VIBRATION-INTERNAL ROTATION INTERACTIONS IN
MOLECULES CONTAINING A SYMMETRIC TOP GROUP

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Vibration-Internal Rotation Interactions in Molecules Containing a Symmetric Top Group*

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The vibration-internal rotation interactions in molecules that contain a single symmetric top are studied by means of a model consisting of two internally rigid groups that are allowed to vibrate as well as rotate relative to each other. The matrix mechanical Hamiltonian for the model is obtained and the diagonalization of the corresponding secular determinant that contains large off-diagonal terms is accomplished. An expression for the \( J = 0 \rightarrow 1, \Delta K = 0 \) transition is obtained. Numerical calculations are carried out for the case of methyl alcohol in order to compare the theory with the observed spectrum. A qualitative fit is found, the major contributions being the in-plane vibrations of the two rigid groups. The lack of detailed agreement is attributed to the neglect of those vibrations which distort the methyl group, and to insufficient knowledge concerning the infrared spectrum of the molecule.

I. INTRODUCTION

Various aspects of the problem of internal rotation in molecules have been discussed by many different approaches. Among these, Dennison and co-workers (1), in a series of papers, have considered in detail the methyl-alcohol molecule. They have used a model in which the only internal motion permitted is the rotation of the symmetric top about its axis of symmetry (we call this a rigid internal rotor model) to explain many features of the microwave rotational spectrum of this molecule. Nevertheless, we shall find that only transitions within the ground torsional state are predicted by this rigid model, and that the transitions involving excited torsional states can only be explained by a vibration-interaction theory.

Kivelson (2), in a series of papers, treated the interaction problem in a rather

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general way, and obtained a semiempirical formula for the fine structure caused by excited torsional states of the $J = 0 \rightarrow 1$, $\Delta K = 0$ transition for methyl silane.

We propose studying the vibration interaction effects by a new method with the object of determining, insofar as possible, the manner in which specific vibrational motions contribute to the observed fine structure of the $J = 0 \rightarrow 1$ transition.

We shall first reformulate the problem of the rigid internal rotor in a matrix mechanics framework. A slightly more general model than Dennison's will be used, and the derivation will be briefly outlined as a basis for the later theory. Then, the fine structure of the $J = 0 \rightarrow 1$ transition of methyl alcohol, which was identified and measured during the course of this work (3), will be compared with the results of the rigid internal rotor theory.

Next, we shall develop our approach to the problem of predicting the observed spectrum and define precisely the model that will be used for the main part of this work. A detailed derivation of the kinetic energy of our model will follow which includes the separation of the internal rotational motion and the choice of internal coordinates for the vibrations, a general expansion of the potential energy, and, finally, the quantum mechanical Hamiltonian for the system. After the pertinent matrix elements have been worked out, a general diagonalization procedure will be derived in order to find the eigenvalues of the resultant secular determinant that contains large off-diagonal terms, from which an explicit formula for the spectrum of the $J = 0 \rightarrow 1$, $\Delta K = 0$ transition will be obtained.

II. THE RIGID INTERNAL ROTOR

As a basis for later work, the problem of the rigid internal rotor will be discussed and solutions will be outlined. Our model will be a general asymmetric rigid frame with a symmetric top attached at some arbitrary angle and allowed to rotate relative to the frame about its axis of symmetry under the influence of a three-fold hindering potential. Moreover, this problem will be solved entirely by matrix methods: consequently, the terms in the resultant Hamiltonian will be more easily identified in terms of the contributions of various components of angular momenta.

**Kinetic Energy**

The classical kinetic energy of our rigid internal rotor can be written in several ways; any particular choice will be in the interest of achieving particular simplifications. Two forms were used in the course of this work, both being set up originally in the principal axes of the molecule. However, in the first case, we transform axes to achieve the usual form of the rigid rotor portion of the Hamiltonian, which was used to investigate the $J = 0 \rightarrow 1$ spectrum of methyl alcohol.
the second case, we transform to axes so that the new z-axis is parallel to the symmetry axis of the top. This choice is much better suited to the vibration interaction problem.

In both methods, we denote by \(xyz\) the principal axes (which do not change with internal rotation of a symmetric top) of the molecule that has an angular velocity \(\omega\) relative to the inertial axes. In addition, the symmetric top has an angular velocity \(\omega'\) about its axis of symmetry relative to the axes \(xyz\). Then, as Crawford (4) (whose notation we adopt for the following work) shows, the rotational kinetic energy can be written

\[
2T = \sum I_{g}\omega_{g}^{2} + I'\omega'^{2} + 2I'\omega'\sum \lambda_{g}\omega_{g} \quad (g = x, y, z)
\]

where the \(I_{g}\) are the principal moments of the entire molecule, \(I'\) is the moment of the symmetric top about its axis of symmetry, and the \(\lambda_{g}\) are the directional cosines of the top axis of symmetry relative to the principal axes \(xyz\) of the molecule.

To give an example of the method, which will be used to advantage later, we find the conjugate momenta and corresponding kinetic energy expression by matrix methods. If we denote the angular velocity of this model with four degrees of freedom by the column vector

\[
\omega = \begin{bmatrix} \omega_{x} \\ \omega_{y} \\ \omega_{z} \\ \omega' \end{bmatrix}
\]

and place the coefficients of (1) in a matrix

\[
I = \begin{bmatrix} I_{x} & 0 & 0 & I'\lambda_{x} \\ 0 & I_{y} & 0 & I'\lambda_{y} \\ 0 & 0 & I_{z} & I'\lambda_{z} \\ I'\lambda_{x} & I'\lambda_{y} & I'\lambda_{z} & I' \end{bmatrix}
\]

the quadratic expression for the kinetic energy can be written in the matrix form

\[
2T = \omega^{T}I\omega,
\]

where \(\omega^T\) denotes the transpose of the column vector \(\omega\).

Then, we define the conjugate angular momentum vector

\[
P = \begin{bmatrix} P_{x} \\ P_{y} \\ P_{z} \\ P' \end{bmatrix} = I\omega
\]

...
so that its components have the usual definitions
\[ P_a = \frac{\partial T}{\partial \omega_a}, \quad P' = \frac{\partial T'}{\partial \omega'} . \] (6)

Then, by straightforward substitution of (5) and its inverse in (4), we obtain
\[ 2T = P'T^{-1}P \]
\[ = \sum_{\alpha \beta} \beta_{\alpha \beta} P_\alpha P_\beta + 2 \sum_\gamma \gamma_\gamma P_\gamma' P'_\gamma + \beta' P'^2 \] (7)
in which the components of the inverse of (3) are denoted by
\[ \Gamma^\dagger = \begin{bmatrix} \beta_{xx} & \beta_{xy} & \beta_{xz} & \gamma_x \\ \beta_{yx} & \beta_{yy} & \beta_{yz} & \gamma_y \\ \beta_{zx} & \beta_{zy} & \beta_{zz} & \gamma_z \\ \gamma_x & \gamma_y & \gamma_z & \beta' \end{bmatrix} . \] (8)

Actual inversion of (3) gives the relations
\[ \beta_{qq'} = \frac{1}{I_q} \left( \delta_{qq'} + \frac{\Gamma \lambda \lambda'}{I_q \Delta} \right), \quad \beta' = \frac{1}{\Delta}, \quad \gamma_q = -\frac{\lambda_q}{\Gamma \Delta}, \]
\[ \Delta = 1 - \sum_q \frac{\Gamma \lambda_q^2}{I_q} . \] (9)

From these relations, it can be shown that if the axis of symmetry of the top is nearly parallel to one of the principal axes, say the z-axis, then the \( \beta_{qq'} \) for \( g \neq g' \) will all be small compared with the diagonal terms. Furthermore, if the molecule possesses a plane of symmetry (which will necessarily include the top axis), say the \( yz \)-plane, then we have
\[ \gamma_z = \beta_{yz} = \beta_{zx} = 0. \]

Both conditions hold for the methyl-alcohol molecule, in which the axis of symmetry is almost parallel to the \( \text{CO} \) bond, which, in turn, is nearly the principal \( z \)-axis, since these are the heavy atoms of the molecule.

In the first method of writing the kinetic energy, we apply a transformation to new axes \( x_d y_d z_d \) so that the submatrix \( \beta_{qq'} \) is diagonalized. This will, of course, introduce new momenta \( P'_q \) and coefficients \( \gamma_q \), as well as new diagonal elements \( \beta_{qq}(g = x_d y_d z_d) \), but note that this transformation leaves the formal definition of \( P' \) and the value of \( \beta' \) unchanged. If the conditions that the \( \beta_{qq'}(g \neq g') \) are small compared with the diagonal terms hold, this transformation is particularly easy to obtain. In any event, the transformation can be made and we obtain
\[ 2T = \sum_q \beta_{qq} P'_q^2 + \beta' P'^2 + \sum_\gamma \gamma_\gamma P_\gamma' P'_\gamma \quad (g = x_d y_d z_d) \] (10)
as the kinetic energy contribution to the rigid internal rotor Hamiltonian.
For the second method of presenting the kinetic energy, we return to (1). At that point, we apply a transformation from the principal axes $xyz$ to a new set of axes $x_s^s y_s^s z_s^s$ with $z_s$ parallel to the axis of symmetry of the top. We then divide the expression into two portions

$$2T = 2T^{(0)} + 2T^{(1)},$$

$$2T^{(0)} = \sum_i I_{gg'} \omega_{g'}^2 + \frac{1}{2} I' \omega^2 + 2I' \omega \omega_z, \quad (11)$$

$$2T^{(1)} = \sum_{g'g''} I_{gg'} \omega_{g'g''}. \quad (g, g' = x_s y_s z_s).$$

If we accept the assumption that the $I_{gg'}$ are small compared with the diagonal terms, $2T^{(0)}$ becomes a small correction to $2T^{(0)}$, which we choose as our "zero-order" kinetic energy. Inversion of $2T^{(0)}$ then gives

$$2T^{(0)} = \sum_i \beta_{gg} P_g^2 + \beta' P'^2 + \gamma_z P_z P', \quad (10)$$

$$\text{(12)}$$

$$\omega_g = \beta_{gg} P_g + \gamma_z P' z_s.$$

Although this inversion procedure appears rather roundabout in the present context, it is convenient because the product of inertia term (only one appears for a molecule with a plane of symmetry) can be treated separately and its effects can be determined quite easily. It should be emphasized, however, that the choice of the $x_s^s y_s^s z_s^s$ axes in preference to the original principal axes or the axes $x_d^d y_d^d z_d$ of (10) is not dictated by this product of inertia term, but by other complications in the interaction theory that follows.

