are consistent with the data on page 16 of Herzberg, Vol. 2 (25).

For cases in which different isotopes of oxygen occur in the molecule, the plane of symmetry is not present and both $g(1)$ and $g(2)$ would be (2J+1) for molecules with $^{12}O_2$ as the central nucleus; 2(2J+1) for molecules with $^{13}O_2$ as the central nucleus. (See p. 11.) It is to be noted that our Hamiltonian is valid only for the symmetric cases.

The lowest vibrational term energies and the statistical weights of the associated rotational levels are summarized in Table 11.
### TABLE 11

The Lowest Vibrational Term Energies of Carbon Dioxide in Its Ground Electronic State Referred to the Lowest Vibrational Term $v_0 = 2536.1$ cm$^{-1}$ and the Statistical Weights of the Associated Rotational Levels (For Carbon 13 central atom, multiply the tabulated statistical weights by 2.) (Note the discussion following this table.)

<table>
<thead>
<tr>
<th>$v_1$</th>
<th>$v_2(1_2)$</th>
<th>$v_3$</th>
<th>$\xi v_1 v_2 v_3 - 0000$ (cm$^{-1}$)</th>
<th>Symm. Species of $\psi$ Vib.</th>
<th>Stat. Wt. of Assoc. Rot. Levels with even $J$</th>
<th>Stat. Wt. of Assoc. Rot. Levels with odd $J$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0(0)</td>
<td>0</td>
<td>0</td>
<td>$\Sigma_g^+$ $\Pi_\gamma$</td>
<td>$(2J+1)$</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>1(1)</td>
<td>0</td>
<td>667.3</td>
<td>$\Sigma_g^+$ $\Pi_\gamma$</td>
<td>$(2J+1)$</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>2(0)</td>
<td>0</td>
<td>1285.8</td>
<td>$\Sigma_g^+$ $\Pi_\gamma$</td>
<td>$(2J+1)$</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>2(2)</td>
<td>0</td>
<td>1335.4</td>
<td>$\Delta_9$ $\Phi_\delta$</td>
<td>0</td>
<td>$(2J+1)$</td>
</tr>
<tr>
<td>0</td>
<td>3(1)</td>
<td>0</td>
<td>1931.9</td>
<td>$\Pi_\gamma$</td>
<td>0</td>
<td>$(2J+1)$</td>
</tr>
<tr>
<td>0</td>
<td>3(3)</td>
<td>0</td>
<td>2004.3</td>
<td>$\Sigma_g^+$ $\Pi_\gamma$</td>
<td>$(2J+1)$</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>4(0)</td>
<td>0</td>
<td>2547.4</td>
<td>$\Sigma_g^+$ $\Delta_9$ $\phi_\gamma$</td>
<td>$(2J+1)$</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>4(2)</td>
<td>0</td>
<td>2583.4</td>
<td></td>
<td>$(2J+1)$</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>4(4)</td>
<td>0</td>
<td>not given</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0(0)</td>
<td>0</td>
<td>1388.1</td>
<td>$\Sigma_g^+$</td>
<td>$(2J+1)$</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0(0)</td>
<td>0</td>
<td>2798.8</td>
<td>$\Sigma_g^+$</td>
<td>$(2J+1)$</td>
<td>0</td>
</tr>
</tbody>
</table>

(continued on next page)
<table>
<thead>
<tr>
<th>( v_1 )</th>
<th>( v_2(1) )</th>
<th>( v_3 )</th>
<th>( \sum_{v_1 v_2 - 2 v_3} G ) (cm(^{-1}))</th>
<th>Symm. Species of ( \psi_{Vib.} )</th>
<th>Stat. Wt. of Assoc. Rot. Levels with even ( J )</th>
<th>Stat. Wt. of Assoc. Rot. Levels with odd ( J )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1(1)</td>
<td>0</td>
<td>2077.1</td>
<td>( \Sigma^+ )</td>
<td>( \Pi^+ )</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>2(0)</td>
<td>0</td>
<td>2626.2</td>
<td>( \Sigma^+ )</td>
<td>( \Pi^+ )</td>
<td>(2J+1)</td>
</tr>
<tr>
<td>1</td>
<td>2(2)</td>
<td>0</td>
<td>2762.2</td>
<td>( \Sigma^+ )</td>
<td>( \Pi^+ )</td>
<td>(2J+1)</td>
</tr>
<tr>
<td>0</td>
<td>0(0)</td>
<td>1</td>
<td>2349.4</td>
<td>( \Sigma^+ )</td>
<td>( \Delta_2 )</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>0(0)</td>
<td>2</td>
<td>not given</td>
<td>( \Sigma^+ )</td>
<td>( \Sigma^+ )</td>
<td>(2J+1)</td>
</tr>
<tr>
<td>0</td>
<td>1(1)</td>
<td>1</td>
<td>not given</td>
<td>( \Sigma^+ )</td>
<td>( \Delta_2 )</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>2(0)</td>
<td>1</td>
<td>3613.2</td>
<td>( \Sigma^+ )</td>
<td>( \Sigma^+ )</td>
<td>(2J+1)</td>
</tr>
<tr>
<td>1</td>
<td>0(0)</td>
<td>1</td>
<td>3715.6</td>
<td>( \Sigma^+ )</td>
<td>( \Sigma^+ )</td>
<td>(2J+1)</td>
</tr>
</tbody>
</table>
From Table 11 it appears that, due to nuclear spin, vibration-rotation bands involving vibrational states of different g-u symmetry (See pp. 12, 13) will have no Q branches while bands involving states with the same g-u symmetry can have no P and R branches. However, we have neglected to mention the phenomenon known as "l-type doubling." *(See pp. 377, 373 of Herzberg, Volume 2 (25).)* This amounts to the fact that each of the $\Pi, \Delta, \ldots$ vibrational levels (i.e., all except the $\Sigma$ ones) have a twofold degeneracy brought about by the equivalence of the two directions of the angular momentum $l_z$. (A splitting occurs which increases with increasing $J$. ) The respective components of each pair of levels have opposite symmetry with respect to inversion. *(See pp. 372, 373 of (25).)* Hence, for each $\Pi, \Delta, \ldots$ state with even $J$ listed in Table 11 as having statistical weight $(2J+1)$ there exists a companion ($J$ even) state with statistical weight 0; and for each $\Pi, \Delta, \ldots$ state with odd $J$ having statistical weight 0 there exists a companion (odd $J$) state with statistical weight $(2J+1)$, etc.

The appropriate parts of Table 11 should then read:

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Pi_\alpha$</td>
<td>$(2J+1)$</td>
<td>0</td>
</tr>
<tr>
<td>$\Delta_g$</td>
<td>0</td>
<td>$(2J+1)$</td>
</tr>
<tr>
<td>$\Sigma_g$</td>
<td>$(2J+1)$</td>
<td>0</td>
</tr>
<tr>
<td>$\Sigma_u$</td>
<td>0</td>
<td>$(2J+1)$</td>
</tr>
</tbody>
</table>

Thus, while no Q branches will occur for $\Sigma_g \leftrightarrow \Sigma_u$ bands
(and no P and R branches would occur for $\Sigma_g \rightarrow \Sigma_g$ and $\Sigma_u \rightarrow \Sigma_u$ bands, were they to have non-negligible intensities), P, Q, and R branches can occur in all other types of bands, as far as nuclear spin is concerned.

Table 12 contains Dennison's numerical values for the $\omega_4$ and the cubic anharmonic potential function constants for CO$_2$. See (15); c.f. Redlich (61) and Eggers and Crawford (13). Table 13 lists the values of the $A_{ij}$ of Equation (209) for the case of CO$_2$, calculated from the $\omega_4$ and $K_{ijk}$ of Table 12. In order that the most appropriate transitions for which to calculate $\Pi r_i'$ be determined, Table 14 was set up. This table, obtained primarily by comparison of Tables 9 and 11, contains the absorptive transitions which can, according to our theory, give rise to non-zero transition probability, in addition to the dipole moment coefficients and $A_{ij}$'s which occur in $\mu$ or $\mu'$. Table 15, obtained from page 274 of Herzberg, Volume 2 (25) lists data on the observed bands of CO$_2$.

It appears that the coefficients $C_{32}$ and $C_{33}$ have negligible values, since transitions whose probabilities involve only these dipole moment coefficients do not appear in the table of observed transitions. This might be expected, since the terms $C_{32}q_3r$ and $C_{33}q_3^2$ do not have the same symmetry as any of the components of the dipole moment of the "point charge atom" model of the molecule. See the discussion on page 43 f. Also, there appear to be some
### TABLE 12

**Numerical Values of Some of the Molecular Constants for CO₂**

[From Dennison (45)]

\[ B_e = \frac{\hbar}{8\pi^2 c I_0} = 0.3895 \text{ cm}^{-1} \]

\[ \omega_1 = 1351.2 \text{ cm}^{-1} \]

\[ \omega_2 = 672.2 \text{ cm}^{-1} \]

\[ \omega_3 = 2396.4 \text{ cm}^{-1} \]

\( \therefore \epsilon = \left( \frac{2B_e}{\omega_1} \right)^\frac{3}{2} = 0.0240 \)

\[ \epsilon K_{111} = -30 \text{ cm}^{-1} \), or \( K_{111} = -12.5 \times 10^2 \text{ cm}^{-1} \)

\[ \epsilon K_{122} = 71.3 \text{ cm}^{-1} \), or \( K_{122} = 29.7 \times 10^2 \text{ cm}^{-1} \)

\[ \epsilon K_{133} = -250 \text{ cm}^{-1} \), or \( K_{133} = -104 \times 10^2 \text{ cm}^{-1} \)
TABLE 13

Numerical Values of the $A_{ij}$ for CO$_2$

(See p. 73.)

<table>
<thead>
<tr>
<th>$A_{ij}$</th>
<th>Formula</th>
<th>Value</th>
<th>$\epsilon A_{ij}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{11}$</td>
<td>$\frac{2K_{111}}{3w_1}$</td>
<td>-0.616</td>
<td>-0.0148</td>
</tr>
<tr>
<td>$A_{12}$</td>
<td>$\frac{K_{111}}{w_1}$</td>
<td>-0.925</td>
<td>-0.0222</td>
</tr>
<tr>
<td>$A_{13}$</td>
<td>$\frac{K_{122}(2w_2^2-w_1^2)}{w_1(4w_2^2-w_1^2)}$</td>
<td>155</td>
<td>3.72</td>
</tr>
<tr>
<td>$A_{14}$</td>
<td>$\frac{K_{133}(2w_3^2-w_1^2)}{w_1(4w_3^2-w_1^2)}$</td>
<td>-3.51</td>
<td>-0.0840</td>
</tr>
<tr>
<td>$A_{15}$</td>
<td>$\frac{2K_{122}w_2}{(4w_2^2-w_1^2)}$</td>
<td>-307</td>
<td>-7.37</td>
</tr>
<tr>
<td>$A_{16}$</td>
<td>$\frac{K_{133}w_3}{(4w_3^2-w_1^2)}$</td>
<td>-1.18</td>
<td>-0.0283</td>
</tr>
<tr>
<td>$A_{17}$</td>
<td>$\frac{2K_{133}w_3^2}{w_1(4w_3^2-w_1^2)}$</td>
<td>-4.18</td>
<td>-0.100</td>
</tr>
<tr>
<td>$A_{18}$</td>
<td>$\frac{2K_{122}w_2^2}{w_1(4w_2^2-w_1^2)}$</td>
<td>-153</td>
<td>-3.67</td>
</tr>
<tr>
<td>$(\Delta v_1 ; \Delta v_2 ; \Delta v_3)$</td>
<td>Constants Occurring</td>
<td></td>
<td></td>
</tr>
<tr>
<td>---------------------------------</td>
<td>-------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(0 ; 0 ; 0)$</td>
<td>$C_{33}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(1 ; 0 ; 0)$</td>
<td>$\epsilon , C_{33} (A_{16}, A_{41})$, $\epsilon^3 , C_{32}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(0 ; 1 ; 0)$</td>
<td>$\beta_2$, $\epsilon , C_{12} (A_{17}, A_{41})$, $\epsilon^3 , C_{12}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(0 ; 0 ; 1)$</td>
<td>$\beta_3$, $\epsilon , C_{13} (A_{16}, A_{17}, A_{41})$, $\epsilon^3 , C_{13}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(1 ; 1 ; 0)$</td>
<td>$C_{12}$, $\epsilon , \beta_2 (A_{15}, A_{41})$, $\epsilon^3 , \beta_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(1 ; 0 ; 1)$</td>
<td>$C_{13}$, $\epsilon , \beta_3 (A_{16}, A_{17}, A_{41})$, $\epsilon^3 , \beta_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(0 ; 1 ; 1)$</td>
<td>$C_{32}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(1 ; -1 ; 1)$</td>
<td>$\epsilon , C_{32} (A_{15}, A_{16}, A_{17}, A_{41})$, $\epsilon^3 , C_{32}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(-1 ; -1 ; 1)$</td>
<td>$\epsilon , C_{33} (A_{16}, A_{17}, A_{41})$, $\epsilon^3 , C_{33}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(0 ; 0 ; 2)$</td>
<td>$C_{33}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(1 ; 0 ; 2)$</td>
<td>$\epsilon , C_{33} (A_{16}, A_{17}, A_{41})$, $\epsilon^3 , C_{33}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(0 ; 1 ; 2)$</td>
<td>$\epsilon , C_{12} (A_{14}, A_{17})$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(2 ; 0 ; 1)$</td>
<td>$\epsilon , C_{13} (A_{11}, A_{12}, A_{14}, A_{41})$, $\epsilon^3 , C_{13}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(2 ; 1 ; 0)$</td>
<td>$\epsilon , C_{12} (A_{11}, A_{12}, A_{15}, A_{41})$, $\epsilon^3 , C_{12}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(0 ; 2 ; 1)$</td>
<td>$\epsilon , C_{13} (A_{13}, A_{41})$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(1 ; 2 ; 0)$</td>
<td>$\epsilon , C_{33} A_{41}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(continued on next page)
**TABLE 14 (Continued)**

<table>
<thead>
<tr>
<th>((\Delta v_1 \quad \Delta v_2 \quad \Delta v_3))</th>
<th>Constants Occurring</th>
</tr>
</thead>
<tbody>
<tr>
<td>((1 \quad \pm 2 \quad 1))</td>
<td>(\epsilon B_3 A_{41})</td>
</tr>
<tr>
<td>((-1 \quad 2 \quad 1))</td>
<td>(\epsilon C_{33} A_{41})</td>
</tr>
<tr>
<td>((1 \quad 2 \quad -1))</td>
<td>(\epsilon C_{13} A_{41})</td>
</tr>
<tr>
<td>((1 \quad \pm 2 \quad 2))</td>
<td>(\epsilon C_{13} (A_{14}, A_{17}))</td>
</tr>
<tr>
<td>((-1 \quad \pm 2 \quad 2))</td>
<td>(\epsilon C_{13} (A_{13}, A_{41}))</td>
</tr>
<tr>
<td>((\pm 2 \quad 2 \quad 1))</td>
<td>(\epsilon B_2 A_{41})</td>
</tr>
<tr>
<td>((2 \quad -2 \quad 1))</td>
<td>(\epsilon C_{32} A_{41})</td>
</tr>
<tr>
<td>((2 \quad 2 \quad -1))</td>
<td>(\epsilon C_{12} A_{41})</td>
</tr>
<tr>
<td>((0 \quad 0 \quad 3))</td>
<td>(\epsilon C_{13} (A_{14}, A_{17}))</td>
</tr>
<tr>
<td>((0 \quad 3 \quad 0))</td>
<td>(\epsilon C_{13} (A_{13}, A_{41}))</td>
</tr>
<tr>
<td>((\pm 1 \quad 3 \quad 0))</td>
<td>(\epsilon C_{32} A_{41})</td>
</tr>
<tr>
<td>((\pm 1 \quad 3 \quad 1))</td>
<td>(\epsilon C_{12} A_{41})</td>
</tr>
<tr>
<td>((1 \quad -3 \quad 1))</td>
<td>(\epsilon C_{32} A_{41})</td>
</tr>
<tr>
<td>((1 \quad 3 \quad -1))</td>
<td>(\epsilon C_{12} A_{41})</td>
</tr>
<tr>
<td>((2 \quad \pm 3 \quad 0))</td>
<td>(\epsilon C_{12} A_{41})</td>
</tr>
</tbody>
</table>
### TABLE 15

Observed Bands of Gaseous CO\(_2\) [from p. 274 of (25)]

("Strength": vs = very strong; s = strong; m = medium; w = weak; vw = very weak; F.R.(U) = Fermi resonance of upper states; F.U.(L) = Fermi resonance of lower states)