**Hamiltonian**

We now add a simple cosine hindering potential as our rigid internal rotor barrier to Eq. (10) and obtain the Hamiltonian

$$H = \frac{1}{2} \sum_i \beta_{gg} P_g^2 + \frac{1}{2} \beta' P'^2 + \sum_i \gamma_z P_z P' + \frac{1}{2} V_0 (1 - \cos 3 \varphi). \quad (14)$$

This can be divided into three terms

$$H_{RR} = \frac{1}{2} \sum_i \beta_{gg} P_g^2,$$

$$H_{tr} = \frac{1}{2} \beta' P'^2 + \gamma_z P_z P' + \frac{1}{2} V_0 (1 - \cos 3 \varphi), \quad (15)$$

$$H_{int} = (\gamma_z P_z + \gamma_z P_z) P',$$

where the interaction Hamiltonian $H_{int}$ is small, from our earlier assumption that the top axis and $z$-axis nearly coincide. The first term is just the free rigid rotor Hamiltonian, and has well-known $(K | K)$ and $(K | K \pm 2)$ matrix elements.
in the usual $JKM$ representation (5). In that representation, $P_z$ has diagonal elements equal to $hK$; thus the internal rotor Hamiltonian $H_{1R}$ is diagonal in the $JKM$ representation.

We choose as our original representation for $H_{1R}$ the one in which $P'$ has diagonal elements $hm(m$ an integer). With the eigenfunctions $(2\pi)^{-1/2}e^{im\varphi}$ that correspond to this, it is easy to calculate directly the matrix elements

$$
(JKm | \cos 3 \varphi | J K m \pm 3) = \frac{1}{2}.
$$

(16)

Thus, we can give the matrix elements of the Hamiltonian $H_{1R}$ as

$$
(JKm | H_{1R} | J K m) = \frac{1}{2}h^2\beta'm^2 + h^2\gamma K m + \frac{1}{2}V_0,
$$

$$
(JKm | H_{1R} | J K m \pm 3) = \frac{1}{4}V_0.
$$

(17)

Except for the case of an extremely low barrier, the off-diagonal term ($\frac{1}{4}V_0$) is quite large compared with the rotational energies; consequently, diagonalizing $H_{1R}$ is a convenient procedure. We note the following properties: The secular determinant that is to be solved factors immediately into three subdeterminants, each of which is labeled by a parameter $\tau(\tau = 1, 2, 3)$, so that the diagonal elements of each subdeterminant contain $m$ values:

$$
\begin{align*}
\tau = 1: m &= \cdots -6, -3, 0, 3, 6, 9, \cdots \\
\tau = 2: m &= \cdots -5, -2, 1, 4, 7, 10, \cdots \\
\tau = 3: m &= \cdots -7, -4, -1, 2, 5, 8, \cdots 
\end{align*}
$$

(18)

Owing to the presence of the quantum number $K$, we have $2J + 1$ sets of determinants for each value of $\tau$, but we note also that the determinant $\tau = 2$ for a particular value of $K$ is identical to that of $\tau = 3$ for minus $K$. Thus the determinants $\tau = 2, 3$ are degenerate, and we need solve for the roots of only one.

The $m$th row of a particular subdeterminant now has diagonal elements

$$
\frac{1}{2}h^2\beta'^2m^2 + h^2\gamma K m + \frac{1}{2}V_0 - E,
$$

where $E$ is the eigenvalue of the particular root being sought, and it has elements off-diagonal by one of the form

$$
-\frac{1}{4}V_0.
$$

For convenience, we divide the entire determinant by the factor $(-\frac{1}{2}h^2\beta')$, thereby obtaining for the $m$th row

$$
\cdots 0 0 \alpha R - \{m\} \alpha 0 0 \cdots
$$

(19)

where we have written

$$
R = (2/h^2\beta') (E - \frac{1}{2}V_0), \quad \alpha = \frac{1}{2}V_0/h^2\beta',
$$

$$
\{m\} = m(m - \epsilon K), \quad \epsilon = -2\gamma/\beta'.
$$

(20)
We now find the root $R$ (hence the particular eigenvalue $E$) by the usual continued-fraction method (5) and obtain the formula

$$
R = \{m\} + \frac{\alpha^2}{R} - \{m + 3\} - \frac{\alpha^2}{R} - \{m + 6\} - \cdots
+ \frac{\alpha^2}{R} - \{m - 3\} - \frac{\alpha^2}{R} - \{m - 6\} - \cdots,
$$

(21)

which are identical in form to the continued fractions obtained by Koehler and Dennison in his treatment of methyl alcohol; the only difference arises in the definition of $\{m\}$.

In accordance with Koehler and Dennison’s procedure, we relabel the roots and eigenvalues $E$ (obtained from the continued fraction expanded about a particular value of $m$, say $m_0$) by a quantum number $n$ in order of increasing values of $E$ for each $\tau$ and $K$. Hence, we have $E^{ Krn}$ for the diagonalized values of $H_{1R}$.

The eigenfunctions corresponding to a particular root are given by the formulas

$$
\alpha_m^{ Krn} = -\alpha m_{-4}/R - \{m\} - \frac{\alpha^2}{R} - \{m + 3\} - \cdots (m > m_0),
$$

$$
\alpha_m^{ Krn} = -\alpha m_{+4}/R - \{m\} - \frac{\alpha^2}{R} - \{m - 3\} - \cdots (m < m_0),
$$

(22)

but the sets $a_m^{ Krn}$ are orthogonal for various values of $n$ only for a particular value of $K$. Thus, since the transformation diagonalizing $H_{1R}$ must in reality be applied to the entire Hamiltonian $H$, we find that any matrix element off-diagonal in $K$ will have a normalizing factor

$$
\sum_m (a_m^{ Krn})^2 = 1.
$$

Thus, we write the matrix elements of our Hamiltonian as

$$
(JKM\tau n \mid H \mid JKM\tau n) = \frac{1}{2} \hbar^2 \beta_+ [J(J + 1) - K^2] + \frac{1}{2} \hbar \beta_+ K^2 + E^{ Krn},
$$

(23)

$$
(JKM\tau n \mid H \mid J K \pm 1 M\tau n') = \frac{1}{2} \hbar^2 \gamma (g(J, K) \sum_m a_m^{ Krn} a_m^{ K'n'}),
$$

$$
(JKM\tau n \mid H \mid J K \pm 2 M\tau n') = \frac{1}{4} \hbar^2 \beta_- f(J, K) \sum_m a_m^{ Krn} a_m^{ K\pm 2n'}
$$

where the following abbreviations have been used:

$$
\beta_\pm = \frac{1}{2} (\beta_{sz} \pm \beta_{sy}),
$$

$$
g(J, K) = [J(J + 1) - K(K \pm 1)]^{1/2},
$$

(24)

$$
f(J, K) = g(J, K) g(J, K \pm 1).
$$

Thus, in the new representation

$$
(K\tau n \mid P' \mid K'\tau n') = \sum_m m a_m^{ Krn} a_m^{ K'n'}
$$

(25)

Equation (23) is the Hamiltonian which will be used to investigate the $J = 0 \rightarrow 1$ spectrum of methyl alcohol; it corresponds closely to Burkhard and Denni-
son's Hamiltonian that was attained by wave equation methods. Note that we use \( \tau \) to label the factors of the original determinant; therefore we do not have cross terms in \( \tau \), as Dennison does.

We postpone the quantum mechanical treatment of the Hamiltonian obtained by use of the kinetic energy of (11).

III. METHYL ALCOHOL

The \( J = 0 \rightarrow 1, \Delta K = 0, \Delta n = 0 \) transition for methyl alcohol has been identified (3). Because of the internal rotation, this transition, which is ordinarily a single absorption frequency, is split into a series of pairs, each pair consisting of one single and one doubly degenerate line. Thus, each pair is split, because of the splitting of the secular determinant into three subdeterminants denoted by \( \tau = 1, 2, \text{and} 3 \), of which 2 and 3 are degenerate, and each of these pairs corresponds to a particular internal torsion state denoted by \( n = 0, 1, 2, \cdots \) in order of increasing energy for each \( \tau \).

The experimental work was carried out with a standard Stark-modulated spectrograph that has been described elsewhere (6). A K-band klystron output was frequency doubled with a crystal doubler to the required range because of the lack of a frequency source in the region of this transition (48,000 Mc/sec). Frequency measurements were made at the K-band frequency with the secondary frequency standard used in our laboratory.

The experimentally observed spectrum is listed in Table I. Tentative identification was made by Stark measurements and intensity measurements; later the observed spectrum was compared with results obtained by applying Kivelson's equation.

**Comparison With Rigid Internal Rotor Theory**

In order to compare our experimental spectrum with the rigid theory, the moments of inertia calculated by Ivash and Dennison (3) were used. The transformation of moments from Dennison's axes to the principal axes gave a matrix \( \beta \)

<table>
<thead>
<tr>
<th>Identification</th>
<th>Frequency</th>
<th>Stark coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>((K\nu n))</td>
<td>(\text{Mc/sec} )</td>
<td>(\text{Mc/sec/(esu)}^3)</td>
</tr>
<tr>
<td>020</td>
<td>48,376.85</td>
<td>0.21</td>
</tr>
<tr>
<td>010</td>
<td>48,372.40</td>
<td>0.20</td>
</tr>
<tr>
<td>011</td>
<td>48,257.19</td>
<td>0.19</td>
</tr>
<tr>
<td>021</td>
<td>48,247.38</td>
<td>0.18</td>
</tr>
<tr>
<td>012</td>
<td>48,191.60</td>
<td>0.252 ( \pm 0.0077 )</td>
</tr>
<tr>
<td>022</td>
<td>48,178.16</td>
<td>0.19</td>
</tr>
</tbody>
</table>
of the form

\[
\mathbf{J} = \begin{bmatrix}
\beta_{zz} & 0 & 0 \\
0 & \beta_{yy} & \beta_{yz} \\
0 & \beta_{yz} & \beta_{xx}
\end{bmatrix},
\]

(26)

where \( \beta_{yz} \ll \beta_{zz} - \beta_{yy} \). This, in turn, was diagonalized to second order by a transformation matrix

\[
\mathbf{A} = \begin{bmatrix}
1 & 0 & 0 \\
0 & \cos \alpha & \sin \alpha \\
0 & -\sin \alpha & \cos \alpha
\end{bmatrix},
\]

where

\[
\sin \alpha = \frac{\beta_{yz}}{\beta_{zz} - \beta_{yy}} \ll 1,
\]

with the result that

\[
\mathbf{J} = \begin{bmatrix}
\beta_{zz} & 0 & 0 \\
0 & \beta_{yy} - \frac{\beta_{yz}^2}{\beta_{zz} - \beta_{yy}} & 0 \\
0 & 0 & \beta_{xx} + \frac{\beta_{yz}^2}{\beta_{zz} - \beta_{yy}}
\end{bmatrix},
\]

(27)

With the use of the Ivash value of 374.8 cm\(^{-1}\) for \( V_0 \) for calculating the Mathieu levels \( E^{\nu_{\nu_n}} \) and the coefficients \( a_m \), the Hamiltonian matrix elements were calculated, the resultant matrix was diagonalized to second order, and the \( J = 0 \rightarrow 1 \) transitions were calculated. There was no recognizable correlation between the resultant spectrum and the observed spectrum. All of the calculated frequency splittings were less than 1 Mc/sec and followed no particular pattern, as compared with the observed splittings up to 200 Mc/sec shown in Table I. The obvious conclusion is that the rigid model is quite insufficient for describing the molecule in its excited internal rotational states.

**APPLICATION OF KIVELSON'S FORMULA**

Kivelson (2) gave the following formula for fitting a symmetric top \( J = 0 \rightarrow 1 \) transition which can be applied to the case of methyl alcohol.

\[
v_{\nu_n} = 2[B + F(1 - \cos 3\phi) + G(P^2)],
\]

(28)

where theoretically the coefficients are related to molecular parameters but practically they are used as empirical constants. The diagonal values \( (1 - \cos 3\phi) \) and \( \langle P^2 \rangle \) are calculated for the particular values of \( \pi n \) that must be considered in the rigid theory. Three observed frequencies are chosen for determin-
TABLE II
METHYL ALCOHOL SPECTRUM FROM KIVELSON'S FORMULA

\( B = 24,224.756 \text{ Mc/sec,} \)
\( F = -71.66076, \)
\( G = -3.538238 \)

<table>
<thead>
<tr>
<th>( n )</th>
<th>( \tau )</th>
<th>Observed</th>
<th>Calculated*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2</td>
<td>48,376.847</td>
<td>48,376.886</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>48,372.399</td>
<td>(48,372.399)</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>48,257.190</td>
<td>(48,257.190)</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>48,247.382</td>
<td>48,247.235</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>48,191.60</td>
<td>(48,191.60)</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>48,178.16</td>
<td>48,177.53</td>
</tr>
</tbody>
</table>

* Values in parentheses were used to determine constants.

The observed Stark effect of normal methyl alcohol is particularly interesting in the anomalous Stark coefficient for the line at 48,191.6 Mc/sec. From Table I, it is seen that the frequency splitting depends on the electric field strength, in accordance with the relation

\[ \Delta \tau = 0.252 \epsilon^2 + 0.0077 \epsilon^4 \text{ Mc/sec,} \]

where \( \epsilon \) is given in esu.

The most probable explanation of the strong fourth-order dependency is the occurrence of an accidental near degeneracy between two levels that are connected by a Stark matrix element. In this case, when the Stark contributions to the Hamiltonian are diagonalized, the nearly degenerate levels permit a large \( \epsilon^2 \) dependence to appear in the denominators of the second-order terms. As an oversimplified illustration of the possible effect, consider the Hamiltonian

\[
\begin{pmatrix}
H_1 & a \mu \epsilon & 0 \\
\mu \alpha & H_2 & b \mu \epsilon \\
0 & b \mu \epsilon & H_3
\end{pmatrix}
\]

where \( H_2 \) and \( H_3 \) are nearly degenerate, and \( H_1 \) is the level under consideration.
A perturbation calculation would then give

\[ E_1 = H_1 + \frac{(a\mu\epsilon)^2}{H_1 - H_2 + \frac{(b\mu\epsilon)^2}{H_2 - H_3}}, \]

where the correction to \( H_2 \) in the denominator is not small compared with \( H_2 \), owing to the degeneracy \( H_2 = H_3 \), but it is small compared with \( H_1 - H_2 \). In this case, we can write

\[ E_1 = H_1 + \frac{(a\mu\epsilon)^2}{H_1 - H_2} \left[ 1 + \frac{(b\mu\epsilon)^2}{(H_1 - H_2)(H_2 - H_3)} \right] \]

\[ = H_1 + \alpha \epsilon^2 + \beta \epsilon^4, \]

where, if we assume for order-of-magnitude purposes that the coefficients \( a \) and \( b \) are equal, we find that

\[ \beta = \frac{\alpha^2}{H_2 - H_3}. \]

Furthermore, if we assume that these are the only terms contributing to Eq. (29), we find that \( H_2 - H_3 \) is an energy corresponding to about 8 Mc/sec.

Thus, we have a means of checking the relative location of levels in the second excited torsional state (at about 500 cm\(^{-1}\)) to within a small fraction of a cm.\(^{-1}\). This depends, of course, on finding the near degeneracy, which may be no mean task if the excited states are not precisely known. This is so because each of the levels of the \( J = 0 \rightarrow 1 \) transition is connected by Stark terms to several levels, each of which, in turn, is connected to several levels with which it might be accidentally nearly degenerate. A search of this sort was made for the rigid model theory, but no near degeneracies were found. This is not surprising, since the levels in question lie well above the top of the assumed cosine barrier, a region in which we would expect that distortions of the barrier shape would alter the levels considerably. However, this Stark effect furnishes an extremely convenient method for evaluating any precise vibration-interaction theory.

\[ ^1 \text{Since the completion of the work reported here (10) two papers dealing with the } J = 0 \rightarrow 1 \text{ transition along somewhat similar lines have appeared. Results similar to those given in Table II have been obtained by Nishikawa (11). Results similar to those shown in Table V have appeared in an article by Hecht and Dennison (12). The latter paper obtains better agreement with experiment than has been presented here, although Hecht and Dennison's agreement was obtained by allowing a variation in constants to achieve a fit to the observed spectrum. That the present work does not show such good agreement with experiment, although it is apparently more complete (namely, in that the contributions of more degrees of freedom of vibrational motion have been considered) merely serves to underline the difficulty of this problem.} \]
IV. VIBRATING INTERNAL ROTOR MODEL

We have shown that the approximation of a rigid internal rotor model is insufficient for predicting the observed splitting of the $J = 0 \rightarrow 1$ transition of methyl alcohol. Since the splitting of this transition is qualitatively the same as that of other internal rotors, we conclude that, in general, a more exact model is required. In the next step, obviously, we must take into account the interactions that arise when internal vibratory motions are considered. However, the presence of large internal motions makes it impossible to use explicitly treatments of the vibration-rotation interaction given in published works.

It has often been noticed, in the study of vibrational spectra of complex molecules, that certain characteristic frequencies appear whenever a particular bond or group of atoms appears in a molecule. Although these group frequencies vary with the bond or group environment, they are sufficiently reliable for some identification purposes. Moreover, the continued presence of these characteristic frequencies indicates that the group of radical maintains its identity, to some extent, in the over-all molecule. In fact, these frequencies are often named under this assumption, for example, we speak of a methyl group rocking vibration, and so forth.

As our example, let us examine the vibrational spectrum of CH$_3$OH. Table III lists the twelve gas spectra frequencies with their designations and descriptions, as given by Herzberg (7). The existence of group frequencies in this molecule becomes immediately apparent, and we note that the five lowest frequencies are of this type, if we consider the molecule as a methyl group and hydroxyl group connected by the CO bond.

### TABLE III

**Vibrational Frequencies of Methyl Alcohol (After Herzberg)**

<table>
<thead>
<tr>
<th>Designation</th>
<th>Description</th>
<th>Frequency (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_6''$</td>
<td>OH-twist</td>
<td>270</td>
</tr>
<tr>
<td>$v_4'$</td>
<td>CO-stretch</td>
<td>1034</td>
</tr>
<tr>
<td>$v_7'$</td>
<td>CH$_3$-rock</td>
<td>1056</td>
</tr>
<tr>
<td>$v_7''$</td>
<td>CH$_3$-rock</td>
<td>1171</td>
</tr>
<tr>
<td>$v_6'$</td>
<td>OH-bend</td>
<td>1340</td>
</tr>
<tr>
<td>$v_6''$</td>
<td>CH$_3$-distort</td>
<td>1430</td>
</tr>
<tr>
<td>$v_6'''$</td>
<td>CH$_3$-distort</td>
<td>1455</td>
</tr>
<tr>
<td>$v_3$</td>
<td>CH$_3$-distort</td>
<td>1477</td>
</tr>
<tr>
<td>$v_2$</td>
<td>CH-stretch</td>
<td>2844</td>
</tr>
<tr>
<td>$v_2''$</td>
<td>CH-stretch</td>
<td>...</td>
</tr>
<tr>
<td>$v_1$</td>
<td>OH-stretch</td>
<td>2977</td>
</tr>
<tr>
<td>$v_1'$</td>
<td>OH-stretch</td>
<td>3682</td>
</tr>
</tbody>
</table>

* Single prime indicates motion in the symmetry plane; double prime indicates motion out of plane.
In ordinary vibration-rotation interaction theory, and also in the case that includes internal rotation, as we shall show later, the interaction terms in the Hamiltonian connect different vibrational states. When the effect of these terms is calculated by means of second-order perturbation theory, they contribute after division by the energy difference of the levels that they connect. Thus, the higher vibrational states have progressively less perturbing effect upon the ground vibrational and the lower excited torsional states.