<table>
<thead>
<tr>
<th>Observed (\nu) (cm(^{-1}))</th>
<th>&quot;Strength&quot;</th>
<th>Initial State (v_1) (V_2(l_2)) (v_3)</th>
<th>(\Delta V_1)</th>
<th>(\Delta V_2(\Delta l_2))</th>
<th>(\Delta V_3)</th>
<th>Type Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>667.3</td>
<td>vs</td>
<td>0 0(0) 0</td>
<td>0 1 (1) 0</td>
<td>(\Sigma_g^+)</td>
<td>(\Pi_u)</td>
<td></td>
</tr>
<tr>
<td>2349.3</td>
<td>vs</td>
<td>0 0 (0) 1</td>
<td>(\Sigma_g^+)</td>
<td>(\Sigma_u^+)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3609</td>
<td>s</td>
<td>0 2 (0) 1</td>
<td>&quot;</td>
<td>&quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3716</td>
<td>F.R.(U)</td>
<td>1 0 (0) 1</td>
<td>&quot;</td>
<td>&quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1932.5</td>
<td>F.R.(U)</td>
<td>0 3 (1) 0</td>
<td>(\Sigma_g^+)</td>
<td>(\Pi_u)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2076.5</td>
<td>m</td>
<td>1 1 (1) 0</td>
<td>&quot;</td>
<td>&quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4860.5</td>
<td>m</td>
<td>0 4 (0) 1</td>
<td>(\Sigma_g^+)</td>
<td>(\Sigma_u^+)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4983.5</td>
<td>F.R.(U)</td>
<td>1 2 (0) 1</td>
<td>&quot;</td>
<td>&quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5109</td>
<td>m</td>
<td>2 0 (0) 1</td>
<td>&quot;</td>
<td>&quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>618.1</td>
<td>m</td>
<td>0 1(1) 0</td>
<td>0 1 (-1) 0</td>
<td>(\Pi_u)</td>
<td>(\Sigma_g^+)</td>
<td></td>
</tr>
<tr>
<td>668.3</td>
<td>?</td>
<td>0 1 (1) 0</td>
<td>(\Pi_u)</td>
<td>(\Delta_g)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>720.5</td>
<td>m</td>
<td>1 -1 (-1) 0</td>
<td>(\Pi_u)</td>
<td>(\Sigma_g^+)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(continued on next page)
<table>
<thead>
<tr>
<th>Observed $\omega$ (cm$^{-1}$)</th>
<th>&quot;Strength&quot;</th>
<th>Initial State $v_1 v_2 l_2 v_3$</th>
<th>$\Delta v_1$</th>
<th>$\Delta v_2 (\Delta l_2)$</th>
<th>$\Delta v_3$</th>
<th>Type Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>2094</td>
<td>m</td>
<td>0 1(1) 0</td>
<td>1</td>
<td>1 (1)</td>
<td>0</td>
<td>$\Pi_u \rightarrow \Delta_g$</td>
</tr>
<tr>
<td>2137</td>
<td>m</td>
<td>$n$</td>
<td>2</td>
<td>-1 (-1)</td>
<td>0</td>
<td>$\Pi_u \rightarrow \Sigma_g^+$</td>
</tr>
<tr>
<td>6077</td>
<td>w</td>
<td>0 0(0) 0</td>
<td>0</td>
<td>6 (0)</td>
<td>1</td>
<td>$\Sigma_g^+ \rightarrow \Sigma_u^+$</td>
</tr>
<tr>
<td>6231</td>
<td>w</td>
<td>$n$</td>
<td>1</td>
<td>4 (0)</td>
<td>1</td>
<td>$n$</td>
</tr>
<tr>
<td>6351</td>
<td>w</td>
<td>$n$</td>
<td>2</td>
<td>2 (0)</td>
<td>1</td>
<td>$n$</td>
</tr>
<tr>
<td>6510</td>
<td>w</td>
<td>$n$</td>
<td>3</td>
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<td>1</td>
<td>$n$</td>
</tr>
<tr>
<td>6976</td>
<td>w</td>
<td>$n$</td>
<td>0</td>
<td>0 (0)</td>
<td>3</td>
<td>$n$</td>
</tr>
<tr>
<td>1586</td>
<td>w</td>
<td>0 1(1) 0</td>
<td>0</td>
<td>3 (-1)</td>
<td>0</td>
<td>$\Pi_u \rightarrow \Sigma_g^+$</td>
</tr>
<tr>
<td>596.8</td>
<td>w</td>
<td>0 2(2) 0</td>
<td>0</td>
<td>1 (1)</td>
<td>0</td>
<td>$\Delta_g \rightarrow \Pi_u$</td>
</tr>
<tr>
<td>647.6</td>
<td>w</td>
<td>0 2(0) 0</td>
<td>0</td>
<td>1 (-1)</td>
<td>0</td>
<td>$\Sigma_g^+ \rightarrow \Pi_u$</td>
</tr>
<tr>
<td>740.8</td>
<td>w</td>
<td>0 2(2) 0</td>
<td>1</td>
<td>-1 (-1)</td>
<td>0</td>
<td>$\Delta_g \rightarrow \Pi_u$</td>
</tr>
<tr>
<td>960.8</td>
<td>w</td>
<td>1 0(0) 0</td>
<td>-1</td>
<td>0 (0)</td>
<td>1</td>
<td>$\Sigma_g^+ \rightarrow \Sigma_u^+$</td>
</tr>
<tr>
<td>1063.6</td>
<td>w</td>
<td>0 2(0) 0</td>
<td>0</td>
<td>-2 (0)</td>
<td>1</td>
<td>$n$</td>
</tr>
</tbody>
</table>

(continued on next page)
<table>
<thead>
<tr>
<th>Observed $\omega$ (cm$^{-1}$)</th>
<th>&quot;Strength&quot;</th>
<th>Initial State $v_1$ $v_2$($l_2$) $v_3$</th>
<th>$\Delta v_1$ $\Delta v_2$($\Delta l_2$) $\Delta v_3$</th>
<th>Type Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>8193</td>
<td>$vw$</td>
<td>0 0(0) 0</td>
<td>0 2 (0) 3</td>
<td>$\Sigma_9^+ \rightarrow \Sigma_\nu^+$</td>
</tr>
<tr>
<td>8293</td>
<td>$vw$</td>
<td>&quot;</td>
<td>1 0 (0) 3</td>
<td>&quot;</td>
</tr>
<tr>
<td>11496.5</td>
<td>$vw$</td>
<td>0 0(0) 0</td>
<td>0 0 (0) 5</td>
<td>&quot;</td>
</tr>
<tr>
<td>12672.4</td>
<td>$vw$</td>
<td>&quot;</td>
<td>0 2 (0) 5</td>
<td>&quot;</td>
</tr>
<tr>
<td>12774.7</td>
<td>$vw$</td>
<td>&quot;</td>
<td>1 0 (0) 5</td>
<td>&quot;</td>
</tr>
<tr>
<td>790.8</td>
<td>$vw$</td>
<td>0 2(0) 0</td>
<td>1 -1 (1) 0</td>
<td>$\Sigma_9^+ \rightarrow \Pi_\nu$</td>
</tr>
</tbody>
</table>

*TABLE 15 (Continued)*
observed high order transitions (most of them "weak" or "very weak") which are not included in our Table 14 of "possible" transitions. This could stem from the fact that we neglected cubic and higher terms in our dipole moment expansion and quartic and higher terms in our anharmonic potential function.

Table 16 contains expressions for the \( \Pi_{\frac{r}{a}}^{\prime} \) going with all of the observed \( \{ \Delta v_1 \Delta v_2(\Delta l_2) \Delta v_3 \} \) except the few high order ones mentioned above. Also included are the non-vanishing \( \Pi_{\frac{r}{a}}^{\prime} \) going with some additional transitions, indicated in the table by the brackets around \( \Delta v_1 \Delta v_2(\Delta l_2) \Delta v_3 \). Numerical values of the constants (excluding the dipole moment expansion coefficients) which appear in the \( \Pi_{\frac{r}{a}}^{\prime} \) expressions are listed for the case of \( CO_2 \) in Table 17.

A number of the expressions for \( \Pi_{\frac{r}{a}}^{\prime} \) in Table 16 illustrate the fact that vibration-rotation interaction can decrease the intensity of one side branch (i.e., a P or an R branch) of a vibration-rotation band and increase the intensity of the other. These expressions are the ones in which the factor \( F_2 \) occurs. \( F_1 \) also gives rise to asymmetry, but, as can be seen from Table 8, the effect is considerably smaller. \( \left[ \text{It should be recalled that both } F_1 = J'(J'+1)-1 \frac{1}{2} \text{ and } F_2 = J'(J'+1)-1 \frac{1}{2} - \{J(J+1)-1 \frac{1}{2}\} \text{ arise purely from the term} \right. \)

\[ H_{11} = 2hcB_c \equiv \frac{(r^2 - F_2^2)}{\hbar^2} \]

in the first order portion of the Hamiltonian. (See p. 73.) It is to
\[ \Pi_{\Pi}^{r'} \text{ for Some Transitions } \{ \Delta V_1, \Delta V_2, \Delta V_3 \} \]

\[ r_2 = \{ v_1v_2\ldots v_9 \} ; \ J = J(J\alpha J'^1J'^1) ; \ F_1 = F_1(J'^1J'^1) ; \ F_2 = F_2(J\alpha J'^1J'^1) \text{ (See Table 5,)} \]

<table>
<thead>
<tr>
<th>( \Delta V_1 )</th>
<th>( \Delta V_2 )</th>
<th>( \Delta V_3 )</th>
<th>( \Pi_{\Pi}^{r'} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0 (0)</td>
<td>0</td>
<td>( \mathcal{J} \mathcal{C}_{33} (v_3 + \frac{1}{2})^2 )</td>
</tr>
</tbody>
</table>
| 0              | 0 (0)          | 1              | \[ \mathcal{J} \frac{3}{2} \mathcal{B}_{3} (v_3 + 1) \left\{ 1 - \epsilon^2(C_{13}/\mathcal{B}_3) \left[ D_1(v_1 + \frac{1}{2}) + D_2(v_3 + 1) + D_3(v_2 + 1) \right] + \epsilon^4(C_{13}/\mathcal{B}_3)^2 \right\} \]
|                |                | \cdot \left[ D_1(v_1 + \frac{1}{2}) + D_2(v_3 + 1) + D_3(v_2 + 1) \right] \right\} + \epsilon^4(C_{13}/\mathcal{B}_3)^2 \;
|                |                | \cdot (F_2 - 2F_1) \] \]
| 0              | 1 (1)          | 0              | \[ \mathcal{J} \frac{3}{2}(v_2 + \frac{1}{2}) \mathcal{B}_{2} \left\{ 1 - 2 \epsilon(C_{13}/\mathcal{B}_2) \left[ D_8(v_1 + \frac{1}{2}) + D_9(v_3 + \frac{1}{2}) + 2D_{10}(3V_2 + 1 + 5) + D_{11} \right] \right\} \]
|                |                | \cdot \epsilon^4(C_{13}/\mathcal{B}_2)^2 \left[ D_8(v_1 + \frac{1}{2}) + D_9(v_3 + \frac{1}{2}) + 2D_{10}(3V_2 + 1 + 5) + D_{11} \right] \right\} + \epsilon^4(C_{13}/\mathcal{B}_2)^2 \;
|                |                | \cdot (F_2 - 2F_1) \right\} + \epsilon^4(C_{13}/\mathcal{B}_2)(F_2 - 2F_1) \] \]

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<table>
<thead>
<tr>
<th>$\Delta v_1$</th>
<th>$\Delta v_2$ ($\Delta l_2$)</th>
<th>$\Delta v_3$</th>
<th>$\Pi'_{n_1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1 (-1)</td>
<td>0</td>
<td>$\mathcal{I}^2_2 (v_{3-1}+\varphi\theta_2^2) \left{1 - 2\varepsilon (c_{12} + \theta_2) \left[ D_8(v_{1+\frac{1}{2}}+D_9(v_{3+\frac{1}{2}})+D_{10}(3v_{2+1}+h)+D_{11} \right] + \varepsilon^3 (C_{12} + \theta_2) \varepsilon^2 (C_{12} + \theta_2) \left[ -D_4 + (v_{3+1} + D_5 \right] + \varepsilon^2 F_2 \left{-D_4 + (v_{3+1} + D_5 + (1/4) \varepsilon^2 F_2 \right} \right} $</td>
</tr>
<tr>
<td>1</td>
<td>0 (0)</td>
<td>0</td>
<td>$\mathcal{I}^2_2 (v_{3+1} + \varphi\theta_2^2) \left{1 - 2\varepsilon (c_{13} + \theta_2) \left[ C_{12} - \varepsilon \theta_3 D_{12} \left{ w_1 - (v_{2+1}+h) w_2 \right} \right} + \varepsilon^2 \theta_2 D_{12}^2 \left{ w_1 - (v_{2+1}+h) w_2 \right} \right} $</td>
</tr>
<tr>
<td>1</td>
<td>1 (1)</td>
<td>0</td>
<td>$\mathcal{I}^2_2 (v_{3+1} + \varphi\theta_2^2) \left{1 - 2\varepsilon (c_{13} + \theta_2) \left[ C_{12} - \varepsilon \theta_3 D_{12} \left{ w_1 - (v_{2+1}+h) w_2 \right} \right} + \varepsilon^2 \theta_2 D_{12}^2 \left{ w_1 - (v_{2+1}+h) w_2 \right} \right} $</td>
</tr>
<tr>
<td>1</td>
<td>1 (-1)</td>
<td>0</td>
<td>$\mathcal{I}^2_2 (v_{3+1} + \varphi\theta_2^2) \left{1 - 2\varepsilon (c_{13} + \theta_2) \left[ C_{12} - \varepsilon \theta_3 D_{12} \left{ w_1 - (v_{2-1}+h) w_2 \right} \right} + \varepsilon^2 \theta_2 D_{12}^2 \left{ w_1 - (v_{2-1}+h) w_2 \right} \right} $</td>
</tr>
<tr>
<td>$\Delta V_1$</td>
<td>$\Delta V_2$ ($\Delta l_2$)</td>
<td>$\Delta V_3$</td>
<td>$\Pi_{\mu}^{\nu}$</td>
</tr>
<tr>
<td>---------</td>
<td>----------------</td>
<td>---------</td>
<td>-----------</td>
</tr>
<tr>
<td>1</td>
<td>-1 (1)</td>
<td>0</td>
<td>$\mathcal{F}<em>{\frac{7}{4}}(v_1+1)(v_2-1)$ ( C</em>{12}^l - \varepsilon \Theta^2 D_{12} \left[ w_1 - (v_2-1)w_2 \right] + \varepsilon^2 \Theta^2 D_{12} \left[ w_1 - (v_2-1)w_2 \right]^2 + \varepsilon^3 D_{12} \left[ w_1 - (v_2-1)w_2 \right]^3 )</td>
</tr>
<tr>
<td>1</td>
<td>-1 (-1)</td>
<td>0</td>
<td>$\mathcal{F}<em>{\frac{7}{4}}(v_1+1)(v_2+1) \cdot C</em>{12}^l - \varepsilon \Theta^2 D_{12} \left[ w_1 - (v_2+1)w_2 \right] + \varepsilon^2 \Theta^2 D_{12} \left[ w_1 - (v_2+1)w_2 \right]^2 + \varepsilon^3 D_{12} \left[ w_1 - (v_2+1)w_2 \right]^3 )</td>
</tr>
<tr>
<td>1</td>
<td>0 (0)</td>
<td>1</td>
<td>$\mathcal{F}<em>{\frac{7}{4}}(v_1+1)(v_3+1) \cdot C</em>{13}^l - \varepsilon \Theta D_3 C_{13} \left[ D_6 - (v_2+1)D_7 \right] + \varepsilon^2 \Theta^2 D_{12} \left[ D_6 - (v_2+1)D_7 \right]^2 + \varepsilon^3 D_3 \left[ D_6 - (v_2+1)D_7 \right]^3 )</td>
</tr>
<tr>
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<td>0 (0)</td>
<td>1</td>
<td>$\mathcal{F}<em>{\frac{7}{4}}(v_1+1)(v_3+1) \cdot C</em>{13}^l - \varepsilon \Theta D_3 C_{13} \left[ D_{14} + (v_3+1)D_7 \right] + \varepsilon^2 \Theta^2 D_{12} \left[ D_{14} + (v_3+1)D_7 \right]^2 + \varepsilon^3 D_3 \left[ D_{14} + (v_3+1)D_7 \right]^3 )</td>
</tr>
<tr>
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<td>$\mathcal{F}<em>{\frac{7}{4}}(v_1+1)(v_1+2)(v_3+1) \cdot C</em>{13}^l \left[ \left{ D_{15} + (v_3+1)D_7 \right}^2 + \varepsilon^2 D_3 \left{ D_{15} + (v_3+1)D_7 \right}^3 \right] )</td>
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<tr>
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<td>0 (0)</td>
<td>-1</td>
<td>$\mathcal{F}<em>{\frac{7}{4}}(v_1+1)(v_1+2) \cdot C</em>{13}^l \left[ \left{ D_{17} + (v_2+1)D_7 \right}^2 + \varepsilon^2 D_3 \left{ D_{17} + (v_2+1)D_7 \right}^3 \right] )</td>
</tr>
<tr>
<td>2</td>
<td>-1 (1)</td>
<td>0</td>
<td>$\mathcal{F}<em>{\frac{7}{4}}(v_1+1)(v_1+2)(v_2-1) \cdot C</em>{13}^l \left[ \left{ D_{18} + (v_2-1)D_5 \right}^2 + \varepsilon^2 D_3 \left{ D_{18} + (v_2-1)D_5 \right}^3 \right] )</td>
</tr>
<tr>
<td>$\Delta v_1$</td>
<td>$\Delta v_2$</td>
<td>$\Delta l_2$</td>
<td>$\Delta v_3$</td>
</tr>
<tr>
<td>-------------</td>
<td>-------------</td>
<td>-------------</td>
<td>-------------</td>
</tr>
<tr>
<td>2</td>
<td>-1 (1)</td>
<td>0</td>
<td>$\epsilon_{1F} \frac{1}{8}(v_{1+1})(v_{2+1})(v_{2+1}+2) C_{12} \left[ \left{ D_{18}+(v_{2+1}+2)D_{5} \right} +2 \epsilon \frac{1}{2} F_2 \left{ D_{18}+(v_{2+1}+2)D_{5}+\frac{1}{2} \epsilon \frac{1}{2} F_2 \right} \right]$</td>
</tr>
<tr>
<td>2</td>
<td>1 (1)</td>
<td>0</td>
<td>$\epsilon_{1F} \frac{1}{8}(v_{1+1})(v_{1+2})(v_{2+1}+2) C_{12} \left[ \left{ D_{18}+(v_{2+1}+2)D_{5} \right} +2 \epsilon \frac{1}{2} F_2 \left{ D_{18}+(v_{2+1}+2)D_{5}+\frac{1}{2} \epsilon \frac{1}{2} F_2 \right} \right]$</td>
</tr>
<tr>
<td>2</td>
<td>1 (-1)</td>
<td>0</td>
<td>$\epsilon_{1F} \frac{1}{8}(v_{2+1}+2)(v_{2}+1)(v_{2}+2) C_{12} \left[ \left{ D_{18}+(v_{2}+2)D_{5} \right} +2 \epsilon \frac{1}{2} F_2 \left{ D_{18}+(v_{2}+2)D_{5}+\frac{1}{2} \epsilon \frac{1}{2} F_2 \right} \right]$</td>
</tr>
<tr>
<td>0</td>
<td>2 (0)</td>
<td>1</td>
<td>$\epsilon_{1F} \frac{1}{8}(v_{2}+2)(v_{2}+1)(v_{3}+1) C_{13} \left{ D_{13} \left[ D_{13}-(v_{2}+2)D_{5} \right) +2 \epsilon \frac{1}{2} F_2 \left{ D_{13}-(v_{2}+2)D_{5}+\frac{1}{2} \epsilon \frac{1}{2} F_2 \right} \right]$</td>
</tr>
<tr>
<td>0</td>
<td>-2 (0)</td>
<td>1</td>
<td>$\epsilon_{1F} \frac{1}{8}(v_{2}+2)(v_{2}+1)(v_{3}+1) C_{13} \left{ D_{13} \left[ D_{13}-(v_{2}+2)D_{5} \right) +2 \epsilon \frac{1}{2} F_2 \left{ D_{13}-(v_{2}+2)D_{5}+\frac{1}{2} \epsilon \frac{1}{2} F_2 \right} \right]$</td>
</tr>
<tr>
<td>-1</td>
<td>-1 (1)</td>
<td>1</td>
<td>$\epsilon_{1F} \frac{1}{8}(v_{2}+1)(v_{2}+2)(v_{3}+1) C_{32} \left[ \left{ D_{32}-(v_{2}+2)D_{5} \right} +2 \epsilon \frac{1}{2} F_2 \left{ D_{32}-(v_{2}+2)D_{5}+\frac{1}{2} \epsilon \frac{1}{2} F_2 \right} \right]$</td>
</tr>
<tr>
<td>-1</td>
<td>1 (1)</td>
<td>1</td>
<td>$\epsilon_{1F} \frac{1}{8}(v_{2}+1)(v_{2}+2)(v_{3}+1) C_{32} \left[ \left{ D_{32}-(v_{2}+2)D_{5} \right} +2 \epsilon \frac{1}{2} F_2 \left{ D_{32}-(v_{2}+2)D_{5}+\frac{1}{2} \epsilon \frac{1}{2} F_2 \right} \right]$</td>
</tr>
<tr>
<td>-1</td>
<td>1 (-1)</td>
<td>1</td>
<td>$\epsilon_{1F} \frac{1}{8}(v_{2}+1)(v_{2}+2)(v_{3}+1) C_{32} \left[ \left{ D_{32}-(v_{2}+2)D_{5} \right} +2 \epsilon \frac{1}{2} F_2 \left{ D_{32}-(v_{2}+2)D_{5}+\frac{1}{2} \epsilon \frac{1}{2} F_2 \right} \right]$</td>
</tr>
</tbody>
</table>
### TABLE 16 (Continued)