Thus we are led to the approximation of considering a model in which the two rigid groups are allowed to rotate about their common bond, and to undergo small vibrations from their equilibrium orientation also. More generally, we shall take as our model any asymmetric rigid frame to which a rigid symmetric top is attached. We consider as possible motions the rotation of the top about its axis of symmetry under a periodic hindering potential and small vibrational changes in the relative positions of the two rigid groups. We follow the generally accepted method of finding the kinetic energy of this model, but we must treat the internal rotation separately from the other internal motions. This complication makes it impossible to put the elegant methodology of Wilson (8) to full use, but we have utilized the parts of his work that were applicable.

V. KINETIC ENERGY

Cartesian Kinetic Energy

If we define \( N_1 \) and \( N_2 \) as the number of atoms in the frame and top, respectively, the molecule will have a total of \( 3N = 3(N_1 + N_2) \) degrees of freedom. Specification of the origin and orientation of the molecule axes (defined precisely below) places the usual six restrictions on the internal coordinates and leaves \( 3N - 6 \) degrees of internal freedom. Our requirement that both the frame and the top remain internally rigid sets an additional \( (3N_1 - 6) + (3N_2 - 6) = 3N - 12 \) restriction (\( 3N - 11 \) if the frame is a linear group) and leaves a final total of six (five for group one linear) degrees of internal freedom. Thus, regardless of the number of atoms in the molecule, we are considering a problem with six (five) internal coordinates, one of which is the internal-rotation angle \( \varphi \).

Define the following axes and coordinates:

\[
\begin{align*}
XYZ &= \text{inertial axes}, \\
xyz &= \text{molecular axes with origin at } R_0 \text{ in } XYZ, \\
\dot{R}_0 &= \text{velocity of } R_0 \text{ relative to } XYZ, \\
\omega &= \text{angular velocity of axes } xyz \text{ relative to } XYZ, \\
R_i &= \text{coordinate of mass } m_i \text{ in } XYZ, \\
r_i &= \text{coordinate of mass } m_i \text{ in } xyz, \\
\dot{R}_i &= \text{velocity of } R_i \text{ relative to } XYZ, \\
\dot{r}_i &= \text{velocity of mass } m_i \text{ relative to } xyz.
\end{align*}
\]
From these definitions, the following relations hold:

\[ \mathbf{R}_i = \mathbf{R}_0 + \mathbf{r}_i, \]
\[ \dot{\mathbf{R}}_i = \dot{\mathbf{R}}_0 + \mathbf{\omega} \times \mathbf{r}_i + \dot{\mathbf{r}}_i. \]  

(30)

Then, twice the kinetic energy becomes

\[ 2T = \sum_i m_i \dot{\mathbf{r}}_i^2 \]
\[ = (\sum_i m_i) \dot{\mathbf{R}}_0^2 + \sum_i m_i (\mathbf{\omega} \times \mathbf{r}_i)^2 \]
\[ + \sum_i m_i \dot{\mathbf{r}}_i^2 + 2\mathbf{\omega} \cdot \sum_i m_i (\mathbf{r}_i \times \mathbf{\dot{r}}_i) \]
\[ + 2(\dot{\mathbf{R}}_0 \times \mathbf{\omega}) \cdot \sum_i m_i \mathbf{r}_i + 2\dot{\mathbf{R}}_0 \cdot \frac{d}{dt} \sum_i m_i \mathbf{r}_i, \]

where use is made of the relation \( \mathbf{A} \times \mathbf{B} \times \mathbf{C} = \mathbf{A} \times \mathbf{B} \times \mathbf{C}. \) We locate the origin of our molecular axes \( xyz \) by the requirement that it always be at the center of mass of the molecule, that is,

\[ \sum_i m_i \mathbf{r}_i = 0. \]  

(32)

This is just sufficient to make the last two terms vanish and to separate the translational energy \( (\sum m_i) \dot{\mathbf{R}}_0^2 \); it also places three restrictions on the coordinates \( \mathbf{r}_i \).

The rotation-vibration kinetic energy then becomes

\[ 2T = \sum_i m_i \dot{\mathbf{r}}_i^2 + \sum_i m_i (\mathbf{\omega} \times \mathbf{r}_i)^2 + 2\mathbf{\omega} \cdot \mathbf{L} \]  

(33)

where

\[ \mathbf{L} = \sum_i m_i (\mathbf{r}_i \times \mathbf{\dot{r}}_i) \]  

(34)

is the angular momentum caused by the internal motion of the atoms.

The next step is usually the specification of the orientation of the instantaneous molecular axes by the requirement that the internal angular momentum \( \mathbf{L} \) vanish to zero order in the small vibrations. We cannot do this immediately, since our internal rotational motion is not small, and it contributes to \( \mathbf{L} \) in zero order. Therefore we must separate the explicit dependence of \( \mathbf{L} \) on the internal-rotation angle \( \phi \).

**Separation of \( \phi \) Dependence of Kinetic Energy**

Let us first specify the orientation of the equilibrium molecular axes \( x_0 y_0 z_0 \). The origin has already been defined by Eq. (32), that is,

\[ \sum_i m_i \mathbf{r}_i = 0, \]  

(35)

where the subscript zero denotes equilibrium values. We now require that \( z_0 \) be parallel to the equilibrium position of the top symmetry axis, and that the
The choice of $z_0$, parallel to the axis of symmetry, simplifies much of the work that follows, and the choice of the $yz_0$-plane takes full advantage of any available symmetry. These axes also correspond to Dennison’s axes.

It will be of value to define a set of auxiliary coordinates $R_i$. Let $R_i$ be identical to $r_i$ for each mass $m_i$, except for the symmetry masses $m$ of the top. In particular, number the coordinates of the ends of the bond that connect the frame and top $R_1$ and $R_2$, respectively. Define a point $R_3$ that is always on the instantaneous axis of symmetry and at a distance $p$ from the apex atom at $R_2$, where $p$ is the distance in the molecular model from the apex atom to any one of the symmetry masses. That is, we define

$$R_3 = R_2 + p\epsilon,$$

where $\epsilon$ is a unit vector along the instantaneous axis of symmetry with equilibrium orientation $e_0$ parallel to $z_0$.

These auxiliary coordinates effect the substitution of a “bond” $R_3 - R_2$ for the symmetric top and, after the $\varphi$ dependence has been explicitly separated in $2T$, the remainder of $2T$ is conveniently expressed in the auxiliary coordinates, which are now of the form

$$R_k = R_{ak} + \delta R_k,$$

where $\delta R_k$ is a small change from equilibrium. We define a summation over upper-case quantities $R$, as a summation over the frame atoms (including $R_1$), and a summation over $R_k$ as including $R_2$ and $R_3$ of the new “bond.”

Then, we describe the purely vibrational motions of the two rigid groups that comprise our model and allow for the rotation of the top about its axis of symmetry. We define axes $x'y'z'$ fixed in the (nonrotating) top with origin at $R_2$, with $z'$ parallel to $\epsilon$, and with $x'$ and $y'$ “nearly” parallel to axes $x$ and $y$ of the molecule. By “nearly” parallel we mean that at equilibrium $x'$ and $y'$ are parallel to $x_0$ and $y_0$, and they only depart from this orientation when small rocking motions of the $z'$-axis occur.

This rocking motion can be more precisely defined. With the apex atom as the origin, an instantaneous rocking orientation of the top defines a plane that includes the vectors $\epsilon$ and $e_0$. Then, the requirement that the instantaneous and equilibrium positions of any particle of the top lie in a plane parallel to that plane defines the instantaneous position of the $x'y'$ axes. This motion can also be described by a set of Eulerian angles

$$\psi, \theta, \chi = \psi, \theta, -\psi$$

where $\psi$ is a precessional angle of $z'$ about $z$, $\theta$ is an azimuthal angle between $z$ and $z'$, and $-\psi$ is the angle of rotation of the top about $z'$. Then, the transfor-
mation \( A(\psi, \theta, -\psi) \), which describes the motion from equilibrium position to the instantaneous \( x'y'z' \) axes, is of the form

\[
A = [a_{ij}] = 
\begin{bmatrix}
\cos^2 \psi + \cos \theta \sin^2 \psi & \sin \psi \cos \psi (1 - \cos \theta) & -\sin \psi \sin \theta \\
\sin \psi \cos \psi (1 - \cos \theta) & \sin^2 \psi + \cos \theta \cos^2 \psi & \cos \psi \sin \theta \\
\sin \psi \sin \theta & -\cos \psi \sin \theta & \cos \theta
\end{bmatrix}.
\]  \( \text{(37)} \)

Thus, if the apex atom is the origin, any vector has components in the two systems that are related by

\[
r(x'y'z') = A(\psi\theta)r(xyz).
\]  \( \text{(38)} \)

In particular, the unit vector \( \epsilon \) has components

\[
\epsilon(x'y'z') = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} = \mathbf{A} \epsilon(xyz) = [a_{ij}] \begin{bmatrix} \xi \\ \eta \\ \zeta \end{bmatrix},
\]  \( \text{(39)} \)

where \( \xi, \eta, \zeta \) are the direction cosines of \( \epsilon \) relative to the molecule axes \( xyz \). Then we have

\[
\epsilon(xyz) = \begin{bmatrix} \xi \\ \eta \\ \zeta \end{bmatrix} = \begin{bmatrix} \sin \psi \sin \theta \\ -\cos \psi \sin \theta \\ \cos \theta \end{bmatrix}.
\]  \( \text{(40)} \)

Since we have restricted the rocking motion to small amplitudes, we have

\[
\sin \theta \ll 1, \quad \xi, \eta \ll 1, \quad \zeta \approx 1,
\]  \( \text{(41)} \)

and we can now write, to second order in the small vibrations,

\[
A = [a_{ij}] = \begin{bmatrix} 1 - \frac{1}{2} \xi^2 & -\frac{1}{2} \xi \eta & -\xi \\
-\frac{1}{2} \xi \eta & 1 - \frac{1}{2} \eta^2 & -\eta \\
\xi & \eta & 1 - \frac{1}{2} \xi^2 - \frac{1}{2} \eta^2 \end{bmatrix}.
\]  \( \text{(42)} \)

The rows of this matrix contain the direction cosines of unit vectors \( \epsilon_x', \epsilon_y', \) and \( \epsilon_z' = \epsilon \) with respect to molecule axes \( xyz \).

Our symmetric top is now composed of three bonds \( 120^\circ \) apart around the axis of symmetry, forming tetrahedral angles with each other and with \(-\epsilon\). Therefore, we can show that the coordinate \( r_j \) of the symmetry mass \( m_j \) can be decom-
posed into the vectors

\[ \mathbf{r}_j = \mathbf{R}_2 + \frac{1}{2} \rho (\mathbf{r} + \sqrt{8} \mathbf{r}_j), \] (43)

where

\[ \mathbf{r}_j = r_{x'} \sin \varphi_j - r_{y'} \cos \varphi_j \] (44)

and

\[ \varphi_j = \varphi + \frac{2\pi}{3}(j - 1) \quad (j = 1, 2, 3). \] (45)

From definition (36), this can also be written

\[ \mathbf{r}_j = \frac{2}{3} \mathbf{R}_2 + \frac{1}{3} \mathbf{R}_3 + \frac{\sqrt{8}}{3} \rho (r_{x'} \sin \varphi_j - r_{y'} \cos \varphi_j). \] (46)

The \( \varphi_j \) have the following properties:

\[ \sum_j \cos \varphi_j = \sum_j \sin \varphi_j = \sum_j \cos \varphi_j \sin \varphi_j = 0, \]
\[ \sum_j \cos^2 \varphi_j = \sum_j \sin^2 \varphi_j = \frac{3}{2}. \] (47)

We are now in a position to evaluate the kinetic energy of the symmetric top, given in (33) and (34), in the new notation:

\[ 2T = \sum_i m_i \mathbf{R}_i^2 = \sum_i m_i (\omega \times \mathbf{R}_i)^2 + 2 \sum_i m_i \omega \cdot (\mathbf{R}_i \times \dot{\mathbf{R}}_i) \]
\[ + m_2 \mathbf{R}_2^2 + m_3 (\omega \times \mathbf{R}_3)^2 + 2 m_3 \omega \cdot (\mathbf{R}_2 \times \dot{\mathbf{R}}_3) \]
\[ + m \sum_i (\dot{r}_j^2 + (\omega \times \mathbf{r}_j)^2 + 2 \omega \cdot (\mathbf{r}_j \times \dot{\mathbf{r}}_j)), \] (48)

if we remember that a summation over upper-case quantities \( \mathbf{R}_i \) is only over the frame atoms. Straightforward substitution of (46) in (48), the use of the properties of (47), and somewhat tedious exercises yield the following results: First,

\[ \mathbf{L} = \left\{ \sum_i m_i (\mathbf{R}_i \times \dot{\mathbf{R}}_i) + [(M_2 + \frac{1}{2} m) \mathbf{R}_2 - \frac{1}{2} m \mathbf{R}_3] \times \dot{\mathbf{R}}_2 \right\} \]
\[ + \left\{ \sum_i m_i (\mathbf{R}_3 \times \dot{\mathbf{R}}_3) + [(M_3 + \frac{1}{2} m) \mathbf{R}_3 - \frac{1}{2} m \mathbf{R}_2] \times \dot{\mathbf{R}}_3 \right\} \]
\[ + \left\{ \sum_i m_i (\mathbf{R}_2 \times \dot{\mathbf{R}}_2) + [(M_2 + \frac{1}{2} m) \mathbf{R}_2 - \frac{1}{2} m \mathbf{R}_3] \times \dot{\mathbf{R}}_2 \right\} \]
\[ + \left\{ \sum_i m_i (\mathbf{R}_3 \times \dot{\mathbf{R}}_3) + [(M_3 + \frac{1}{2} m) \mathbf{R}_3 - \frac{1}{2} m \mathbf{R}_2] \times \dot{\mathbf{R}}_3 \right\} \] (49)

The dependence of \( \mathbf{L} \) on \( \varphi \) takes on the simple form

\[ \mathbf{L}(\varphi) = I'(\varepsilon_0 + \delta \varepsilon) \varphi, \]

where \( I' = \frac{1}{2} m \rho^2 \) is the moment of inertia of the top about its axis of symmetry.

Second, the remaining terms contain cross terms between coordinates \( \mathbf{R}_2 \) and \( \mathbf{R}_3 \), and so they do not correspond to the Eckart conditions of a molecule that is ob-
tained by placing some mass at $R_i$. For this reason, we cannot utilize the full value of Wilson’s formulation (8) for obtaining immediately the inverse metric of $2T$.

However, the first three terms of the zero-order portion of $L$ can be written in the form

$$\frac{d}{dt} \left[ \sum m_i (R_i \times \delta R_i) \right]$$

so that the quantity acted upon by the time derivative can be set equal to zero as a sort of pseudo-Eckart condition defining the instantaneous orientation of the molecule axes and placing three additional constraints on the coordinates $\delta R_i$.

Therefore, we have

$$\sum_i m_i (R_i \times \delta R_i) + [(M_2 + \frac{8}{3}m)R_{o2} - \frac{2}{3}mR_{o3}] \times \delta R_2$$

$$+ [\frac{8}{3}mR_{o3} - \frac{2}{3}mR_{o3}] \times \delta R_3 = 0$$

(50)

and

$$L = I' \phi(\epsilon_0 + \delta \epsilon) + \sum_i m_i (\delta R_i \times \delta \dot{R}_i)$$

$$+ [(M_2 + \frac{4}{3}m)\delta R_2 + \frac{2}{3}m\delta R_3] \times \delta \dot{R}_2 + [\frac{2}{3}m\delta R_3 + \frac{4}{3}m\delta R_3] \times \delta \dot{R}_3$$

(51)

$$= I' \phi(\epsilon_0 + \delta \epsilon) + \sum_{kk'} N_{kk'} (\delta R_k \times \delta \dot{R}_{k'})$$.

For frame atoms, by comparison, we have

$$N_{22} = M_2 + \frac{4}{3}m, \quad N_{23} = N_{32} = \frac{2}{3}m, \quad N_{33} = \frac{4}{3}m, \quad N_{kk'} = m_i.$$ (52)

Moreover, the total kinetic energy can be written

$$2T = \sum_{\alpha \alpha'} (I' \phi(\epsilon_0 + \delta \epsilon) + 4 \phi^2 + \sum_{kk'} M_{kk'} (\delta R_k \times \delta \dot{R}_{k'})$$

$$+ 2I' \phi(\epsilon_0 + \delta \epsilon) \cdot \omega - I' \phi(\delta \epsilon \times \delta \dot{\epsilon}) \cdot \omega_0$$

$$+ 2 \sum_{kk'} N_{kk'} (\delta R_k \times \delta \dot{R}_{k'}) \cdot \omega,$$

(53)

where we have

$$1' = \frac{8}{3}mp^2, \quad \epsilon = \epsilon_0 + \delta \epsilon = \begin{bmatrix} 0 \\ \xi \\ 1 \end{bmatrix} + \begin{bmatrix} 0 \\ \eta \\ 0 \end{bmatrix},$$

and

$$I' = I_{\alpha \alpha} (\epsilon_0 + \delta \epsilon)$$

$$= \sum_k m_k (G_{k0} \epsilon^2 + G_{k0} \epsilon^2) + I'(\delta \epsilon \cdot \delta \dot{\epsilon} + \frac{1}{4} \delta \dot{\epsilon} \cdot \delta \dot{\epsilon})$$

$$+ 2 \sum_k m_k (G_{k0} \delta \dot{R}_k \cdot \delta \dot{R}_k) + \frac{1}{2} \sum \delta \dot{R}_k \cdot \delta \dot{R}_k;$$
\[
I_{\phi'} = I_{\phi'}^{(0)} + \delta I_{\phi'}
= - \sum_k m_k^* G_k \delta \phi' - \sum_k m_k^* (G_{ik} \delta \phi_k + G_{ik} \delta \phi_k) \\
- 2m \rho (\delta G_2 - \delta G_3) \delta \phi, + (\delta G_2 + \delta G_3) \delta \phi)
\]

\[
m_k^* = M_2 + 2m, \quad m_i^* = m, \quad m_k^* = m_k \quad \text{for} \quad k = i,
M_{22} = M_2 + \frac{3}{2}m, \quad M_{33} = \frac{3}{2}m, \quad M_{23} = M_{32} = -\frac{3}{2}m,
M_{kk'}^* = m_i \quad \text{for} \quad k = k' = i.
\]

All other coefficients are zero.

From these last definitions, we can rewrite (50), defining the orientation of the molecule axes as follows.

\[
\sum_{kk'} M_{kk'} (R_{ik} \times \delta R_{ik}) = 0. \quad (54)
\]

Similarly, the \(m_k^*\) can be used to rewrite (32) and (35), defining the origin of the molecule axes:

\[
\sum_k m_k^* R_{ik} = \sum_k m_k^* \delta R_{ik} = 0. \quad (55)
\]

**INTERNAL VIBRATIONAL COORDINATES**

We assume that five (four for group one linear) internal coordinates \(q_t\) exist with coefficients \(l_t'\) (we revert to the subscripts \(ij\) for \(kk'\)), related to the \(\delta G_i\) by the equation

\[
\delta G_i = \sum_{ii'} l_{ii'} q_{ii'}, \quad (56)
\]

which describe the motions that contribute the terms in \(2T\) independent of \(\varphi\). These motions are essentially the perpendicular rocking motions of each of the two rigid groups and the stretching vibration of the bond connecting them. However, Eqs. (56) can only be obtained for an explicit geometrical model. In Appendix 1 we obtain their inverses for methyl alcohol by the method of Wilson's s-vectors. This gives each of the quantities \(q_t\) in terms of the Cartesian displacements \(\delta G_i\), and the equilibrium interatomic distances and angles, including those of the "bond" \(R_{23}\) which replaced the symmetric top.