<table>
<thead>
<tr>
<th>( \Delta v_1 )</th>
<th>( \Delta v_2 (\Delta l_2) )</th>
<th>( \Delta v_3 )</th>
<th>( \Pi_{q}^{n} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-1 (-1)</td>
<td>1</td>
<td>( \varepsilon^{4} \frac{1}{8} (v_{1}+1)(v_{2}+l_{3})(v_{3}+1) C_{33}^{2} \left{ \left{ D_{13} - (v_{2}+l_{3})D_{5} \right}^{2} - 2 \varepsilon^{1} F_{2} \left{ D_{13} - (v_{2}+l_{3})D_{5} - \frac{1}{2} \varepsilon^{1} F_{3} \right} \right} )</td>
</tr>
<tr>
<td>1</td>
<td>2 (0)</td>
<td>1</td>
<td>( \varepsilon^{4} \frac{1}{4} (v_{1}+1)(v_{2}+l_{3}+2)(v_{3}+1) B_{3}^{2} D_{5}^{2} )</td>
</tr>
<tr>
<td>-1</td>
<td>-2 (0)</td>
<td>1</td>
<td>( \varepsilon^{4} \frac{1}{4} v_{1}(v_{2}-l_{3}+2)(v_{2}+l_{3}+2)(v_{3}+1) B_{3}^{2} D_{5}^{2} )</td>
</tr>
<tr>
<td>1</td>
<td>2 (0)</td>
<td>-1</td>
<td>( \varepsilon^{4} \frac{1}{4} (v_{1}+1)(v_{2}-l_{3}+2)(v_{2}+l_{3}+2) v_{3} B_{3}^{2} D_{5}^{2} )</td>
</tr>
<tr>
<td>2</td>
<td>2 (0)</td>
<td>1</td>
<td>( \varepsilon^{4} \frac{1}{8} (v_{1}+2)(v_{2}-l_{3}+2)(v_{2}+l_{3}+2)(v_{3}+1) C_{13} D_{5}^{2} )</td>
</tr>
<tr>
<td>2</td>
<td>2 (0)</td>
<td>1</td>
<td>( \varepsilon^{4} \frac{1}{8} (v_{1}+2)(v_{2}-l_{3}+2)(v_{2}+l_{3}+2)(v_{3}+1) C_{13} D_{5}^{2} )</td>
</tr>
<tr>
<td>-2</td>
<td>-2 (0)</td>
<td>1</td>
<td>( \varepsilon^{4} \frac{1}{8} (v_{1}+1)(v_{1}+2)(v_{2}+l_{3})(v_{3}+1) C_{13} D_{5}^{2} )</td>
</tr>
<tr>
<td>2</td>
<td>2 (0)</td>
<td>-1</td>
<td>( \varepsilon^{4} \frac{1}{8} (v_{1}+1)(v_{1}+2)(v_{2}-l_{3}+2)(v_{2}+l_{3}+2) v_{3} C_{13} D_{5}^{2} )</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>2</td>
<td>( \varepsilon^{4} \frac{1}{4} (v_{3}+2) C_{33}^{2} )</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>3</td>
<td>( \varepsilon^{4} \frac{1}{8} (v_{3}+1)(v_{3}+2)(v_{3}+3) C_{13} D_{19}^{2} )</td>
</tr>
<tr>
<td>$\Delta v_1$</td>
<td>$\Delta v_2$ ($\Delta l_2$)</td>
<td>$\Delta v_3$</td>
<td>$\Pi_{11}^{0}$</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>0</td>
<td>3 (1)</td>
<td>0</td>
<td>$\epsilon^2 \mathcal{F} \left( \frac{1}{8} (v_2+1 \omega+2)(v_2+1 \omega+4)(v_2-1 \omega+2) \right) \mathcal{C}<em>{12} \mathcal{D}</em>{3}$</td>
</tr>
<tr>
<td>0</td>
<td>3 (-1)</td>
<td>0</td>
<td>$\epsilon^2 \mathcal{F} \left( \frac{1}{8} (v_2+1 \omega+2)(v_2-1 \omega+4)(v_2-1 \omega+2) \right) \mathcal{C}<em>{12} \mathcal{D}</em>{3}$</td>
</tr>
<tr>
<td>1</td>
<td>3 (1)</td>
<td>0</td>
<td>$\epsilon^2 \mathcal{F} \left( \frac{1}{4} (v_1+1)(v_2-1 \omega+2)(v_2+1 \omega+2)(v_2+1 \omega+4) \right) \mathcal{B}<em>{2} \mathcal{D}</em>{5}$</td>
</tr>
<tr>
<td>1</td>
<td>3 (-1)</td>
<td>0</td>
<td>$\epsilon^2 \mathcal{F} \left( \frac{1}{4} (v_1+1)(v_2-1 \omega+2)(v_2+1 \omega+2)(v_2-1 \omega+4) \right) \mathcal{B}<em>{2} \mathcal{D}</em>{5}$</td>
</tr>
<tr>
<td>-1</td>
<td>3 (1)</td>
<td>0</td>
<td>$\epsilon^2 \mathcal{F} \left( \frac{1}{4} v_1(v_2-1 \omega+2)(v_2+1 \omega+2)(v_2+1 \omega+4) \right) \mathcal{B}<em>{2} \mathcal{D}</em>{5}$</td>
</tr>
<tr>
<td>-1</td>
<td>3 (-1)</td>
<td>0</td>
<td>$\epsilon^2 \mathcal{F} \left( \frac{1}{4} v_1(v_2-1 \omega+2)(v_2+1 \omega+2)(v_2-1 \omega+4) \right) \mathcal{B}<em>{2} \mathcal{D}</em>{5}$</td>
</tr>
<tr>
<td>2</td>
<td>3 (1)</td>
<td>0</td>
<td>$\epsilon^2 \mathcal{F} \left( \frac{1}{8} (v_1+1)(v_1+2)(v_2-1 \omega+2)(v_2+1 \omega+2)(v_2+1 \omega+4) \right) \mathcal{C}<em>{12} \mathcal{D}</em>{5}$</td>
</tr>
<tr>
<td>2</td>
<td>3 (-1)</td>
<td>0</td>
<td>$\epsilon^2 \mathcal{F} \left( \frac{1}{8} (v_1+1)(v_1+2)(v_2-1 \omega+2)(v_2+1 \omega+2)(v_2-1 \omega+4) \right) \mathcal{C}<em>{12} \mathcal{D}</em>{5}$</td>
</tr>
<tr>
<td>2</td>
<td>-3 (1)</td>
<td>0</td>
<td>$\epsilon^2 \mathcal{F} \left( \frac{1}{8} (v_1+1)(v_1+2)(v_2-1 \omega+2)(v_2-1 \omega)(v_2+1 \omega) \right) \mathcal{C}<em>{12} \mathcal{D}</em>{5}$</td>
</tr>
<tr>
<td>2</td>
<td>-3 (-1)</td>
<td>0</td>
<td>$\epsilon^2 \mathcal{F} \left( \frac{1}{8} (v_1+1)(v_1+2)(v_2+1 \omega-2)(v_2-1 \omega)(v_2+1 \omega) \right) \mathcal{C}<em>{12} \mathcal{D}</em>{5}$</td>
</tr>
</tbody>
</table>
TABLE 17
Numerical Values of the Constants $D_\kappa$
for the Case of CO₂

<table>
<thead>
<tr>
<th>$D_\kappa$</th>
<th>$K_{1\mu\kappa}$ Occurring</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_1 = 3A_{11} + A_{12} + 2A_{15} = -5.14$</td>
<td>$K_{111}$ ; $K_{133}$</td>
</tr>
<tr>
<td>$D_2 = \frac{1}{2}(3A_{14} + A_{17}) = -8.86$</td>
<td>$K_{133}$</td>
</tr>
<tr>
<td>$D_3 = A_{13} = 155$</td>
<td>$K_{133}$</td>
</tr>
<tr>
<td>$D_4 = 2A_{16} = -2.36$</td>
<td>$K_{133}$</td>
</tr>
<tr>
<td>$D_5 = A_{41} = -153$</td>
<td>$K_{133}$</td>
</tr>
<tr>
<td>$D_6 = 2(A_{16} - A_{17}) = 6.00$</td>
<td>$K_{133}$</td>
</tr>
<tr>
<td>$D_7 = 2A_{11} = -306$</td>
<td>$K_{122}$</td>
</tr>
<tr>
<td>$D_8 = 3A_{11} + A_{12} + A_{15} = -310$</td>
<td>$K_{111}$ ; $K_{122}$</td>
</tr>
<tr>
<td>$D_9 = A_{14} + A_{17} = -7.69$</td>
<td>$K_{133}$</td>
</tr>
<tr>
<td>$D_{10} = \frac{1}{2}A_{13} = 77.5$</td>
<td>$K_{122}$</td>
</tr>
<tr>
<td>$D_{11} = A_{41} = -153$</td>
<td>$K_{122}$</td>
</tr>
<tr>
<td>$D_{12} = (1/\omega_2)A_{41} = -0.228$</td>
<td>$K_{122}$</td>
</tr>
<tr>
<td>$D_{13} = A_{15} + 2A_{16} - 2A_{17} = -300$</td>
<td>$K_{133}$</td>
</tr>
<tr>
<td>$D_{14} = 2(A_{16} + A_{17}) = 10.7$</td>
<td>$K_{133}$</td>
</tr>
<tr>
<td>$D_{15} = 3A_{11} - A_{12} = -0.923$</td>
<td>$K_{111}$</td>
</tr>
<tr>
<td>$D_{16} = 3A_{11} - A_{12} - 2A_{16} + 2A_{17} = -6.92$</td>
<td>$K_{111}$ ; $K_{133}$</td>
</tr>
<tr>
<td>$D_{17} = 3A_{11} - A_{12} - 2A_{16} - 2A_{17} = 9.80$</td>
<td>$K_{111}$ ; $K_{133}$</td>
</tr>
<tr>
<td>$D_{18} = 3A_{11} - A_{12} - A_{15} = 306$</td>
<td>$K_{111}$ ; $K_{122}$</td>
</tr>
<tr>
<td>$D_{19} = A_{14} - A_{17} = 0.67$</td>
<td>$K_{133}$</td>
</tr>
</tbody>
</table>
be noted that everywhere either $F_1$ or $F_2$ occur, a factor $\varepsilon^3$ is also present. If the vibration-rotation interaction asymmetry effect is to be at all appreciable, some of the other factors occurring in the respective terms must be large enough to offset this. The most likely transitions for this to be the case appear to be $\{\Delta v_1 \Delta v_2(\Delta l_2) \Delta v_3\} = \{1 1(\pm 1) 0\}, \{1 -1(\pm 1) 0\}, \{\pm 1 0(0) 1\}, \{2 0(0) 1\}$, and $\{2 -1(\pm 1) 0\}$. One should also note that the $J(\Delta l_2^2 J_2^1)$ factors also give rise to band asymmetry, as is evidenced by their values for the different branches given in Table 8.

The effects of cubic anharmonicity enter into our results by way of the $D_k$ factors in the $\Pi f^L_2$ expressions. (See Table 17.) From the quantities multiplying most of the $D_k$'s it is seen that these anharmonicity effects increase with some or all of the vibrational quantum numbers specifying the initial states of the respective transitions.
APPENDIX I

THE NORMAL COORDINATES FOR THE LINEAR SYMMETRIC X-Y-X MOLECULE

Consider the positions of the atoms of the molecule referred to the $x'y'z'$ reference frame shown on page 38.

If the equilibrium position of the $i$th atom is represented by $\hat{r}_i^o = (x_i^o, y_i^o, z_i^o)$, the equilibrium configuration of the molecule is specified in the following table, where $m_i$ is the mass of the $i$th atom, and $a$ is the equilibrium X-Y distance.