Actually, up to this point, we have not utilized the original requirement that the framework group be internally rigid. In fact, additional coordinates \(q_t\) could be chosen for internal vibrations of the frame without disturbing what has been done. However, we would expect the added freedom (and complication) to contribute little, since distortion of the symmetric top itself would undoubtedly be as important, if not more so. And the rigidity of the top has been used to a great extent to separate the \(\varphi\) dependence of the kinetic energy. Thus, we shall assume instead the existence of \(3N_1 - 6\) \((3N_1 - 5)\) equations that relate the \(\delta R_{ik}\) of the frame, similar to those used in Appendix 1 for the top group.

Now we have:
(a) five (four) equations defining the \( q_t \);
(b) six equations specifying the origin and orientation of the instantaneous axes;
(c) \( 3N_1 - 6 \) (\( 3N_1 - 5 \)) equations specifying the rigidity of the frame; and
(d) one equation requiring that the bond length \( \rho \) remain constant.

This makes a total of \( 3N_1 + 6 \) equations that are functions of the \( \delta G_i \). Since we have \( 3N_1 + 3(2) \) Cartesian coordinates \( \delta G_j \), these equations must be just sufficient to invert and obtain the desired relations (56).

Two difficulties present themselves. First, the six pseudo-Eckart conditions, (54) and (55) do not correspond to true Eckart conditions for any molecule, since they contain cross terms between different masses \( m_i \). More to the point, on account of the way they were obtained, they are not orthogonal to (although they are independent of) the equations defining the \( q_t \). Hence, the inverse metric of \( 2T \) cannot be obtained immediately by the methods of Wilson, but must be obtained after an explicit inversion of the \( 3N_1 + 6 \) equations. Second, it is impracticable to obtain this inversion analytically; hence we must resort to a numerical inversion for each molecule that is being investigated. This is accomplished in Appendix 2 for the case of methyl alcohol and numerical values for the \( l_{it}^{\varphi} \) are obtained.

With these new coordinates \( q_t \) and coefficients \( l_{it}^{\varphi} \), Eq. (53) can be rewritten

\[
2T = \left\{ \sum_{\alpha\beta} \delta I_{\alpha\beta}^{(0)} \omega_\alpha^0 \omega_\beta^0 + I' \bar{\phi}^2 + 2I' \bar{\phi} \sum_{\gamma} m_{\gamma \alpha} q_\gamma q_\gamma + \sum_{\alpha\beta} \delta I_{\alpha\beta} \right\} + \left\{ \sum_{\alpha\beta} \delta I_{\alpha\beta} (q_t) \omega_\alpha \omega_\beta + 2\bar{\phi} \sum_{\alpha} \delta \lambda_\alpha (q_t) \omega_\alpha + 2 \sum_{\alpha} m_{\alpha \gamma} n_{\alpha \gamma} \delta_{\gamma \alpha} + 2 \sum_{\alpha} \omega_\alpha \delta_{\alpha \alpha} \right\}
\]

where the zero-order and first-order terms have been grouped in brackets, and

\[
\delta I_{\alpha\beta} = \sum_{\gamma} \delta I_{\alpha\beta} (q_t) ;
\]

\[
\delta I_{\alpha\beta}^{(0)} = 2 \sum_{\gamma} m_{\gamma \alpha} (G_0 \delta_{\gamma \beta} + G_0 \delta_{\gamma \beta}) \quad (g = g') ;
\]

\[
\delta I_{\alpha\beta}^{(1)} = - \sum_{\gamma} m_{\gamma \alpha} (G_0 \delta_{\gamma \beta} + G_0 \delta_{\gamma \beta}) + 2m_p [(l_{3t}^{\varphi} - l_{2t}^{\varphi}) \delta_{g \alpha} + (l_{3t}^{\varphi} - l_{2t}^{\varphi}) \delta_{g \alpha}] \quad (g \neq g') ;
\]

\[
\rho \lambda_\alpha (q_t) = (l_{3t}^{\varphi} - l_{2t}^{\varphi}) q_t ;
\]

\[
m_{\alpha \beta} = \sum_{\gamma} \sum_{\kappa} k_{\alpha \kappa} M_{\gamma \kappa} ;
\]

\[
n_{\alpha \beta} (q_t) = \sum_{\gamma} \omega_{\alpha \gamma} q_\gamma ;
\]

\[
n_{\alpha \beta} (q_t) = \sum_{\gamma} \omega_{\alpha \gamma} q_\gamma ;
\]

\[
n_{\alpha \beta} (q_t) = \sum_{\gamma} \omega_{\alpha \gamma} q_\gamma ;
\]

\[
n_{\alpha \beta} (q_t) = \sum_{\gamma} \omega_{\alpha \gamma} q_\gamma ;
\]

\[
\rho \lambda_\alpha (q_t) = (l_{3t}^{\varphi} - l_{2t}^{\varphi}) (l_{2t}^{\varphi} - l_{2t}^{\varphi}) \quad (g \neq g') .
\]
Two simplifications of the zero-order terms are now possible. If the internal coordinates \( q_t \) are good approximations to the normal coordinates of the problem, the coefficients \( m_{tt'} \) for \( t \neq t' \) will be small compared with the diagonal coefficients \( m_{tt} \). Next, if the molecular axes are close to the principal axes of the molecule, the products of inertia \( I_{pp'}^{(0)} \) will be small compared with the diagonal moments \( I_{pp}^{(0)} \). This will generally be true for molecules in which the atoms of the bond that connects the two groups are the only heavy ones in the molecule, such as methyl alcohol and methyl mercaptan, since this bond is almost the principal z-axis and is also nearly parallel to the axis of symmetry of the top because of bonding considerations. It will also be true for molecules of higher symmetry, such as nitromethane, methyl silane, and so forth. If these conditions hold, it will be convenient to include the terms \( I_{pp'}^{(0)} \) and \( m_{tt'} \) in the first-order terms, thereby simplifying the zero-order terms to a great extent. If not, then a transformation must be applied to diagonalize the zero-order terms. We shall assume, henceforth, that these conditions hold; therefore we give the kinetic energy in two expressions:

\[
2T^{(0)} = \sum_q I_{qq}^{(0)} \omega_q^2 + 2 I'_{pp} \phi \omega_p + \sum_t m_{tt} q_t^2,
\]

\[
2T^{(1)} = \sum_{pp'} (I_{pp'}^{(0)} + \delta I_{pp'}^{(0)}(q_t)) \omega_q \omega_{p'} + 2 I'_{pp} \sum_q \delta \lambda_p(q_t) \omega_q \\
+ \sum_{pp'} m_{tt'} q_t q_{p'} + 2 \sum_p \sum_{pp'} n_{pp'}(q_t) q_{p'} \omega_q \\
+ 2 \sum_{pp'} n_{pp'}(q_t) q_{p'} \phi.
\]

(59)

Utilizing the matrix inversion procedure outlined above, we define

\[
\omega = [\omega] = \begin{bmatrix} \omega_x \\ \omega_y \\ \omega_z \\ \phi \\ \ddot{q}_1 \\ \ddot{q}_2 \\ \ddot{q}_3 \\ \ddot{q}_4 \end{bmatrix} \quad \text{and} \quad P = [P] = \begin{bmatrix} P_x \\ P_y \\ P_z \\ \dot{p}_1 \\ p_2 \\ \dot{p}_3 \\ p_4 \end{bmatrix}
\]

(60)

where

\[
P = \Gamma^{(0)} \omega; \quad P_f = \frac{\partial T^{(0)}}{\partial \omega_f};
\]

(61)
and
\[
\mathbf{I}^{(0)} = [I_{ij}^{(0)}] = \begin{bmatrix}
I_x^{(0)} \\
I_y^{(0)} \\
I_z^{(0)} \\
I_x^{(0)}' I' \\
I_y^{(0)}' I' \\
m_{11} \\
m_{22} \\
m_{33} \\
m_{44} \\
m_{55}
\end{bmatrix}
\]

Then
\[
2T^{(0)} = \sum_{ij'} I_{ij'}^{(0)} \omega_j \omega_{j'} = \boldsymbol{\omega}^T \mathbf{I}^{(0)} \boldsymbol{\omega}
\]
\[
= \sum_{ij'} \beta_{ij'}^{(0)} P_i P_{j'} = \mathbf{P}^T \mathbf{\beta}^{(0)} \mathbf{P},
\]

where
\[
\mathbf{\beta}^{(0)} = \mathbf{I}^{(0)} \quad (63)
\]

and
\[
\mathbf{g}^{(0)} = [\mathbf{g}_{ij'}^{(0)}] = \begin{bmatrix}
\delta_{xx} & \delta_{yy} & \delta_{xz} & \delta_{yz} & \delta_{x'z} & \delta_{y'z} & \delta_{x'z'} & \delta_{y'z'} & \mu_{11} & \mu_{22} & \mu_{32} & \mu_{41} & \mu_{42} & \mu_{44} & \mu_{55}
\end{bmatrix}
\]
which gives

\[ \beta_{yy} = \frac{1}{I_{yy}^{(0)}} (y = x, y) \quad \beta' = \frac{I_{xx}^{(0)}}{I'(I_{xx}^{(0)} - I')} , \]

\[ \beta_{zz} = \frac{1}{I_{zz}^{(0)} - I' } , \quad \gamma = -\frac{1}{I_{zz}^{(0)} - I} \]

\[ \mu_{tt} = (m_{tt})^{-1}. \]

Thus, if we use the inverse of (61) and

\[ I^{(1)} = [I_{ff'}^{(1)}] = \]

\[ \begin{bmatrix}
\delta I_{xx} & I_{xy}^{(0)} + \delta I_{xy} & I_{xt}^{(0)} + \delta I_{xt} & I'\delta x & n_{x1} & n_{x2} & n_{x3} & n_{x4} & n_{x5} \\
\delta I_{yy} & I_{yx}^{(0)} + \delta I_{yx} & I'\delta y & n_{y1} & n_{y2} & n_{y3} & n_{y4} & n_{y5} \\
\delta I_{zz} & 0 & n_{z1} & n_{z2} & n_{z3} & n_{z4} & n_{z5} \\
0 & n_{p1} & n_{p2} & n_{p3} & n_{p4} & n_{p5} \\
0 & m_{12} & m_{13} & m_{14} & m_{15} \\
0 & m_{23} & m_{24} & m_{25} \\
0 & m_{34} & m_{35} \\
0 & m_{45} \\
0
\end{bmatrix}, \] (67)

we can write

\[ 2T^{(1)} = \omega T^{(1)} \omega = P^T g^{(0)} T^{(1)} g^{(0)} P \]

\[ = P^T g^{(1)} P = \sum_{ff'} \beta_{ff'}^{(1)} P_f P_{f'} , \] (68)

where

\[ \beta_{ff'}^{(1)} = \sum_{l'l''} \beta_{ll'}^{(0)} I_{l'l''}^{(1)} \beta_{l'l''}^{(0)} \] (69)