<table>
<thead>
<tr>
<th>i</th>
<th>$m_i$</th>
<th>$x_i^o$</th>
<th>$y_i^o$</th>
<th>$z_i^o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$m$</td>
<td>0</td>
<td>0</td>
<td>$-a$</td>
</tr>
<tr>
<td>2</td>
<td>$M$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>$m$</td>
<td>0</td>
<td>0</td>
<td>$a$</td>
</tr>
</tbody>
</table>

Let the displacement of the $i$th atom from equilibrium be given by $\delta x_i^o = (\delta x_i, \delta y_i, \delta z_i)$, so that the instantaneous position of the $i$th atom is given by $x_i' = (x_i^o + \delta x_i)$, where $x_i' = x_i^o + \delta x_i^o$, $y_i' = y_i^o + \delta y_i$, and $z_i' = z_i^o + \delta z_i$. The Eckart condition,

$$ \sum_i m_i \delta x_i = 0 ,$$

that the origin of the $x'y'z'$ frame remain at the center of mass of
the configuration leads to

\[ \begin{align*}
    m\delta x_1' + M\delta x_2' + m\delta x_3' &= 0 \\
    m\delta y_1' + M\delta y_2' + m\delta y_3' &= 0 \\
    m\delta z_1' + M\delta z_2' + m\delta z_3' &= 0
\end{align*} \]  

(I-1)

The Eckart condition,

\[ \sum_i r_{0i}' \times n_i \frac{\dot{r}_i'}{m_i} = 0 \]

is satisfied if

\[ \begin{align*}
    m\delta y_1' - ma\delta y_3' &= 0, \text{ i.e., } \delta y_1' = \delta y_3' \\
    -ma\delta x_1' + ma\delta x_3' &= 0, \text{ i.e., } \delta x_1' = \delta x_3'
\end{align*} \]  

(I-2)

Hence

\[ \begin{align*}
    0 &= \frac{1}{m} \delta x_1' + \frac{1}{M} (\delta x_1' + \delta x_3') = \frac{1}{m} \delta x_1' + 2 \delta x_1' \\
    0 &= \frac{1}{m} \delta y_1' + \frac{1}{M} (\delta y_1' + \delta y_3') = \frac{1}{m} \delta y_1' + 2 \delta y_1' \\
    0 &= \frac{1}{m} \delta z_1' + \frac{1}{M} (\delta z_1' + \delta z_3') 
\end{align*} \]  

(I-3)

To find suitable normal coordinates, we must find \( 3N-5 = 4 \) linearly independent linear combinations of the \( \delta x_1', \delta y_1', \delta z_1' \) in terms of which the kinetic energy and the quadratic portion of the potential energy contain no cross product terms. Upon examination of the linear dependencies of the \( \delta x_1', \delta y_1', \) and \( \delta z_1' \) given by relations (I-3) it is seen that a possible tentative choice of such combinations is

\[ Q_1 = \frac{1}{2} (\delta z_1' - \delta z_3') \]
\[ Q_{2a} = \delta x_2' - \frac{1}{3} (\delta x_1' + \delta x_3') = \delta x_2' - \delta x_1' \]
\[ Q_{2b} = \delta y_2' - \frac{1}{3} (\delta y_1' + \delta y_3') = \delta y_2' - \delta y_1' \]
\[ Q_3 = \delta z_2' - \frac{1}{3} (\delta z_1' + \delta z_3') \]

These linear combinations were chosen, not only to be linearly independent but also to be such that they will readily combine with the Eckart relations (I-3) upon the determination of the inverse relations giving the \((\delta x_1' \delta y_1' \delta z_1')\) in terms of the \(Q_j\)'s. Also, each of our \(Q_j\)'s is seen to go with a particular kind of simple motion consistent with the Eckart conditions as pictured on page 40. For example, \(Q_1\) involves only \(\delta z\) motion in opposite directions of particles 1 and 3.

By direct operation it is seen that the kinetic energy,

\[ T = \sum_1 \frac{1}{2} m_1 (\dot{x}_1^2 + \dot{y}_1^2 + \dot{z}_1^2) \]

becomes

\[ T = \frac{1}{2} \left[ 2m \dot{Q}_1^2 + \mu(\dot{Q}_{2a}^2 + \dot{Q}_{2b}^2) + \mu \dot{Q}_3^2 \right] \]

where

\[ \mu = \frac{2mM}{(2m+M)} . \]

Also, the quadratic portion of the potential energy expressed in the form

\[ V = \frac{1}{2} \left[ k_1(\delta x_1^2 - \delta x_2^2) + k_1(\delta x_1^2 - \delta x_3^2) \right. \]
\[ + k_2(\delta x_1^2 + \delta x_3^2) + k_3 \delta x_2^2 \]
\[ + k_2(\delta y_1^2 + \delta y_3^2) + k_4 \delta y_2^2 \]
becomes

$$v = \frac{1}{2} \left[ K_1 q_1^2 + K_2 (q_{2a}^2 + q_{2b}^2) + K_3 q_3^2 \right]$$

where

$$K_1 = 2k_1 \quad ; \quad K_2 = 2k_2 \left( \frac{\mu}{2m} \right)^2 + k_4 \left( \frac{\mu}{\lambda} \right)^2 \quad ;$$

$$K_3 = 2k_1 \left( \frac{\mu}{2m} \right)^2 + 2 \left( \frac{\mu}{\lambda} \right) k_1 \left( \frac{\mu}{\lambda} \right)^2$$

Hence, our choice of the $Q_4$ diagonalizes both $T$ and $V$.

The quantum mechanical Hamiltonian $H_v$ corresponding to our $T + V$ becomes

$$H_v = \frac{1}{2} \left[ -\frac{h}{2m} \frac{\partial^2}{\partial q_1^2} + K_1 q_1^2 - \frac{h}{\mu} \frac{\partial^2}{\partial q_3^2} + K_3 q_3^2 \right]$$

$$- \frac{h}{\mu} \left\{ \frac{\partial^2}{\partial q_{2a}^2} + \frac{\partial^2}{\partial q_{2b}^2} \right\} + K_2 (q_{2a}^2 + q_{2b}^2) \right]$$

Now, in terms of the normal frequencies, $K_1 = \frac{4\pi^2}{3} (2\mu c^2 \omega_1^2$,

$K_2 = \frac{4\pi^2}{3} \mu c^2 \omega_2^2$, and $K_3 = \frac{4\pi^2}{3} \mu c^2 \omega_3^2$. (Recall the relation $\nu =

\frac{1}{2\pi} \sqrt{\frac{\text{"force constant"}}{\text{"mass"}}} = c\omega$.)

We mass adjust our normal coordinates so that

$$H_v = \frac{h\omega_1}{2} \left( -\frac{\partial^2}{\partial q_1^2} + q_1^2 \right) + \frac{h\omega_3}{2} \left( -\frac{\partial^2}{\partial q_3^2} + q_3^2 \right)$$

$$+ \frac{h\omega_2}{2} \left( -\frac{\partial^2}{\partial q_{2a}^2} - \frac{\partial^2}{\partial q_{2b}^2} + q_{2a}^2 + q_{2b}^2 \right)$$

where

$$q_1 = 2\pi \left( \frac{2mcw_1}{h} \right)^{1/3} \quad q_3 = 2\pi \left( \frac{2mcw_1}{h} \right)^{1/3} \left( \delta z_1 - \delta z_2 \right)$$
\[ q_{an} = 2\pi \left( \frac{\mu \omega_2}{h} \right)^{\frac{1}{2}} q_{2n} = 2\pi \left( \frac{\mu \omega_2}{h} \right)^{\frac{1}{2}} \left\{ \delta x_2^i - \frac{1}{2} \left( \delta x_1^i + \delta x_3^i \right) \right\} \]

\[ q_{2b} = 2\pi \left( \frac{\mu \omega_2}{h} \right)^{\frac{1}{2}} q_{2b} = 2\pi \left( \frac{\mu \omega_2}{h} \right)^{\frac{1}{2}} \left\{ \delta y_2^i - \frac{1}{2} \left( \delta y_1^i + \delta y_3^i \right) \right\} \]

\[ q_{3} = 2\pi \left( \frac{\mu \omega_2}{h} \right)^{\frac{1}{2}} q_{3} = 2\pi \left( \frac{\mu \omega_2}{h} \right)^{\frac{1}{2}} \left\{ \delta x_2^i - \frac{1}{2} \left( \delta x_1^i + \delta x_3^i \right) \right\} \]

where \( \omega \) is the \( k \)th normal frequency expressed in \( \text{cm}^{-1} \).
APPENDIX II.

THE QUANTUM MECHANICAL HAMILTONIAN FOR THE LINEAR SYMMETRIC X-Y-X MOLECULE

The method for obtaining the Hamiltonian here is essentially that of Wilson and Howard (46). Some additional remarks are added to clarify the method's application to the case of the linear symmetric X-Y-X molecule.

The Classical Kinetic Energy

Consider first a system of point masses \( m_i \), the motions of which are described by means of an \( XYZ \) "space fixed" reference frame and an \( xyz \) reference frame with origin at the center of mass of the system, the orientation of which will be specified later. The arrangement is pictured below.

\[ \hat{R} \] locates the center of mass of the system with respect to the origin of the "space fixed" \( XYZ \) frame. \( \hat{R}_i = (x_i,y_i,z_i) \) is the instantaneous position of the \( i \)th particle referred to the \( xyz \) frame. If the particles are bound together by molecular binding
forces, each particle can vibrate about an equilibrium position.

For the ith particle, we specify the equilibrium position by the vector \( \mathbf{r}_{0i} = (x_{0i}, y_{0i}, z_{0i}) \), and the displacement from equilibrium by the vector \( \delta \mathbf{r}_i = (\delta x_i, \delta y_i, \delta z_i) = \mathbf{r}_i - \mathbf{r}_{0i} \). If the angular velocity of the \( xyz \) reference frame is given by \( \omega \) and the velocity of the ith particle with respect to the \( xyz \) frame is given by

\[
\mathbf{v}_i = (\dot{x}_i, \dot{y}_i, \dot{z}_i) = \left[ (\ddot{x}_i)(\ddot{y}_i)(\ddot{z}_i) \right], \tag{II-1}
\]

then the velocity of the ith particle with respect to the \( XYZ \) "space fixed" frame is given by the vector quantity,

\[
\dot{\mathbf{R}} + \omega \times \mathbf{r}_i + \dot{\mathbf{v}}_i.
\]

The kinetic energy of the system,

\[
T = \frac{1}{2} \sum_i m_i \left[ \dot{\mathbf{R}} + \omega \times \mathbf{r}_i + \dot{\mathbf{v}}_i \right]^2,
\]

(where the square of a vector shall mean its dot product with itself), becomes

\[
T = \frac{1}{2} \dot{\mathbf{R}}^2 \sum_i m_i + \frac{1}{2} \sum_i m_i (\omega \times \mathbf{r}_i)^2 + \omega \cdot \sum_i m_i \mathbf{r}_i \times \mathbf{v}_i,
\]

since the \( xyz \) origin is located at the center of mass of the system of particles, i.e.,

\[
\sum_i m_i \mathbf{r}_i = 0 \tag{II-2}
\]

(Note also that \( \frac{d}{dt} \sum_i m_i \mathbf{r}_i = 0 = \sum_i m_i \dot{\mathbf{r}}_i + \omega \times \sum_i m_i \mathbf{r}_i = \sum_i m_i \mathbf{v}_i \).
It is convenient to choose the orientation of the $x\ y\ z$ system so that

$$\sum_i \vec{r}_{oi} \times m_i \vec{v}_i = 0 \quad \text{ (II-3)}$$

Note that the angular momentum of the configuration with respect to the $x\ y\ z$ system is

$$\sum_i \vec{r}_i \times m_i \vec{v}_i = \sum_i \vec{r}_{oi} \times m_i \vec{v}_i + \sum_i \delta \vec{r}_i \times m_i \vec{v}_i \quad \text{ (II-4)}$$

Thus, with our choice of $x\ y\ z$ reference frame, the only kind of angular momentum that the system of particles can have with respect to it will be the kind arising from the term $\sum_i \delta \vec{r}_i \times m_i \vec{v}_i$. Note that for this to be non-vanishing, some of the $\vec{v}_i$ must have components perpendicular to their respective $\delta \vec{r}_i$. These conditions usually imply that the $x\ y\ z$ frame is such that the molecular configuration as a whole cannot rotate with respect to it. However, consider the case of the linear $X-Y-X$ molecule with its perpendicular $v_2$ mode of vibration excited, as pictured below.
(The X Y Z axes are such as to always remain parallel to the respective X Y Z "space fixed" axes.) It is seen that this kind of motion can take place within a reference frame defined according to Eckart conditions (II-2) and (II-3). It is also seen that both the \( x'y'z' \) frames in the picture above satisfy conditions (II-2) and (II-3), so that we can use either one in setting up our Hamiltonian, providing we use the proper angular velocity \( \omega \). We shall use the \( x'y'z' \) frame in our description of the X-Y-Z molecule since our vibrational coordinates are expressed with respect to this frame. (See Appendix I.) However, we shall not include the primes in the general portion of this discussion. From (II-2) and (II-3), the kinetic energy becomes

\[
T = \frac{1}{2} \sum_i m_i \left( \frac{\mathbf{v}_i}{m_i} \right)^2 + \frac{1}{2} \sum_i \mathbf{m}_i (\mathbf{\omega} \times \mathbf{r}_i)^2 + \sum_i \mathbf{m}_i \mathbf{v}_i \cdot \mathbf{\omega} \cdot \sum_i \mathbf{m}_i (\delta \mathbf{r}_i \times \mathbf{v}_i) .
\]

\[
\frac{1}{2} \sum_i m_i = \text{the translational energy of the molecule, and is a function of the time derivatives of the center of mass coordinates X Y Z, which occur nowhere else in T. (We have, from the beginning, assumed that no external field is present.) We shall neglect this term hereafter.}

\[
\frac{1}{2} \sum_i m_i (\mathbf{\omega} \times \mathbf{r}_i) = \text{Rotational Energy}
\]

\[
= \frac{1}{2} \left[ I_{xx} \omega_x^2 + I_{yy} \omega_y^2 + I_{zz} \omega_z^2 \right]
\]
\[-2I_{xy}w_{xy} - 2I_{yz}w_{yz} - 2I_{zx}w_{zx} \right\}, \quad (II-6)\]

where

\[I_{xx} = \sum m_i \left(y_{1i}^2 + z_{1i}^2\right), \text{ etc. and} \]

\[I_{xy} = \sum m_i x_{1i} y_{1i}, \text{ etc.} \]

\[\frac{1}{2} \sum m_i v_{1i}^2 = \text{ Vibrational Energy} \]

\[= \frac{1}{2} \sum q_k^l \]

\[\text{where } q_k^l \text{ is the } k\text{th normal coordinate multiplied by the appropriate constant to make} \]

\[\sum m_i v_{1i}^2 = \sum q_k^l. \]

\[\omega \sum m_i \left(8x_{1i} y_{1i} z_{1i}\right) = \text{ the contribution to the kinetic energy due to coupling between vibration and rotation.} \]

Now \[\delta x_i = (\delta x_{1i}, \delta y_{1i}, \delta z_{1i}), \quad \text{and} \]

\[\delta x_{1i} = \sum l_{ik} q_k^l, \quad \text{or} \quad (\delta x_{1i}) = \sum l_{ik} \dot{q}_k^l \]

\[\delta y_{1i} = \sum m_{ik} q_k^l, \quad \text{or} \quad (\delta y_{1i}) = \sum m_{ik} \dot{q}_k^l \quad (II-10) \]

\[\delta z_{1i} = \sum n_{ik} q_k^l, \quad \text{or} \quad (\delta z_{1i}) = \sum n_{ik} \dot{q}_k^l \]

\[\text{where } l_{ik}, m_{ik}, \text{ and } n_{ik} \text{ are constants. From (II-1), (II-10), and direct operation,} \]
\[ \sum_{i} m_{i} (\delta \mathbf{r}_{i} \times \mathbf{r}_{i}) = \left( \sum_{k} X_{k} \mathbf{q}_{k}, \sum_{k} Y_{k} \mathbf{q}_{k}, \sum_{k} J_{k} \mathbf{q}_{k} \right) \quad \text{(II-11)} \]

(the components being along \( x, y, \) and \( z \))

where

\[
\begin{align*}
X_{k} &= \sum_{i} \sum_{j} m_{i} (m_{i}^{j} \mathbf{r}_{i}^{j} - n_{i}^{j} \mathbf{r}_{i}^{j})q_{j}^{i} \\
Y_{k} &= \sum_{i} \sum_{j} m_{i} (n_{i}^{j} \mathbf{r}_{i}^{j} - l_{i}^{j} \mathbf{r}_{i}^{j})q_{j}^{i} \\
J_{k} &= \sum_{i} \sum_{j} m_{i} (l_{i}^{j} \mathbf{r}_{i}^{j} - m_{i}^{j} \mathbf{r}_{i}^{j})q_{j}^{i}
\end{align*}
\]

(II-12)

Thus,

\[
T = \frac{1}{2} \left[ I_{xx} \omega_{x}^{2} + I_{yy} \omega_{y}^{2} + I_{zz} \omega_{z}^{2} \\
- 2I_{xy} \omega_{x} \omega_{y} - 2I_{yz} \omega_{y} \omega_{z} - 2I_{xz} \omega_{x} \omega_{z} \right] \\
+ \frac{1}{2} \sum_{k} \mathbf{q}_{k}^{2} \\
+ \omega_{x} \sum_{k} X_{k} \mathbf{q}_{k}^{i} + \omega_{y} \sum_{k} Y_{k} \mathbf{q}_{k}^{i} + \omega_{z} \sum_{k} J_{k} \mathbf{q}_{k}^{i} \quad \text{(II-13)}
\]

Now, the total angular momentum of the molecule is

\[ \mathbf{L} = \sum_{i} m_{i} (\mathbf{r}_{i} \times \mathbf{v}_{i}) = \sum_{i} m_{i} (\mathbf{r}_{i} \times \mathbf{v}_{i}) \]

Making use of this, Equations (II-1), (II-3), (II-4), (II-7), (II-8), (II-11), and the mathematical relation,

\[ \mathbf{r}_{1} \times (\mathbf{\omega} \times \mathbf{r}_{1}) = \mathbf{r}_{1}^{2} \mathbf{\omega} - (\mathbf{r}_{1} \cdot \mathbf{\omega}) \mathbf{r}_{1} \]
we obtain the relations

\[ P_x = \sum_k x_k^i \dot{q}_k^i + I_{xx} \omega_x - I_{xy} \omega_y - I_{xz} \omega_z = \frac{\partial T}{\partial \omega_x} \]

\[ P_y = \sum_k y_k^i \dot{q}_k^i - I_{xy} \omega_x + I_{yy} \omega_y - I_{yz} \omega_z = \frac{\partial T}{\partial \omega_y} \] (II-14)

\[ P_z = \sum_k \frac{1}{2} \dot{k}^i_k \dot{q}_k^i - I_{xz} \omega_x - I_{yz} \omega_y + I_{zz} \omega_z = \frac{\partial T}{\partial \omega_z} \]

The momentum conjugate to the normal coordinate \( q_k^i \) is

\[ p_k^i = \frac{\partial T}{\partial \dot{q}_k^i} = q_k^i + x_k^i \dot{x}_k + y_k^i \dot{y}_k + \frac{1}{2} \dot{k}^i_k \] (II-15)

From the above it can be readily shown that

\[ T = \frac{1}{2} \left[ P_x \omega_x + P_y \omega_y + P_z \omega_z + \sum_k p_k^i \dot{q}_k^i \right] \]

and further manipulation yields

\[ T = \frac{1}{2} \left[ (P_x - \rho_x) \omega_x + (P_y - \rho_y) \omega_y + (P_z - \rho_z) \omega_z + \sum_k \rho_k^3 \right] \] (II-16)

where

\[ \rho_x = \sum_k x_k^i p_k^i \]

\[ \rho_y = \sum_k y_k^i p_k^i \] (II-17)

\[ \rho_z = \sum_k \frac{1}{2} \dot{k}^i_k p_k^i \]

Also, from relations (II-14), (II-15), and (II-17), one readily obtains the relations

\[ (P_x - \rho_x) = I_{xx} \omega_x - I_{xy} \omega_y - I_{xz} \omega_z \] (II-18)

(continued on next page)
\[(P_y - \rho_y) = -I_{xy}w_x + I_{yy}w_y - I_{yz}w_z\]

\[(P_z - \rho_z) = -I_{xz}w_x - I_{yz}w_y + I_{zz}w_z\]

\[\text{where} \quad I'_{XX} = I_{XX} - \sum_{k} \gamma_k^2, \quad \text{etc., and} \]

\[I'_{XY} = I_{XY} + \sum_{k} \gamma_k\gamma_k, \quad \text{etc.}\]

\[
\begin{pmatrix}
\omega_x \\
\omega_y \\
\omega_z
\end{pmatrix}
= 
\begin{pmatrix}
\mu_{xx} & \mu_{xy} & \mu_{xz} \\
\mu_{yx} & \mu_{yy} & \mu_{yz} \\
\mu_{zx} & \mu_{zy} & \mu_{zz}
\end{pmatrix}
\begin{pmatrix}
P_x - \rho_x \\
P_y - \rho_y \\
P_z - \rho_z
\end{pmatrix}
\]

and denote the determinant of the transformation matrix \(\mu'_{\alpha'\beta'}\) by \(\mu\).

Now consider the case of the linear X-Y-X molecule, where our "moving" reference frame is the \(x'y'z'\) frame pictured on page 148. (Also see the discussion on page 148.) Since \(\omega_{x'}^1, \omega_{y'}^1, \omega_{z'}^1\) are the projections of the angular velocity vector of the \(x'y'z'\) frame on the \(x'y'z'\) axes,

\[
\begin{align*}
\omega_{x'}^1 &= - \sin \psi \dot{\phi} \\
\omega_{y'}^1 &= \dot{\phi} \\
\omega_{z'}^1 &= \cos \psi \dot{\phi}
\end{align*}
\]
so that \( w_{z'} = - (\text{cote}) w_{x'} \).

Hence, Equation (II-18) becomes

\[
(P_{x'} - \rho_{x'}) = (I_{x'y'y'} + \text{cote} I_{x'y'y'} w_{x'} - I_{x'y'y'} w_{x'})
\]

\[
(P_{y'} - \rho_{y'}) = (-I_{x'y'y'} + \text{cote} I_{x'y'y'} w_{y'} + I_{x'y'y'} w_{y'})
\]

\[
(P_{z'} - \rho_{z'}) = (-I_{x'y'y'} + \text{cote} I_{x'y'y'} w_{z'} - I_{x'y'y'} w_{z'})
\]

Now for linear symmetric X-Y-X, it can be readily shown by substitution and direct operation that

\[
I_{x'y'y'} = I_{x'y'y'} = I_{x'y'y'} = 0
\]

\[
I_{z'z'} = 0
\]

\[
I_{x'x'} = I_{y'y'} = I_{0} (1 - \frac{1}{I_{0}} d_{1}^2),
\]

where \( I_{0} = 2m a^2 \), where \( a \) is the equilibrium X-Y distance, i.e., \( I_{0} \) is the equilibrium moment of inertia of the molecule. For \( e = 0 \), it is seen that \( \text{cote} I_{x'y'} = 0 \) and \( \text{cote} I_{x'y'y'} = 0 \). (Where \( \delta Y \) can be \( z'x' \), \( x'y' \), or \( y'z' \).)

For \( e = 0 \), however, \( \text{cote} = \infty \), so that \( \text{cote} I_{x'y'} \) and \( \text{cote} I_{x'y'y'} \) are indeterminate. But if \( (P_{x'} - \rho_{x'}) \), \( (P_{y'} - \rho_{y'}) \), and \( (P_{z'} - \rho_{z'}) \) are continuous functions of \( e \), then \( \text{cote} I_{x'y'} \) and \( \text{cote} I_{x'y'y'} \) must equal zero for \( e = 0 \). If this is true, \( \text{cote} I_{x'y'} = 0 \) and \( \text{cote} I_{x'y'y'} = 0 \) for all \( e \). Then,

\[
(P_{x'} - \rho_{x'}) = I_{x'y'y'} w_{x'}
\]

\[
(P_{y'} - \rho_{y'}) = I_{y'y'y'} w_{y'}
\]

\[
(P_{z'} - \rho_{z'}) = 0.
\]

The inverse transformation is seen to be
\begin{equation}
\begin{pmatrix}
(\omega_x^1) \\
(\omega_y^1)
\end{pmatrix} = \begin{pmatrix}
\mu_{x'x'} & 0 \\
0 & \mu_{y'y'}
\end{pmatrix} \begin{pmatrix}
(P_{x'} - \Phi_{x'}) \\
(P_{y'} - \Phi_{y'})
\end{pmatrix}
\tag{II-26}
\end{equation}

where

\begin{equation}
\mu_{x'x'} = \mu_{y'y'} = \frac{1}{2} \frac{1}{I_0} (1 - \frac{1}{2} q_1^2)^{-2}
\tag{II-27}
\end{equation}

Also, the determinant of the matrix of this inverse transformation, \(\mu\), becomes

\begin{equation}
\mu = \mu_{x'x'}^2 = \frac{1}{\frac{1}{2} I_0} (1 - \frac{1}{2} q_1^2)^{-1}
\tag{II-28}
\end{equation}

The classical kinetic energy according to Equation (II-16) becomes

\begin{equation}
T = \frac{1}{2} \left[ (P_{x'} - \Phi_{x'})^2 + (P_{y'} - \Phi_{y'})^2 + 0 \omega_x^2 + 0 \omega_y^2 + \frac{1}{2} \sum_{k} p_k^2 \right]
\tag{II-29}
\end{equation}

and, from Equation (II-27), this becomes

\begin{equation}
T = \frac{1}{2} \mu_{x'x'} \left[ (P_{x'} - \Phi_{x'})^2 + (P_{y'} - \Phi_{y'})^2 \right] + \frac{1}{2} \sum_{k} p_k^2
\tag{II-30}
\end{equation}

THE VIBRATIONAL POTENTIAL

ENERGY FUNCTION

In general, the vibrational potential energy function \(V\) can be expressed in terms of the normal coordinates \(q_i\) as a power series

\begin{equation}
V = \frac{1}{2} \left\{ \sum_{ij} K_{ij} q_i q_j + \sum_{ijk} K_{ijk} q_i q_j q_k + \cdots \right\}
\tag{II-31}
\end{equation}

In the case of a completely unsymmetric molecule, all the coefficients \(K_{ij}, K_{ijk}, K_{ijkl}, \ldots\) are different from zero. For a molecule with some symmetry, some of these coefficients may be zero. This is true because the potential energy must have the same symmetry as the molecule.
itself and therefore must remain unchanged upon the carrying out of all of the symmetry operations included in the point group of the molecule.

The linear symmetric X-Y-X molecule belongs to the point group D_{\infty h}. The axes and planes of symmetry are illustrated in the diagram below, where the angle \( \theta \) of course can take on any real value.

Among the infinite number of symmetry operations are the following:

- \( \text{E} \) = Leaving the molecule unchanged;
- \( \text{C}_{2}(\theta) \) = Rotating the molecule \( \pi \) about an axis through the central atom perpendicular to the z axis, making an angle \( \theta \) with the pictured x axis. (An infinite number of such operations exist, going with the infinite number of possible values of \( \theta \); also, as far as these considerations go, there are an infinite number of possible orientations for the x y axes.)
- \( \text{C}_{\gamma} \) = Rotating the molecule an angle about the z axis. (There are also an infinite number of these operations.)
- \( \sigma_{h} \) = Reflecting the molecular constituents in the x y plane.
\( \varphi(\phi) = \) Reflecting the molecular constituents in a plane making an angle \( \phi \) with the \( x \) axis. (For any real value of \( \phi \).)

\( S_\psi = \) Rotating the molecule by an angle \( \psi \) about the \( z \) axis and then reflecting in the \( xy \) plane. (An infinitude of these operations exist.)

\( S_3(\phi) = C_2(\phi) \) followed by reflection in the \( xy \) plane. (For any real value of \( \phi \).)

The following table will illustrate how each of the normal coordinates is affected upon the performance of a representative set of these symmetry operations. It is seen that, for the operations in the table,

\[ q_1 \text{ always goes over into } q_1, \]

\[ \begin{pmatrix} q_{2a} \\ q_{2b} \end{pmatrix} \text{ goes over into } \begin{pmatrix} +q_{2a} \\ +q_{2b} \end{pmatrix} \text{ or } \begin{pmatrix} -q_{2a} \\ -q_{2b} \end{pmatrix}, \text{ and} \]

\[ q_3 \text{ goes over into } q_3 \text{ or } -q_3. \]

Thus, all powers of \( q_1 \) can occur in \( V \), but only even powers of \( q_3 \). \( q_{2a} \) and \( q_{2b} \) can occur only together in the form \( q_{2a}^2 + q_{2b}^2 \), and any integral power of this quantity has the proper symmetry. As has been indicated, not all of the infinite number of possible symmetry operations have been included in the table, although all types of operations have been included. Nevertheless, it can be shown that the above terms are still the only ones with the proper symmetry for inclusion in the potential energy.
TABLE 18

Effects of Symmetry Operations on the Normal Coordinates

<table>
<thead>
<tr>
<th>Normal Mode</th>
<th>Symmetry Operation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E$</td>
</tr>
<tr>
<td>$\rightarrow$</td>
<td>q₁</td>
</tr>
<tr>
<td>$\rightarrow$</td>
<td>q₂a</td>
</tr>
<tr>
<td>$\rightarrow$</td>
<td>q₃b</td>
</tr>
<tr>
<td>$\rightarrow$</td>
<td>q₃</td>
</tr>
</tbody>
</table>

(A minus sign in front of a $q_i$ indicates a resulting configuration in which all of the arrows on the diagram of the respective $q_i$ are reversed in direction.)
\[ V = \frac{1}{\hbar} \hbar c \left\{ w_1 q_1^2 + w_2 \left( q_{2a}^2 + q_{2b}^2 \right) + w_3 q_3^2 \right\} \]
\[ + \varepsilon \hbar c \left\{ K_{111} q_1^2 + K_{122} q_1 \left( q_{2a}^2 + q_{2b}^2 \right) + K_{133} q_1 q_3 \right\} \]
\[ + \varepsilon^2 \hbar c \left\{ K_{1111} q_1^4 + K_{1122} q_1 \left( q_{2a}^2 + q_{2b}^2 \right) + K_{1133} q_1^2 q_3 \right\} \]
\[ + K_{2222} \left( q_{2a}^2 + q_{2b}^2 \right)^2 + K_{2233} \left( q_{2a}^2 + q_{2b}^2 \right) q_3 \]
\[ + K_{3333} q_3^4 \right\} + \ldots \]  

where the above forms of the constants were chosen as a matter of convenience. \[ \varepsilon = \left( \frac{2B_0}{\omega_1} \right)^{1/3}. \]

THE QUANTUM MECHANICAL HAMILTONIAN \( H \)

According to Wilson and Howard (46), the quantum mechanical Hamiltonian \( H \) can be expressed as

\[ H = \frac{1}{2} \sum_{\alpha \beta} \left( P_\alpha - \Phi_\alpha \right) \mu_{\alpha \beta} \mu^{-\frac{1}{2}} \left( P_\beta - \Phi_\beta \right) \]
\[ + \frac{1}{2} \mu^{\frac{3}{2}} \sum_k p_k^4 \mu^{-\frac{1}{2}} p_k^4 + V \]  

where \( P_\alpha, \Phi_\alpha, \) and \( p_k^4 \), etc., are the quantum mechanical operators associated with the respective classical mechanical quantities of the first section of this appendix. \( \alpha \) and \( \beta \) of course can be \( x, y, \) or \( z \) (or \( x', y', \) or \( z' \)). The \( P_\alpha, \) which are functions of \( \phi, \phi', \frac{2}{\phi}, \frac{2}{\phi'}, \) and \( \frac{2}{\phi''}, \) are given in Appendix III. The quantum mechanical \( p_k^4 \) are merely \( - \frac{1}{2} \frac{2}{\phi'_{\alpha}} \), and the \( \Phi_\alpha \) can be obtained from Equations (II-17) and
(II-12), making use of the quantum mechanical $p^k_k$. (See p.162.) The
$\mu_{\alpha\beta}$ and $\mu$ are defined on p. 153.