We denote the elements \( \beta_{ff'}^{(1)} \) by the symbols

\[ g^{(1)} = \begin{bmatrix}
\delta \beta_{gg'} & \delta \gamma_{gg'} & \delta \varepsilon_{gg'} \\
\delta \gamma_{gg'} & \delta \beta_{gg'} & \delta \varepsilon_{gg'} \\
\delta \varepsilon_{gg'} & \delta \varepsilon_{gg'} & \mu_{gg'}
\end{bmatrix}. \] (70)

The terms \( \mu_{ll'} \) are functions only of the \( m_{ll'} \), and the remaining terms are either those that arise from the small terms \( I_{gg'}^{(0)} (g \neq g') \) or they are linear functions of the \( q_i \), through the coefficients \( l_{ii'} \), as given by (58). The first type
is denoted by the symbols
\[ \delta \beta_{f''}(I_{y^0}) = \delta \beta_{f''}, \]
and the second by
\[ \delta \beta_{f''}(q_t) = \delta \beta_{f''}, q_t. \]

We then obtain explicitly
\[ \delta \beta_{g''}(q_t) = I_{g''}(q_t) \beta_{g''}, \]
\[ \delta \gamma_{g''}(q_t) = I_{g''}(q_t) \beta_{g''}, \]
\[ \delta \beta_{g''}(q_t) = I_{g''}(q_t) \beta_{g''}, \]
\[ \delta \gamma_{g''}(q_t) = I_{g''}(q_t) \beta_{g''}, \]
\[ \delta \epsilon_{g''}(q_t) = n_{g''}(q_t) \mu_{g''}, \]
\[ \delta \epsilon_{g''}(q_t) = n_{g''}(q_t) \mu_{g''}, \]
\[ \mu_{g''} = m_{g''} \mu_{g''}, \]

Then, \( 2T^{(1)} \) can be written as
\[ 2T^{(1)} = \sum_{g''} \delta \beta_{g''}(0) P_{g''} P' + 2 \sum_{g} \delta \gamma_{g}(0) P_{g} P' \]
\[ + \sum_{t} \left[ \sum_{g''} \delta \beta_{g''}(0) P_{g''} P' + 2 \sum_{g} \delta \gamma_{g}(0) P_{g} P' + \delta \beta'(0) q_t \right] \]
\[ + \sum_{t'} \mu_{g''}(q_t) P_{g''} P' \]
(74)

This expression constitutes the kinetic energy contribution to the rotation-internal rotation-vibration Hamiltonian discussed below.

VI. POTENTIAL ENERGY

We assume that the potential energy for our model is a function \( V(q_t, \varphi) \) that has a minimum at \( \varphi = q_t = 0 \) about which it can be expanded in the most general way.
\[ V(q_t, \varphi) = V(q_t) + \sum_{g} V(q_t)^3 \cos 3q_t + \sum_{g'} V(q_t)^3 \sin 3q_t, \]
(75)
where the last summation expresses the possibility that the torsional equilibrium position, as a function of the \( q_t \), may not occur at \( \varphi = 0 \). We then expand
\[ V(q_t, \varphi) = V_0 + \sum_{t} k_t q_t + \frac{1}{2} \sum_{t'} k_{t} q_{t'} q_{t'} + \cdots \]
\[ + \left[ \sum_{g} V_0^3 + \sum_{g} k^3 q_t + \frac{1}{2} \sum_{t'} k_{t} q_{t'} q_{t'} + \cdots \right] \times (\cos 3q_t) \]
\[ + \left[ \sum_{g'} V_0^3 + \sum_{g'} k_{g'} q_t + \frac{1}{2} \sum_{t'} k_{g'} q_{t'} q_{t'} + \cdots \right] \times (\sin 3q_t). \]
(76)
The requirement that the partial derivative of $V$ with respect to $\phi$ vanish when it is evaluated at (torsional plus vibrational) equilibrium requires that, for all $s'$,

$$V_o^{3s'} = 0.$$  

The similar condition that the partial with respect to $q_t$ vanish at equilibrium requires that $k_t = 0$ and $k_t^{3s'} = 0$ for all $s$. Thus, omitting an additive constant, we have to second order in the $q_t$:

$$V(q_t, \phi) = \frac{1}{2} \sum_{s'} q_{t's'} q_{t's'} + \frac{1}{2} \sum_{s} V_o^{3s'(1 - \cos 3s\phi)}$$

$$+ \left( \sum_{s'} \frac{1}{2} \sum_{t'=t''} k_{t'3s'}^{3s'} q_{t's'} \right) (1 - \cos 3s\phi)$$

$$+ \left( \sum_{s'} \sum_{t'} k_{t't'}^{3s'} q_t + \frac{1}{2} \sum_{t'=t''} k_{t'3s'}^{3s'} q_{t's'} \right) \sin 3s\phi).$$  

We have redefined the $k_{t3s'}$ and $V_o^{3s'}$ in order to achieve a more convenient form. Then, to zero order in the vibrational coordinates, the internal rotational potential is just the usual

$$V_{rot} = \frac{1}{2} \sum_s V_o^{3s'(1 - \cos 3s\phi)}.$$  

In the limit that $\phi$ is restricted to small vibrations $\delta\phi$ about an equilibrium position, the potential energy becomes to second order in the $q_t$ and $\delta\phi$:

$$V(q_t, \delta\phi) = \frac{1}{2} \sum_{s} q_{t's'} q_{t's'} + \frac{1}{2} \sum_{s} 9g_s^2 V_o^{3s'} \delta\phi^2$$

$$+ \sum_t \left( \sum_{s'} 3s'k_{t3s'} \right) q_t \delta\phi.$$  

In this limit, we can make the correspondences:

$$k_{\phi\phi} = \sum_s 9g_s^2 V_o^{3s'} = \frac{9}{2} V_o^{(3)}$$

$$k_{\phi t} = \sum_s 3s'k_{t3s'}.$$  

If the values of $V_o = 374.8$ cm$^{-1}$ and $I' = 5.331 \times 10^{-40}$ g cm$^2$ are used in the relation $\omega^2 = k_{\phi\phi}/I'$ (with the definition of $k_{\phi\phi}$), the value of $\omega^2$ will be $133$ cm$^{-1}$. If it is compared with the value of about $270^{-1}$ quoted for methyl alcohol by Herzberg (7), we get some indication of the extent to which the top is not a torsional harmonic oscillator.

**Addition of a Small Six-Fold Periodic Term**

Within the framework of the rigid rotor theory, it is of interest to investigate the effect of the addition of a small six-fold periodic term to the Hamiltonian $H_{IR}$ of (15). This involves the substitution of a term $\frac{1}{2}(V^3 + V^4)$ for $\frac{1}{2}V_o$ in the diagonal elements of $H_{IR}$, and the addition of a term $-\frac{1}{2}V_o$ off-diagonal by two in the factored secular determinant. The $m$th row of the subdeterminant now becomes

$$\cdots 0 0 a_6 a_3 R - |m| a_5 a_6 0 0 \cdots,$$
in which \(|m|\) is defined as before, and
\[
R = \left(2/h^2 \beta' \right) \left(E - \frac{1}{2} V^3 - \frac{1}{2} V^6 \right),
\]
\[
\alpha_3 = \frac{1}{2} V^3 / h^2 \beta',
\]
\[
\alpha_6 = \frac{1}{2} V^6 / h^2 \beta'.
\]

If we assume that \(\alpha_6 \ll \alpha_3\), then any root \(R\) can be found by the usual method of clearing rows and columns and retaining terms to the first order in \(\alpha_6/\alpha_3\).

The results are expressed in continued-fraction form, with the assumption that
\[
|\alpha_6| \ll |R - |m + 9| |
\]
or, equivalently, that the quantity on the right is of the order of or larger than \(\alpha_3\). Although it must be checked during the calculation, this requirement was always satisfied in the roots calculated for methyl alcohol. The resultant continued fractions take the form
\[
R = |m| + \left[\alpha_3^2/R - |m + 3| - \alpha_3^2/R - |m + 6| - \cdots\right] \\
\times \left[1 + 2\alpha_6/R - |m + 6| - \cdots\right] \\
+ \left[\alpha_3^2/R - |m - 3| - \alpha_3^2/R - |m - 6| - \cdots\right] \\
\times \left[1 + 2\alpha_6/R - |m - 6| - \cdots + 2\alpha_6/R - |m + 3| - \cdots\right].
\]

Thus, the simple continued fractions that appeared in the original theory have been altered by expressions that contain essentially only portions of the original fractions themselves. This addition is trivial in terms of computational work, and so we have obtained an extremely easy method of investigating the addition of a small six-fold potential.

For the determination of order-of-magnitude effects, a small \(V_6\) term was added to a barrier that was approximately that of methyl alcohol, and a few energy levels were calculated. The parameters and results are summarized in Table IV. Note that the choice of \(\alpha_6/\alpha_3\) negative (\(V_6\) opposite in sign to \(V^3\))

<table>
<thead>
<tr>
<th>(K_{mn})</th>
<th>(E_{Kmn}) (cm(^{-1}))</th>
<th>Without (V_6)</th>
<th>With (V_6)</th>
<th>(\Delta E_{Kmn}) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>010</td>
<td>128.84</td>
<td>125.72</td>
<td>-3.12</td>
<td></td>
</tr>
<tr>
<td>012</td>
<td>483.71</td>
<td>479.86</td>
<td>-3.85</td>
<td></td>
</tr>
<tr>
<td>112</td>
<td>583.56</td>
<td>583.65</td>
<td>-1.91</td>
<td></td>
</tr>
</tbody>
</table>
which corresponds to a narrowing of the potential “hill” and a broadening of
the “valley,” gives an over-all lowering of the energy levels. The change in relative
location of the various levels is of the order of one or two wave numbers;
evitably it would be of great importance in any theory that depends critically
on these spacings. Conversely, it might be possible to determine that the relative
magnitude of \( V_6 \) is smaller than the value of 1.5 percent of \( V_3 \) used here.