For the linear symmetric X-Y-X molecule, we have shown that, if
we use the $x' y' z'$ system for our moving reference frame, the non-
vanishing $\mu_{\alpha\beta}$ are

$$\mu_{x'x'} = \mu_{y'y'} = \frac{1}{I_{x'x'}} = \frac{1}{I_0} (1 - \frac{1}{2} q_1^2)^{-2} \quad (II-34)$$

and $\mu = \mu_{x'x'}$. Hence, the Hamiltonian becomes

$$H = \frac{1}{2} \mu_{x'x'} \left[ (P_{x'} - P_{x'}) \cdot \cdot (P_{x'} - P_{x'}) + (P_{y'} - P_{y'}) \cdot \cdot (P_{y'} - P_{y'}) \right]
+ \frac{3}{2} \mu_{x'x'} \frac{1}{P_1} + \frac{1}{2} \left[ \frac{P_{2a}^2}{2} + \frac{P_{2b}^2}{2} + \frac{P_{3}^2}{2} \right] + V \quad (II-35)$$

It is readily shown that

$$\frac{3}{2} \mu_{x'x'} \frac{1}{P_1} + \frac{1}{2} \frac{1}{P_1} = \frac{1}{2} \frac{1}{P_1} + \frac{1}{2} \mu_{x'x'} \frac{1}{P_1} \quad (II-36)$$

Let us switch, for convenience, to the normal coordinates $q_k$ of Appendix
I with momenta $p_k$. First, note that $p_k$ and $p_k^i$ are such that

$$\sum_k p_k^2 = \sum_k \hbar c \omega_k \frac{p_k^2}{\hbar^2} \quad (II-37)$$

(C.f. p. 141.) It is seen that $p_k^i = -i \hbar \frac{2}{a q_k} (\hbar c \omega_k)^{\frac{1}{2}} p_k / \hbar$ where

$$p_k = -i \hbar \frac{2}{a q_k} \quad \text{and} \quad q_k = \frac{1}{2 \pi} \left( \frac{\hbar}{\omega_k} \right) q_k$$

$$\quad (II-38)$$

Also,

$$\mu_{x'x'} = I_0^{-1} \left( 1 - \varepsilon q \right)^{-2} = I_0^{-1} \left( 1 + 2 \varepsilon q_1 + 3 \varepsilon^2 q_1^2 + 4 \varepsilon^3 q_1^3 + \ldots \right) \quad (II-39)$$
Combining these expressions, we obtain for the quantum mechanical Hamiltonian of the linear symmetric X-Y-X molecule the following expression:

\[
H = \hbar c B_e \left( 1 + 2 \epsilon q_1 + 3 \epsilon^2 q_1^2 + 4 \epsilon^3 q_1^3 + \ldots \right)
\]

\[
+ \frac{1}{\hbar^2} \left[ (P_{x'}^2 - \rho_{x'}^2)^2 + (P_{y'}^2 - \rho_{y'}^2)^2 \right]
\]

\[
+ \frac{\hbar^2 c}{\omega_1} \left[ \omega_1 \left( \frac{P_1^2}{\hbar^2} + q_1^2 \right) + \omega_2 \left( \frac{P_{2a}^2 + P_{2b}^2}{\hbar^2} + q_{2a}^2 + q_{2b}^2 \right) + \omega_3 \left( \frac{P_3^2}{\hbar^2} + q_3^2 \right) \right]
\]

\[
+ \epsilon \hbar c \omega_1 \left( 1 + \epsilon q_1 + \epsilon^2 q_1^2 + \epsilon^3 q_1^3 + \ldots \right) P_{y'} / \hbar
\]

\[
+ \epsilon \hbar c \left[ X_{111} q_1^3 + X_{122} \left( q_{2a}^2 + q_{2b}^2 \right) + X_{133} q_1 q_3^2 \right]
\]

\[
+ \epsilon^2 \hbar c \left[ X_{111} q_1^3 + X_{122} q_1 q_3^2 \left( q_{2a}^2 + q_{2b}^2 \right) + X_{133} q_1 q_3^2 \right]
\]

\[
+ X_{222} \left( q_{2a}^2 + q_{2b}^2 \right)^2 + X_{223} \left( q_{2a}^2 + q_{2b}^2 \right) q_3^2
\]

\[
+ X_{333} q_3^4 \right] + \ldots \right) \quad (II-43)
\]

where \( P_{x'} \) and \( P_{y'} \) are to be found in Appendix III. Recall from Equations (II-17) that
\[ \boldsymbol{\rho}_x' = \sum_k \nu'_k \nu_k' \]
\[ \boldsymbol{\rho}_y' = \sum_k \gamma'_k \nu_k' \quad (\text{II-44}) \]
\[ \boldsymbol{\rho}_z' = \sum_k \lambda'_k \nu_k' \]

where \( \nu'_k \), \( \gamma'_k \), and \( \lambda'_k \) are the normal coordinate dependent coefficients in

\[ \Sigma_m \left( \delta r'_i x'_j \right) = \left\{ \sum_k \nu'_k \dot{\nu}_k', \sum_k \gamma'_k \dot{\gamma}_k', \sum_k \lambda'_k \dot{\lambda}_k' \right\} \quad (\text{II-45}) \]

[See Equations (II-11) and (II-12).] For the linear symmetric X-Y-X molecule, these quantities are found to be

\[ \nu'_1 = \nu'_{2a} = 0 ; \quad \nu'_{2b} = -q'_3, \quad \nu'_3 = q'_2b \]
\[ \gamma'_1 = \gamma'_{2b} = 0 ; \quad \gamma'_{2a} = q'_3, \quad \gamma'_3 = -q'_2a \quad (\text{II-46}) \]
\[ \lambda'_1 = \lambda'_{2a} = 0 ; \quad \lambda'_{2b} = -q'_2b, \quad \lambda'_{ab} = q'_2a \]

Therefore,

\[ \boldsymbol{\rho}_x' = -q'_3 p'_{2b} + q'_2b p'_{3} = -(\omega_2/\omega_3)^{\frac{1}{2}} q_3 p_{2b} + (\omega_3/\omega_2)^{\frac{1}{2}} q_{2b} p_{3} \]
\[ \boldsymbol{\rho}_y' = q'_3 p'_{2a} - q'_2a p'_{3} = (\omega_2/\omega_3)^{\frac{1}{2}} q_3 p_{2a} - (\omega_3/\omega_2)^{\frac{1}{2}} q_{2a} p_{3} \quad (\text{II-47}) \]
\[ \boldsymbol{\rho}_z' = -q'_2b p'_{2a} + q'_2a p'_{2b} = -q_{2b} p_{2a} + q_{2a} p_{2b} \]
\[ = - \frac{\partial^2 \omega}{\partial \nu'_{2b} \partial \nu'_{2a}} \]
A method for obtaining the quantum mechanical operators associated with the projections of the total angular momentum vector $\mathbf{P}$ along various axes is to be found in Chapter VII of (22). Consider the sets of axes pictured below.

\[
\begin{align*}
\mathbf{P} &= \cos(X, Z') \mathbf{P}_X + \cos(Y, Z') \mathbf{P}_Y + \cos(Z, Z') \mathbf{P}_Z \\
\mathbf{P} &= \cos(X, y') \mathbf{P}_X + \cos(Y, y') \mathbf{P}_Y + \cos(Z, y') \mathbf{P}_Z \\
\mathbf{P} &= \cos(X, z') \mathbf{P}_X + \cos(Y, z') \mathbf{P}_Y + \cos(Z, z') \mathbf{P}_Z,
\end{align*}
\]

where $\mathbf{P}_x$, $\mathbf{P}_y$, and $\mathbf{P}_z$ are the operators associated with the projections of $\mathbf{P}$ along $X$, $Y$, and $Z$ respectively. Hence,
\[
\begin{align*}
- \sin \frac{2}{\varrho} &= 0 + 0 + P_z, \\
- \sin \frac{2}{\varphi} &= \cos \varphi P_x + \cos \varphi P_y + 0 \quad \text{(III-2)} \\
- \sin \frac{2}{\varphi} &= \cos \varphi \sin \varphi P_x + \sin \varphi \sin \varphi P_y + \cos \varphi P_z,
\end{align*}
\]
from which we readily obtain
\[
\begin{align*}
P_x &= -\sin \varphi \cot \varphi \frac{2}{\varphi} - \sin \frac{2}{\varphi} + \cos \varphi \frac{2}{\varphi} \quad \text{(III-3)} \\
P_y &= -\sin \varphi \cot \varphi \frac{2}{\varphi} + \cos \varphi \frac{2}{\varphi} + \sin \frac{2}{\varphi} \\
P_z &= -\sin \frac{2}{\varphi}
\end{align*}
\]
Similarly,
\[
\begin{align*}
- \sin \frac{2}{\varrho} &= \cos(\varphi, Z) P_{x_1} + \cos(\varphi, X) P_{y_1} + \cos(\varphi, Z) P_{z_1} \\
- \sin \frac{2}{\varrho} &= \cos(\varphi, Y) P_{x_1} + \cos(\varphi, Y) P_{y_1} + \cos(\varphi, Y) P_{z_1} \quad \text{(III-4)} \\
- \sin \frac{2}{\varrho} &= \cos(\varphi, Z) P_{x_1} + \cos(\varphi, Z) P_{y_1} + \cos(\varphi, Z) P_{z_1},
\end{align*}
\]
or
\[
\begin{align*}
- \sin \frac{2}{\varrho} &= -\sin \varphi P_{x_1} + 0 + \cos \varphi P_{z_1} \\
- \sin \frac{2}{\varrho} &= 0 + P_{y_1} + 0 \quad \text{(III-5)} \\
- \sin \frac{2}{\varrho} &= 0 + 0 + P_{z_1}
\end{align*}
\]
from which
\[
\begin{align*}
P_{x_1} &= -\sin \left( -\frac{1}{\sin \varphi} \frac{2}{\varphi} + \cot \frac{2}{\varphi} \right) \\
P_{y_1} &= -\frac{2}{\varphi} \quad \text{(III-6)} \\
P_{z_1} &= -\frac{2}{\varphi}
\end{align*}
\]
[\text{Ask Sayvetz, (47).}]

Also
\[- \frac{\partial}{\partial \phi} = \cos(x, z) P_x + \cos(y, z) P_y + \cos(z, z) P_z \]
\[- \frac{\partial}{\partial \theta} = \cos(x, y') P_x + \cos(y, y') P_y + \cos(z, y') P_z \quad (III-7) \]
\[- \frac{\partial}{\partial \psi} = \cos(x, z') P_x + \cos(y, z') P_y + \cos(z, z') P_z \]
so that
\[- \frac{\partial}{\partial \phi} = - \sin \phi \cos \theta P_x + \sin \phi \sin \theta P_y + \cos \phi P_z \]
\[- \frac{\partial}{\partial \theta} = \sin \theta P_x + \cos \theta P_y + 0 \quad (III-8) \]
\[- \frac{\partial}{\partial \psi} = 0 + 0 + P_z . \]

Therefore,
\[P_x = -i \hbar (- \cos \phi \frac{\partial}{\partial \phi} + \sin \phi \frac{\partial}{\partial \theta} + \cos \phi \cot \psi \frac{\partial}{\partial \psi}) \]
\[P_y = -i \hbar (\sin \phi \frac{\partial}{\partial \phi} + \cos \phi \frac{\partial}{\partial \theta} - \sin \phi \cot \psi \frac{\partial}{\partial \psi}) \quad (III-9) \]
\[P_z = -i \hbar \frac{\partial}{\partial \psi} \]

By direct operation, one obtains
\[
\begin{bmatrix} P_x \end{bmatrix} \begin{bmatrix} P_y \end{bmatrix} = i \hbar P_z \\
\begin{bmatrix} P_y \end{bmatrix} \begin{bmatrix} P_z \end{bmatrix} = i \hbar P_x \quad (III-10) \\
\begin{bmatrix} P_z \end{bmatrix} \begin{bmatrix} P_x \end{bmatrix} = i \hbar P_y \; ; \; \text{and} \\
\]
\[P_x^2 + P_y^2 + P_z^2 = - \hbar^2 \left( \frac{1}{\sin \phi} \frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin \theta} \frac{\partial^2}{\partial \theta^2} + \cot \phi \frac{\partial}{\partial \phi} - \cot \psi \frac{\partial}{\partial \psi} \right) \quad (III-11) \]

Similarly,
\[
\begin{bmatrix} P_x \end{bmatrix} \begin{bmatrix} P_y \end{bmatrix} = - i \hbar P_z \\
\begin{bmatrix} P_y \end{bmatrix} \begin{bmatrix} P_z \end{bmatrix} = - i \hbar P_x \quad (III-12) \\
\begin{bmatrix} P_z \end{bmatrix} \begin{bmatrix} P_x \end{bmatrix} = - i \hbar P_y \; ; \]
and

\[
P^2_x + P^2_y + P^2_z = -\hbar^2 \left( \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} + \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} - 2 \frac{\cot \theta}{\sin \theta} \frac{\partial}{\partial \varphi} \frac{\partial}{\partial \varphi} \right)
\]

\[
= P^2_x + P^2_y + P^2_z
\]

(III-13)

Note, however, that if \( P^x_1, P^y_1, \) and \( P^z_1 \) are the operators given by Equation (III-6), one obtains

\[
\begin{bmatrix} P^x_1 & P^y_1 \end{bmatrix} = -\hbar^2 \left( -\cot \theta \frac{\partial}{\partial \varphi} + \frac{1}{\sin^3 \theta} \frac{\partial}{\partial \varphi} \right)
\]

\[
= -i \hbar P^z_1 - i \hbar \cot \theta P^x_1
\]

(III-14)

\[
\begin{bmatrix} P^y_1 & P^z_1 \end{bmatrix} = \begin{bmatrix} P^z_1 & P^x_1 \end{bmatrix} = 0,
\]

and

\[
P^2_x + P^2_y + P^2_z
\]

\[
= -\hbar \left( \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} + \frac{\partial^2}{\partial \theta^2} - 2 \frac{\cot \theta}{\sin \theta} \frac{\partial}{\partial \varphi} \frac{\partial}{\partial \varphi} \right)
\]

(III-15)

in which the term \( \cot \theta \frac{\partial}{\partial \varphi} \) appears to be lacking. It would seem that the method for deriving the operators presented here breaks down. Perhaps the fact that only two, rather than three angles relate \( XYZ \) to \( x'y'z' \) has something to do with this. Also, note the connection between \( w^x_1 \) and \( w^z_1 \) given by Equations (II-21) and (II-22). In any event, we assume in our work that \( P^2 \) is invariant under rotation of axes.
Equations (183) and (184) on p. 67, i.e.

\[ P_x = \cos \gamma P_x - \sin \gamma P_y \]

\[ P_y = \sin \gamma P_x + \cos \gamma P_y \quad \text{(III-16)} \]

\[ P_z = P_z \]

are just

\[ P_x = \cos (x',x) P_x + \cos (x',y) P_y + \cos (x',z) P_z \]

\[ P_y = \cos (y',x) P_x + \cos (y',y) P_y + \cos (y',z) P_z \quad \text{(III-17)} \]

\[ P_z = \cos (z',x) P_x + \cos (z',y) P_y + \cos (z',z) P_z . \]

It is likely that the factors mentioned in the preceding paragraph affect the validity of these relationships. Note that combination of Equations (III-16) and (III-17) yield the expressions for \( P_x, P_y, \) and \( P_z \) given by Equations (III-6).

On page 162 of Appendix II it was shown that the operators \( \mathcal{P}_x, \mathcal{P}_y, \) and \( \mathcal{P}_z \) are given by

\[ \mathcal{P}_x = -(w_2/w_3)^{\frac{1}{3}} q_{3a}p_{3b} + (w_2/w_3)^{\frac{1}{3}} q_{3b}p_3 \]

\[ \mathcal{P}_y = (w_2/w_3)^{\frac{1}{3}} q_{3a}p_{3a} - (w_3/w_2)^{\frac{1}{3}} q_{3a}p_3 \]

\[ \mathcal{P}_z = -q_{3b}p_{3a} + q_{3a}p_{3b} . \]

If \( q_{3a} = r \cos \gamma \), \( q_{3b} = r \sin \gamma \)

\[ p_{3a} = - \frac{2}{q_{3a}} = - \frac{2}{q_{3a}} - \frac{1}{r} \sin \gamma \frac{2}{2\gamma} \]

and

\[ p_{3b} = - \frac{2}{q_{3b}} = - \frac{2}{q_{3b}} - \frac{1}{r} \cos \gamma \frac{2}{2\gamma} \]
then, by direct operation, one can obtain the relations

$$P^1_{z} = -i\frac{\partial}{\partial y},$$

(III-18)

$$[P^1_{x}, P^1_{y}] = i\hbar P^1_{z},$$

(III-19)

$$[P^1_{y}, P^1_{z}] = i\hbar P^1_{x},$$

$$[P^1_{z}, P^1_{x}] = i\hbar P^1_{y}.$$
APPENDIX IV

SOME COMMUTATION RELATIONS INVOLVING QUANTITIES $q$ and $-\frac{2}{5q}$

The following relationships can be very readily obtained by direct operation. See Table 1 of Herman and Shaffer, (36). ($n = a$ positive integer.)

\[
\begin{align*}
[p^n, q] &= -n\hbar p^{n-1} \\
[p, q^n] &= -n\hbar q^{n-1} \\
[p^3, q^2] &= -3\hbar (p^2q + qp^2) \\
[p^2, q^3] &= -3\hbar (pq^2 + q^2p) \\
[p^2, q^2] &= -2\hbar (pq + qp) \\
[p^3, q^3] &= -3\hbar \left\{ \frac{3}{2} (p^2q^2 + q^2p^2) + n^2 \right\} \\
[q^n, qpq] &= n\hbar q^{n+1} \\
[p^n, pqp] &= -n\hbar p^{n+1} \\
[p^2, qpq] &= -2\hbar (pqq + qqp) \\
[pq + qp, q] &= -2i\hbar q \\
[pq + qp, q^2] &= -3i\hbar q^2
\end{align*}
\]
The non-vanishing matrix elements of some functions of $q$ and $p$ (for non-degenerate simple harmonic oscillator wave functions) are the following: 

$q$ is a normal vibrational coordinate, mass adjusted in the manner indicated on p. 144; $p$ is the associated quantum mechanical momentum operator; $v$ can be any non-negative integer. See (57).

\[
(v|q|v-1) = \sqrt{\frac{v}{v+1}} = (v-1|q|v) \quad (V-1)
\]

\[
(v|q|v+1) = \sqrt{\frac{v}{v+2}} = (v+1|q|v) \quad (V-2)
\]

\[
\frac{1}{\hbar}(v|p|v-1) = i \sqrt{\frac{v}{v+1}} = -(1/\hbar)(v-1|p|v) \quad (V-3)
\]

\[
\frac{1}{\hbar}(v|p|v+1) = -i \sqrt{\frac{v}{v+2}} = -(1/\hbar)(v+1|p|v) \quad (V-4)
\]

\[
(v|q^2|v-2) = \frac{1}{2} \sqrt{v(v-1)} = (v-2|q^2|v) \quad (V-5)
\]

\[
(v|q^2|v) = v+\frac{1}{2} \quad (V-6)
\]

\[
(v|q^2|v+2) = \frac{1}{2} \sqrt{(v+1)(v+2)} = (v+2|q^2|v) \quad (V-7)
\]

\[
(1/\hbar^2)(v|p^2|v-2) = -\frac{1}{2} \sqrt{v(v-1)} = (1/\hbar^2)(v-2|p^2|v) \quad (V-8)
\]

\[
(1/\hbar^2)(v|p^2|v) = v+\frac{1}{2} \quad (V-9)
\]

\[
(1/\hbar^2)(v|p^2|v+2) = -\frac{1}{2} \sqrt{(v+1)(v+2)} = (1/\hbar^2)(v+2|p^2|v) \quad (V-10)
\]

\[
(1/\hbar)(v|pq|v-2) = \frac{1}{2} \sqrt{v(v+1)} = -(1/\hbar)(v-2|pq|v) \quad (V-11)
\]

\[
(1/\hbar)(v|pq|v) = -\frac{1}{2} \quad (V-12)
\]

\[
(1/\hbar)(v|pq|v+2) = -\frac{1}{2} \sqrt{(v+1)(v+2)} = -(1/\hbar)(v+2|pq|v) \quad (V-13)
\]
\begin{align*}
(1/\mathcal{N})(v|qp|v-2) &= \frac{1}{2} \sqrt{v(v-1)(v-2)} = -(1/\mathcal{N})(v-2|qp|v) \\
(1/\mathcal{N})(v|qp|v) &= \frac{1}{2} \\
(1/\mathcal{N})(v|qp|v+2) &= -\frac{1}{2} \sqrt{(v+1)(v+2)} = -(1/\mathcal{N})(v+2|qp|v)
\end{align*}

\begin{align*}
(v|q^3|v-3) &= \sqrt{(1/8)v(v-1)(v-2)} = (v-3|q^3|v) \\
(v|q^3|v-1) &= (3/2)v \sqrt{\frac{1}{2}v} = (v-1|q^3|v) \\
(v|q^3|v+1) &= (3/2)(v+1) \sqrt{\frac{1}{2}(v+1)} = (v+1|q^3|v) \\
(v|q^3|v+3) &= \sqrt{(1/8)(v+1)(v+2)(v+3)} = (v+3|q^3|v)
\end{align*}

\begin{align*}
(1/\mathcal{N})(v|p^3|v-3) &= -i \sqrt{(1/8)v(v-1)(v-2)} = -(1/\mathcal{N})(v-3|p^3|v) \\
(1/\mathcal{N})(v|p^3|v-1) &= i(3/2)v \sqrt{\frac{1}{2}v} = -(1/\mathcal{N})(v-1|p^3|v) \\
(1/\mathcal{N})(v|p^3|v+1) &= -i(3/2)(v+1) \sqrt{\frac{1}{2}(v+1)} = -(1/\mathcal{N})(v+1|p^3|v) \\
(1/\mathcal{N})(v|p^3|v+3) &= i \sqrt{(1/8)(v+1)(v+2)(v+3)} = -(1/\mathcal{N})(v+3|p^3|v).
\end{align*}

The following matrix elements are readily obtained from the non-vanishing \((v|p^2|v')\) and \((v|q|v')\).

\begin{align*}
(1/\mathcal{N})(v|p^2q|v-3) &= -\frac{1}{2} \sqrt{\frac{1}{2}v(v-1)(v-2)} \\
(1/\mathcal{N})(v|p^2q|v-1) &= \frac{1}{2}(v+2) \sqrt{\frac{1}{2}v} \\
(1/\mathcal{N})(v|p^2q|v+1) &= \frac{1}{2}(v-1) \sqrt{\frac{1}{2}(v+1)} \\
(1/\mathcal{N})(v|p^2q|v+3) &= -\frac{1}{2} \sqrt{\frac{3}{2}(v+1)(v+2)(v+3)}
\end{align*}

\begin{align*}
(1/\mathcal{N})(v|q^2p|v-3) &= -\frac{1}{2} \sqrt{\frac{1}{2}v(v-1)(v-2)} \\
(1/\mathcal{N})(v|q^2p|v-1) &= \frac{1}{2}(v-2) \sqrt{\frac{1}{2}v} \\
(1/\mathcal{N})(v|q^2p|v+1) &= \frac{1}{2}(v+3) \sqrt{\frac{1}{2}(v+1)} \\
(1/\mathcal{N})(v|q^2p|v+3) &= -\frac{1}{2} \sqrt{\frac{3}{2}(v+1)(v+2)(v+3)}.
\end{align*}

It is seen that
so that the non-vanishing matrix elements are
\[
(1/h)(v_1v_3v_2\lambda \lambda JM|p_1|v_1v_3v_21\lambda \lambda J'M') = i \sqrt{\frac{2}{v_1}}
\]
\[
(1/h)(v_1v_3v_2\lambda \lambda JM|p_1v_1-1v_3v_2\lambda \lambda JM) = -i \sqrt{\frac{2}{v(v+1)}}
\]

[See Equations (7-2).]

To obtain the non-vanishing
\[
(1/h^2)(v_1v_3v_2\lambda \lambda JM|p_{2a}^2 + p_{2b}^2|v_1v_3v_21\lambda \lambda J'M')
\]
we make use of the following relations:
\[
p_{2a} + p_{2b} = (p_{2a} + ip_{2b})(p_{2a} - ip_{2b})
\]
\[
p_{2a} = r \cos \chi, \quad p_{2b} = r \sin \chi
\]
\[
p_{2a} = -i h \frac{2}{\partial \phi_a}, \quad p_{2b} = i h \frac{2}{\partial \phi_b}
\]
where \( p_{\phi} = -i h \frac{2}{\partial \phi} \) and \( p_{\chi} = -i h \frac{2}{\partial \chi} \), so that
\[
(p_{2a} + i p_{2b}) = e^{i \phi_a}\left\{ p_{\phi} + i(1/r)p_{\chi} \right\}
\]
\[
(p_{2a} - i p_{2b}) = e^{-i \phi_a}\left\{ p_{\phi} - i(1/r)p_{\chi} \right\}
\]

From p. 98 of (37), we obtain for the non-vanishing matrix elements of the above two quantities the following expressions:
\[
(V 1|e^{i \phi_a}\left\{ p_{\phi} + i(1/r)p_{\chi} \right\} | V-1 \ 1-1)_{\phi \chi}
\]
\[
= -(V-1 \ 1-1|e^{-i \phi_a}\left\{ p_{\phi} - i(1/r)p_{\chi} \right\} | V \ 1)_{\phi \chi} = -i h \sqrt{\frac{2}{v(v+1)}}
\]
\[
(\mathbf{1} \mid e^{-i\gamma} \{ \mathbf{p}_r - i(1/r)\mathbf{p}_r \} \mid \mathbf{1} + 1)_r \gamma \\
= -(\mathbf{1} \mid e^{i\gamma} \{ \mathbf{p}_r + i(1/r)\mathbf{p}_r \} \mid \mathbf{1} + 1)_r \gamma = \frac{1}{\hbar} \sqrt{2^{1/2}(\mathbf{1} \mid \mathbf{1})} 
\]
\[(v-18)\]
(The wave functions here are those for the twofold degenerate simple harmonic oscillator, and the subscript \(r \gamma\) merely indicates that both \(r\) and \(\gamma\) portions are included.) From the above relations and application of the product rule we obtain for the non-vanishing
\[
(1/\hbar^2)(\mathbf{1} \mid \mathbf{2}_a^2 + \mathbf{2}_b^2 \mid \mathbf{1} + 1)_r \gamma
\]
the expressions
\[
(1/\hbar^2)(\mathbf{1} \mid \mathbf{2}_a^2 + \mathbf{2}_b^2 \mid \mathbf{2} \mid \mathbf{1}) = \frac{1}{\hbar} \sqrt{(\mathbf{1} \mid \mathbf{1})} 
\]
\[(v-19)\]
\[
(1/\hbar^2)(\mathbf{1} \mid \mathbf{2}_a^2 + \mathbf{2}_b^2 \mid \mathbf{2} \mid \mathbf{1}) = \mathbf{v} + 1
\]
\[
(1/\hbar^2)(\mathbf{1} \mid \mathbf{2}_a^2 + \mathbf{2}_b^2 \mid \mathbf{2} \mid \mathbf{1}) = \frac{1}{\hbar} \sqrt{(\mathbf{1} \mid \mathbf{1})} 
\]
(In our work, \(\mathbf{1}\) and \(\mathbf{1}\) become \(\mathbf{v}_2\) and \(\mathbf{l}_2\).) Now
\[
(1/\hbar^2)(v_1v_3v_2\mathbf{1}^2\mathbf{M}\mid \mathbf{2}_a^2 + \mathbf{2}_b^2 \mid v_1v_3v_2\mathbf{1}^2\mathbf{M}^\dagger) 
\]
\[
= (1/\hbar^2)(v_2^2 \mid \mathbf{2}_a^2 + \mathbf{2}_b^2 \mid v_2^2) \int_{\mathbf{J}_2\mathbf{M}^\dagger} F_{\mathbf{J}_2\mathbf{M}^\dagger}(\varphi \rho) F_{\mathbf{J}_2\mathbf{M}^\dagger}(\varphi \rho) \varphi \rho \rho \rho 
\]
\[
\cdot (v_1 \mid 1 \mid v_1) (v_3 \mid 1 \mid v_3) 
\]
\[
= \left\{ \frac{1}{\hbar} \sqrt{(v_2^2 + 1)(v_2^2 - 1)} \delta_1 \delta_1 \delta_1 \delta_1 + \frac{1}{\hbar} \sqrt{(v_2^2 - 1)(v_2^2 + 1)} \delta_1 \delta_1 \delta_1 \delta_1 \right\} \int F^*_{\mathbf{J}_2\mathbf{M}^\dagger} F_{\mathbf{J}_2\mathbf{M}^\dagger} \varphi \rho \rho \rho 
\]
\[
\cdot \delta_1 \delta_1 \delta_1 \delta_1 \delta_1 
\]
\[(v-20)\]
where \(F_{\mathbf{J}_2\mathbf{M}^\dagger}(\varphi \rho)\) is the \(\varphi \rho\) portion of a symmetric rotator wave function, \(F_{\mathbf{J}_2\mathbf{M}^\dagger}(\varphi \rho)(1/2\pi)^{1/2} e^{i\lambda_2 \mathbf{Y}}\). (See pp. 55 f.) Since these
functions are normalized,

\[ \delta_{J_1 J_2} \delta_{M_1 M_2} = (1/2\pi) \int_{J_1}^{J_2} e^{iM_1 \ell} e^{-iM_2 \ell} e^{i\ell_1 \phi} e^{-i\ell_2 \phi} d\phi \]

\[ = 1 \cdot \int_{J_1}^{J_2} F^{J_1 J_2} \ell F^{J_1 J_2} \ell^* d\phi. \]  

(Note that all terms in Equation (V-20) are multiplied by \( \delta_{1_J 2_J} \)).

Hence, the non-vanishing matrix elements of \( p_{2a}^2 + p_{2b}^2 \) are

\[ (1/\hbar^2) (v_1 v_3 \ell_2 l_2 \lambda) p_{2a}^2 + p_{2b}^2 (v_1 v_3 \ell_2 l_2 \lambda) = \frac{1}{3} (v_2 - 1) (v_2 + 1) \]  

\[ (1/\hbar^2) (v_1 v_3 \ell_2 l_2 \lambda) p_{2a}^2 + p_{2b}^2 (v_1 v_3 \ell_2 l_2 \lambda) = v_2 + 1 \]  

\[ (1/\hbar^2) (v_1 v_3 \ell_2 l_2 \lambda) p_{2a}^2 + p_{2b}^2 (v_1 v_3 \ell_2 l_2 \lambda) = \frac{1}{3} (v_2 + 1) (v_2 + 2) \]

The non-vanishing "radial" matrix elements, \( (V \ell | r^n | V' \ell') _r \), for \( n = 1, 2, \) and \( 3 \) are given below. The wave functions here are the \( r \) dependent portions of the wave functions for the twofold degenerate simple harmonic oscillator given by Equation (158) on p. 57; \( r = (q_{2a}^2 + q_{2b}^4)^{1/2} \), and the restrictions on \( V \) and \( l \) (in our work, \( V_2 \) and \( l_2 \)) are given on p. 60. [See (57).]

\[ (V \ell | r | V-1 \ell-1) _r = -\frac{1}{2} (V+1) = (V-1 \ell-1 | r | V \ell) _r \]

\[ (V \ell | r | V-1 \ell+1) _r = \frac{1}{2} (V-1) = (V-1 \ell+1 | r | V \ell) _r \]  

\[ (V \ell | r | V+1 \ell-1) _r = \frac{1}{2} (V-1) = (V+1 \ell-1 | r | V \ell) _r \]

\[ (V \ell | r | V+1 \ell+1) _r = -\frac{1}{2} (V+1) = (V+1 \ell+1 | r | V \ell) _r \]

\[ (V \ell | r^2 | V-2 \ell-2) _r = \frac{1}{3} (V+1) (V+1) = (V-2 \ell-2 | r^2 | V \ell) _r \]

\[ (V \ell | r^2 | V-2 \ell) _r = -\frac{1}{3} (V+1) (V-1) = (V-2 \ell | r^2 | V \ell) _r \]  

\[ (V \ell | r^2 | V-2 \ell+2) _r = \frac{1}{3} (V-1) (V-1) = (V-2 \ell+2 | r^2 | V \ell) _r \]

(continued on next page)
\[
\begin{aligned}
(V_l | r^2 | V_{l-2} \rho)_{r} &= -\sqrt{(V+1)(V-1+2)} = (V_{l-2} | r^2 | V_{l} \rho)_{r} \\
(V_l | r^2 | V_{l-1} \rho)_{r} &= V_{l+1} \\
(V_l | r^2 | V_{l+2} \rho)_{r} &= -\sqrt{(V+1+2)(V-1)} = (V_{l+2} | r^2 | V_{l} \rho)_{r} \\
(V_l | r^2 | V_{l+3} \rho)_{r} &= \frac{1}{3} \sqrt{(V+1+2)(V-1+4)} = (V_{l+3} | r^2 | V_{l} \rho)_{r} \\
(V_l | r^2 | V_{l+4} \rho)_{r} &= \frac{1}{3} \sqrt{(V+1+4)(V-1+6)} = (V_{l+4} | r^2 | V_{l} \rho)_{r}
\end{aligned}
\]
APPENDIX VI

SOME PROPERTIES OF THE REPRESENTATION COEFFICIENTS $D^j_{km}$ AND THE VECTOR ADDITION COEFFICIENTS $(j_1 j_2 m_1 m_2 | jm)$

Consider the cartesian reference frames $XYZ$ and $X'Y'Z'$ which are related by Eulerian angles $\varphi$, $\theta$, and $\chi$ as pictured below. Let $(\phi, \theta)$ and $(\phi', \theta')$ be the azimuthal and polar angles locating a fixed point on the unit sphere centered at the origin, referred to the $XYZ$ and $X'Y'Z'$ frames, respectively.

The representation coefficients $D^j_{km}$ are merely the coefficients in the transformation giving the spherical harmonics, $Y^j_k(\phi', \theta')$ in terms of the spherical harmonics $Y^j_m(\phi, \theta)$. [The basic concepts here do not require the specific choice of angles employed here. However, a particular choice is necessary in order that we be able to define certain quantities exactly. Our spherical harmonics (solutions of Laplace's equation) are the $\Theta(jm) \Phi(m)$ given in Chapter III of Condon and Shortley (28), normalized so that]
\[ \int \int \int Y_m^j Y_m^j' \sin \Theta \, d\Theta \, d\Phi = \delta_{jj'} \delta_{mm}. \]

The \( D_{km}^j \) are then defined by the relationship

\[ Y_k^j (\phi', \Theta') = \sum m D_{km}^j (\phi \theta \phi' \Theta') Y_m^j (\phi, \Theta ). \quad (VI-1) \]

[The infinite number of transformation matrices \( D_{km}^j (\phi \theta \phi' \Theta') \) going with all of the possible sets of values of \( \gamma, \epsilon, \) and \( \gamma' \) form representations of the three dimensional rotation group.] According to Tsao and Curnutte [Appendix B of (20)], the \( D_{km}^j (\phi \theta \phi' \Theta') \) for our choice of Eulerian angles can be expressed as

\[ D_{km}^j (\phi \theta \phi' \Theta') = \sqrt{\frac{(j+k)! (j-k)!}{(j+m)! (j-m)!}} e^{-im \phi} e^{-ik \gamma} (-1)^{j-m} \]

\[ \times \frac{2^{j+k}}{(j+k)!} (\cos^{k+m} (\sin \phi)^{k-m} \]

\[ \times \frac{d^{j+k}}{d(\cos \phi)^{j+k}} \left\{ (\sin \phi)^{2j+2m} (\cos \phi)^{2j-2m} \right\} \quad (VI-2) \]

The non-vanishing \( D_{km}^j \) for \( j + 1 \) tabulated on p. 37 in Table 5 were obtained from the above reference, which also lists the \( D_{km}^j \) for \( j = 0 \) and \( j = 2 \). [C.f. p. 182 of Wigner, (58).]

If one makes use of the relation,

\[ \frac{d^{J-M}}{d(\cos \phi)^{J-M}} (\cos \phi)^{2J} = 2^{J-M} 2J(2J-1) \ldots (J+M+1)(\cos \phi)^{2J+2M} \ldots \quad (VI-3) \]

Equations (153) and (154) on pp. 56 and 57 yield, for the normalized symmetric rotator wave functions, the expression
\[ \psi_{JKM}(\phi, \Theta) = \mathcal{F}_{JKM}(\phi, \Theta) e^{iK\Theta}/(2\pi)^{\frac{1}{2}} \]

\[ = (1/2\pi) \sqrt{(J+M)! (J-K)!(2J+1)} e^{iM\phi} e^{iK\Theta} (-1)^{J-K} \]

\[ \cdot \frac{2^{J-K}}{J+M} (\sin^2\Theta)^{M-K} (\cos^2\Theta)^{K-M} \]

\[ \cdot \frac{d^{J-K}}{d(\cos\Theta)^{J-K}} \left\{ (\sin^2\Theta)^{2J-2M} (\cos^2\Theta)^{2J+2M} \right\} \ldots \quad \text{(VI-4)} \]

Comparison of this expression with Equation (VI-2) yields the proportionality between the symmetric rotator wave functions and the representation coefficients,

\[ \psi_{JKM}(\phi, \Theta) = (-1)^{-K-M} (1/2\pi) \sqrt{\frac{1}{2}(2J+1)} D_{K-M}^J(\phi, \Theta) \ldots \quad \text{(VI-5)} \]

The fact that the symmetric rotator wave functions and the representation coefficients are proportional to each other has also been demonstrated by Wigner, who makes use of group theoretical methods. See Chapter XIX of (58).

It turns out that the product of two \( D_{km}^j \) can be expanded in a series of terms involving \( D_{km}^j \)'s to the first power only, each coefficient in the expansion being the product of two of the so-called "vector addition coefficients," \((j_1j_2k_1k_2|j_m)\). More specifically,

\[ D_{kJ_1}^{j_1} D_{kJ_2}^{j_2} \]

\[ = \sum_{k_{1+2} = |j_1-j_2|} (j_1j_2k_{1+2}|n k_{1+2})(j_1j_2m_{1+2}|n m_{1+2}) \cdot D_{kJ_1+k_2}^n m_{1+m_2} \quad \text{(VI-6)} \]
[See Equation B-13 of (20); Chapter XVII of (58).] This expansion is known as the Clebsch-Gordan series, and the \((j_1 j_2 k_1 k_2 | jk)\) are often called the Clebsch-Gordan coefficients. In terms of the symmetric rotator wave functions, the above expansion becomes, from Equation (VI-5),

\[
\psi_{J_1 K_1 M_1} \psi_{J_2 K_2 M_2} = \frac{1}{\sqrt{2\pi}} \sum_{J=|J_1-J_2|}^{J_1+J_2} \frac{(2J_1+1)(2J_2+1)}{2\pi} (J_1 J_2 - K_1 - K_2) (J - K_1 - K_2)
\]

\[
\cdot (J_1 J_2 - M_1 M_2) (J - M_1 - M_2) \psi_{J_1+K_1 M_1+M_1} \psi_{J_2+K_2 M_2+M_2} \quad (VI-7)
\]

Hence, the orthonormality of the symmetric rotator wave functions enable one to obtain the relation

\[
\int \psi_{J_2 K_2 M_2}^* \psi_{J_1 K_1 M_1} d\tau = \frac{1}{\sqrt{2\pi}} \frac{(2J_1+1)(2J_2+1)}{2\pi} (J_1 J_2 - K_1 - K_2) (J_2 - K_2) (J_1 J_2 - M_1 - M_2) (J_2 M_2) \quad (VI-8)
\]

(In this instance, \(\psi_{J_2 K_2 M_2}^* \psi_{J_1 K_1 M_1} = \psi_{J_1 K_1 M_1} \psi_{J_2 K_2 M_2} \) was expanded.)

The vector addition coefficients \((j_1 j_2 m_1 m_2 | jm)\) are discussed in Chapter III of Condon and Shortley (58), and Chapter XVII of Wigner (58). [See also Simon (59), and Biedenharn, Blatt, and Rose (62).] A brief resume follows, in which the \((j_1 j_2 m_1 m_2 | jm)\) turn up in the quantum mechanical addition of angular momentum.

Consider the angular momentum operators \(P_X\), \(P_Y\), and \(P_Z\), which satisfy the commutation relations

\[
[P_X, P_Y] = i\hbar P_Z
\]
\[
\begin{bmatrix}
P_Y, P_Z \end{bmatrix} = \mathbf{i} \hbar P_X \\
P_Y, P_X = \mathbf{i} \hbar P_Y;
\]
the "square" of the total angular momentum,

\[P^2 = P_X^2 + P_Y^2 + P_Z^2,\]

and a set, \( P \), of operators, which, together with \( P^2 \) and \( P_Z \), make up a complete set of independent commuting observables. [A complete set of commuting observables is a set in terms of whose simultaneous eigenstates one can describe the state of a system completely. See p. 18 of Condon and Shortley (28).] The set of eigenvalues of the set of operators \( \{ P, P^2, P_Z \} \) can be represented by \( \{ \gamma, J(J+1)\hbar^2, M \} \), where \( 2J \) is a non-negative integer and \( M \) can take on the values \( J, J-1, \ldots, -J \). [See p. 47 of (28).] The eigenfunctions, which are simultaneously eigenfunctions of all of the above operators, will be denoted by \( \psi(\gamma J M) \). These will be assumed to be normalized to unity, the arbitrary phase factor which occurs being chosen, as a matter of convenience, so that

\[(P_X + \mathbf{i} P_Y) \psi(\gamma J M) = \hbar \sqrt{(J-M)(J+M+1)} \psi(\gamma J M \pm 1).\]

[See p. 43 of (28).]

The states of a system of two commuting angular momentum vectors \( P_1 \) and \( P_2 \) can be represented by \( \Phi(\gamma J_1 J_2 M_1 M_2) \), where \( J_i \) and \( M_i \) \((i = 1, 2)\) are the quantum numbers going with \( P_i^2 \) and \( P_i Z \) respectively, and \( \gamma \) is a set of quantum numbers going with a set of observables which commute with the \( P_i^2 \) and \( P_i Z \) and is such that \( \{ \gamma, P_i, P_i^2, P_i Z \} \) form a complete set. However, if \( P = P_1 + P_2 \) so that \( P^2 = P_1^2 + P_2^2 \), the set of operators, \( \{ \gamma, P_1, P_2, P_1^2, P_2^2, P, P_Z \} \), is equally
complete. The eigenfunctions in this latter case can be represented by
\[ \psi (\mathcal{W} J_1 J_2 M) \]. [The arbitrary phase of \( \Phi \) will be chosen here so that
\[ (p_x + i p_y) \Phi (\mathcal{W} J_1 J_2 M_1 M_2) = \sqrt{(j_1^2 - M_1)(j_1^2 + M_1 + 1)} \Phi (\mathcal{W} J_1 J_2 M_1 M_2), \]
\[ (p_x - i p_y) \Phi (\mathcal{W} J_1 J_2 M_1 M_2) = \sqrt{(j_2^2 - M_2)(j_2^2 + M_2 + 1)} \Phi (\mathcal{W} J_1 J_2 M_1 M_2), \]
and the phase of \( \Phi \) will be chosen so that
\[ (p_x \pm i p_y) \psi (\mathcal{W} J_1 J_2 M) = \sqrt{(j_1^2 M)(j_1 M + 1)} \psi (\mathcal{W} J_1 J_2 M^2). \]

The vector addition coefficients are the coefficients in the expansion which expresses the \( \psi (\mathcal{W} J_1 J_2 M) \) in terms of the \( \Phi (\mathcal{W} J_1 J_2 M_1 M_2) \). This expansion can be written as
\[ \psi (\mathcal{W} J_1 J_2 M) = \sum_{M_1 M_2} (J_1 J_2 M_1 M_2 | JM) \Phi (\mathcal{W} J_1 J_2 M_1 M_2) \quad (VI-9) \]
See p. 73 of (28). Wigner has obtained the general form of the vector addition coefficients by means of group theoretical methods. [See p. 206 of (58), p. 75 of (28).] His result is
\[ (j_1 j_2 m_1 m_2 | j m) = \delta_{m, m_1 + m_2} \]
\[ \sqrt{(j + j_1 - j_2)!(j - j_1 + j_2)!(j_1 + j_2 - j)!(j + m)!(j - m)!(2j + 1)!} \]
\[ (j + j_1 + j_2 - 1)!(j_1 - j_2)!(j_1 + j_2 - j)!(j_1 + m_1)!(j_2 - m_2)!(j_2 + m_2)! \]
\[ \sum_{k} (-1)^{k+j_2+m_2}(j+j_2+m_1-k)!(j_1-m_1+k)! \]
\[ k (j-j_1+j_2-k)!(j+m-k)!k!(k+j_1-j_2-m)! \quad (VI-10) \]
where \( k \) takes on all integral values consistent with the factorial notation, the factorial of a negative number being meaningless. Small case letters will be used when we consider the vector addition coefficients as purely mathematical quantities. The non-vanishing \( (j_1 j_2 m_1 m_2 | j m) \)
for \( j_2 = 0, \frac{1}{2}, 1, 3/2, \) and 2 are given on pp. 75-77 of Condon and Shortley (23). [Table 7 on p. 97 giving the \((j_1m_1m_2|jm)\) was obtained from this source.] A table of \((j_1m_1m_2|jm)\) is given by Falkoff, Colladay, and Sells (64).

The limitations on the possible values of \( j_1, j_2, m_1, m_2, j, \) and \( m \) are the following: [See Simon (59), or Racah (63).]

\[
\begin{align*}
\{ j_1, j_2, j \} & \text{ are non-negative integers or half integers;} \\
\{ m_1, m_2, m \} & \text{ are positive or negative integers or half integers;} \\
\quad & \text{ such that} \\
\qquad j_1 + j_2 + j & = \text{ an integer} \\
\{ j_1 + j_2 - j \} & \geq 0; \\
\{ j_1 - j_2 + j \} & \\
\{ -j_1 + j_2 + j \} \\
\end{align*}
\]

\[
\begin{align*}
|m_1| & \leq j_1, \\
|m_2| & \leq j_2, \\
|m| & \leq j; \text{ and} \\
\{ j_1 + m_1 \} & \text{ are integers.} \\
\{ j_2 + m_2 \} & \\
\{ j + m \} & \\
\end{align*}
\]

Note from Equation (VI-10) that \((j_1j_2m_1m_2|jm) = 0\) unless \(m_1+m_2 = m\).

The following symmetry relations hold: [See (59), Appendix A of (20); (62), and (63).]

\[
\begin{align*}
(j_1j_2m_1m_2|jm) &= (-1)^{j_1+j_2-j}(j_1j_2 -m_1 -m_2 | j -m) \quad (VI-11) \\
&= (j_2j_1 -m_2 -m_1 | j -m) \quad (VI-12) \\
&= (-1)^{j_1+j_2-j}(j_2j_1m_2m_1 | jm) \quad (VI-13)
\end{align*}
\]
(j_1j_2m_1m_2 | jm) = \sqrt{\frac{2j_1+1}{2j_1}} \frac{(-1)^{j_1-m_1}(-1)^{j_2-m_2}}{\sqrt{2j_2+1}} (j_2m_2 | j_1m_1) \quad (VI-14)

= \sqrt{\frac{2j_1+1}{2j_1}} \frac{(-1)^{j_1-m_1}}{\sqrt{2j_2+1}} (j_2m_2 | j_1m_1) \quad (VI-15)

= \sqrt{\frac{2j_1+1}{2j_2+1}} \frac{(-1)^{j_1-m_1}}{\sqrt{2j_2+1}} (j_2m_2 | j_1m_1) \quad (VI-16)

= \sqrt{\frac{2j_1+1}{2j_2+1}} \frac{(-1)^{j_1-m_1}}{\sqrt{2j_2+1}} (j_2m_2 | j_1m_1) \quad (VI-17)

= \sqrt{\frac{2j_1+1}{2j_2+1}} \frac{(-1)^{j_1-m_1}}{\sqrt{2j_2+1}} (j_2m_2 | j_1m_1) \quad (VI-18)

The application of Symmetry Relation (VI-11) causes Equation (VI-8) for \( \int \psi^* J_2 K_2 M_2 \psi J_1 K_1 M_1 \, d\tau \) to go over into

\[
\int \psi^* J_2 K_2 M_2 \psi J_1 K_1 M_1 \, d\tau = \frac{1}{2\pi} \sqrt{\frac{(2j_1+1)(2j_2+1)}{2(2j_2+1)}}
\]

\[ 
\cdot (j_1j_2 | j_1j_2) (J_1 M_1 | J_2 M_2) \quad (VI-19)
\]

This is Equation (251) on p. 94. If one replaces \( \{ k \text{ and } m \} \) by \( \{ -k \text{ and } -m \} \) everywhere in this equation and makes use of Equation (VI-5), one obtains

\[
\int \psi^* J_2 K_2 M_2 \psi J_1 K_1 M_1 \, d\tau = (-1)^{k+m} \sqrt{\frac{(2j_1+1)}{(2j_2+1)}} (j_1j_2 \rightarrow k | j_2j_2) (J_1 M_1 | J_2 M_2). \quad (VI-20)
\]

This is Equation (255) on p. 95.

It happens that the \( (j_1j_2 | jm) \) form a unitary matrix, this property giving rise to the relations
\[ \sum \sum (j_1 j_2 m_1 m_2 | j m) (j_1 j_2 m_1 m_2 | j' m) = \delta_{jj'} \]  
(VI-21)

\[ \sum \sum (j_1 j_2 m_1 m_2 | j m) (j_1' j_2' m_1' m_2' | j m) = \delta_{m_1 m_1'} \delta_{m_2 m_2'} \]  
(VI-22)

[See Appendix A of (20), Chapter XVII of Wigner (53).] From (VI-21)

and Symmetry Relation (VI-14), it can be shown that

\[ \sum \sum (j_1 j_2 m_1 m_2 | j m) (j_1' j_2 m_1 m_2 | j m) = \delta_{m_1 m_2} \frac{2j+1}{2j_1+1} \]  
(VI-23)

In a similar manner, it can be shown from Equations (VI-21) and (VI-17) that

\[ \sum \sum (j_1 j_2 m_1 m_2 | j m) (j_1' j_2 m_1 m_2 | j m) = \delta_{j_1 j_2} \frac{2j+1}{2j_2+1} \]  
(VI-24)

[In considering these summations it is well to bear in mind the restrictions on the values that \( m_1, m_2, j \), and \( m \) can assume, particularly the one, \( m_1 + m_2 = m \).] This last relation is Equation (272) on p. 102 which proved so useful in simplifying the calculation of the

\[ \sum \sum \sum (J_1 l_1 M_1 | \lambda \gamma | J_2 M_2)^2 \]  
and the \[ \sum \sum \sum (J_1 l_1 M_1 | \lambda \gamma | J_2 M_2)^2 \]  
\[ \sum \sum \sum (M M' \gamma) \]
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