VII. HAMILTONIAN

**Classical Hamiltonian**

If we collect terms from (63), (74), and (77), we have the following Hamiltonian:

\[
H^{(0)} = H_{RR}^{(0)} + H_{1R}^{(0)} + H_{V}^{(0)}
\]

\[
= [\frac{1}{2} \sum \beta_{\mu \nu} P_{\mu}^2] + [\frac{1}{2} \beta P^2 + \gamma P P' + \frac{1}{2} V_3 (1 - \cos 3\phi)] + \frac{1}{2} \sum_i \mu_i q_i^2 + \frac{1}{2} \sum_{i'j} k_{ij} q_{i}^2],
\]

\[
H^{(1)} = H_{RR}^{(1)} + H_{1R}^{(1)} + H_{V}^{(1)} + H_{int}^{(1)}
\]

\[
= [\frac{1}{2} \sum_{\mu' \mu''} \delta \beta_{\mu' \mu''} P_{\mu}' P_{\mu}'' + \frac{1}{2} \sum_{i} \sum_{\mu' \mu''} \delta \beta_{\mu' \mu''} q_{i}' P_{\mu}' P_{\mu}''] + \frac{1}{2} \sum_{i} \delta \beta \gamma q_{i}' P_{\mu}' P_{\mu}'' + \frac{1}{2} \sum_{i} V_3 (1 - \cos 3\phi) + \frac{1}{2} \sum_{ij} k_{ij} q_{i}^2 q_{j}^2 + \frac{1}{2} \sum_{i} \mu_{i} q_{i}^2 \sin 3\phi]
\]

where, except in \( H_{V}^{(0)} \), we have retained terms only to first order in the \( q_{i} \).

**Vibrational Hamiltonian**

The vibrational Hamiltonian has the form

\[
H_{V} = H_{V}^{(0)} + H_{V}^{(1)}
\]

\[
= \frac{1}{2} \sum_{i} (\mu_{i} q_{i}^2 + k_{ii} q_{i}^2) + \frac{1}{2} \sum_{i'j} \mu_{i'j} q_{i} q_{j} + \frac{1}{2} \sum_{i'j} k_{i'j} q_{i} q_{j}.
\]

A transformation can be applied to diagonalize \( H_{V} \); thus the normal modes and
frequencies are obtained. However, we note the following points. If the coordinates \( q_{i} \) are aptly chosen, the coefficients \( \mu_{i'j}(l' \neq l) \) are small compared with
the diagonal terms. Likewise, if the valence force constants constitute a good
description of the actual force constants, the terms \( k_{i'j}(l' \neq l) \) will be small
compared with the diagonal terms \( k_{ii} \).

If this is the case, the frequencies calculated from just \( H_{V}^{(0)} \) will be very close
to the experimentally observed frequencies. We find, from our earlier work, that
the assumption concerning the \( \mu_{i'j} \) is met by the \( q_{i} \) that we have chosen, and we
now make the above assumption with regard to the $k_{tt'}$. We then use the observed frequencies $v_t$ and the calculated $\mu_t$ to evaluate the desired matrix elements in the perturbation Hamiltonian.

For each coordinate $q_t$ we have

$$H_{tt'}(\text{cm}^{-1}) = \frac{\hbar}{8\pi^2 c} \mu_t (p_t / h)^2 + \frac{1}{2\hbar c} k_{tt'} q_t^2$$

$$= \frac{1}{2} \mu_t* (p_t / h)^2 + \frac{1}{2} k_{tt'}* q_t^2,$$

(82)

where $H_{tt'}$, $\mu_t*$ and $k_{tt'}*$ are in reciprocal centimeters, and $q_t$ and $(p_t / h)$ are dimensionless. The quantum mechanical solution of this harmonic oscillator problem is

$$E_{st} = v_t (v_t + 1)$$

$$= (v_t = 0, 1, 2, \ldots),$$

(83)

where the frequency $v_t$ is given by

$$v_t = (k_{tt'}* \mu_t*).$$

(84)

The matrix elements of interest in the perturbation Hamiltonian are

$$(0 \mid q_t \mid v_t \pm 1) = (\mu_t*/2v_t) (v_t')^{1/2} = q_{ot}(v_t')^{1/2},$$

$$(0 \mid p_t \mid v_t \pm 1) = \mp \frac{1}{2} \hbar q_{ot}^{-1}(v_t')^{1/2},$$

(85)

where $v_t' = v_t$ or $v_t \pm 1$, whichever is the larger.

In particular, the matrix elements of interest in investigating the ground vibrational state are

$$0 \mid q_t \mid 1) = q_0; \quad (0 \mid p_t \mid 1) = -\frac{1}{2} \hbar q_{ot}^{-1}.$$  

(86)

We have, in essence, chosen $H_v^{(0)}$ as our vibrational representation and can now evaluate $H_v^{(1)}$ in this representation. However, we shall find that the terms of $H_v^{(1)}$ cannot affect the $J = 0 \rightarrow 1$ spectrum with which we shall be concerned.

**Rigid Rotor Hamiltonian**

We choose the usual $JKM$ representation for the zero-order rigid rotor Hamiltonian $H_{RR}^{(0)}$, with the following matrix elements for the components $P_\phi$:

$$(JK \mid P_\phi \mid JK \pm 1) = \mp i (JK \mid P_\phi \mid JK \pm 1) = \frac{1}{2} \hbar g(J, K),$$

$$(JK \mid P_z \mid JK) = \hbar K,$$

(87)

wherein we adopt the notation

$$g(J, K) = |J(J + 1) - K(K \pm 1)|^{1/2},$$

$$f(J, K) = g(J, K)g(J, K \pm 1).$$

(88)
Then the Hamiltonian \( H_{RR}^{(0)} \) has matrix elements

\[
\langle JK | H_{RR}^{(0)} | JK \rangle = \frac{1}{2} \hbar^2 \beta_+ [J(J + 1) - K^2] + \frac{1}{2} \hbar^2 \beta_2 K^2,
\]

\[
\langle JK | H_{RR}^{(0)} | JK \pm 2 \rangle = \frac{1}{4} \hbar^2 \beta f(J, K),
\]

where

\[
\beta_\pm = \frac{1}{2} (\beta_{zz} \pm \beta_{yy}).
\]

**Internal Rotor Hamiltonian**

The zero-order internal rotor Hamiltonian has the form

\[
H_{IR}^{(0)} = \frac{1}{2} \hbar^2 \beta' P'^2 + \gamma P P' + \frac{1}{2} \hbar^2 V_0^2 (1 - \cos 3\phi).
\]

We choose the representation in which \( P' \) has diagonal elements \( \hbar m \), with \( m \) an integer. Then, \( H_{IR}^{(0)} \) has matrix elements

\[
\langle Km | H_{IR}^{(0)} | Km \rangle = \frac{1}{2} \hbar^2 \beta' m^2 + \frac{1}{2} \hbar^2 V_0^2 K^2 + \frac{1}{2} \hbar^2 V_0^2 + \gamma V_0^3,
\]

\[
\langle Km | H_{IR}^{(0)} | Km \pm 3 \rangle = -\frac{1}{4} \hbar^2 V_0^2,
\]

wherein we have used the matrix elements

\[
\langle m | \cos 3\phi | m \pm 3 \rangle = \mp i \langle m | \sin 3\phi | m \pm 3 \rangle = \frac{1}{2}.
\]

This, of course, is not strictly an internal rotor Hamiltonian, because of the presence of \( P' \). However, we use the label for convenience, since the interaction term \( P P' \) is not small and a true separation of the rigid rotor and internal rotor Hamiltonians is impossible.

**Total Hamiltonian**

We are now in a position to write the matrix elements of the total Hamiltonian of Eq. (80). Since we are interested in the ground vibrational state, we list only off-diagonal \((v | v')\) elements \((0 | 1)\) and \((0 | 2)\), and note that \( H^{(3)} \) can contribute no diagonal elements to the ground state through terms of the type \( p_{q'q'} \). For convenience in tabulation, we use the notation

\[
\langle JKmv | H | JK'm'v' \rangle = \langle K'm'v' \rangle.
\]

Thus we have elements diagonal in \( m \) and \( v \):

\[
| Km(m) = \hbar^2 [\frac{1}{2} \beta_+ [J(J + 1) - K^2] + \beta_{zz} K^2 + \frac{1}{2} \beta' m^2 + \gamma V_0^2 K]
+ \frac{1}{2} \hbar \epsilon_c \sum_i \nu_i \nu_i + \frac{1}{2} \hbar \epsilon_c \sum_i \nu_i \nu_i + \frac{1}{2} \hbar \epsilon_c \sum_i \nu_i + \nu_i,
| K \pm 1mv = \frac{1}{2} \hbar^2 [i \beta_+ (\delta_{zz} \nu_0 \pm i \delta_{yy} \nu_0) (K \pm \frac{1}{2}) + (\bar{\delta}_{zz} \nu_0 \pm i \delta_{yy} \nu_0) \nu_j |g(J, K),
| K \pm 2mv = -\frac{1}{4} \hbar^2 [\beta_+ \mp i \delta_{xx} \nu_0)] |f(J, K).
The elements off-diagonal in $v$ are:

$$|Km1| = \hbar^2 \sum_{t} \left[ \frac{1}{2} \delta_{\varepsilon t} (J(J+1) - K^2) + \delta_{\varepsilon t}^\prime K^2 ight] + \frac{1}{2} \delta_{\varepsilon t}^\prime m^2 + \delta_{\varepsilon t}^\prime Km |q_{tt'},$$

$$|K \pm 1m1| = \frac{1}{2} \hbar^2 \sum_{t} \left[ (\delta_{\varepsilon t}^\prime \pm i \delta_{\varepsilon t}^\prime) (K \pm \frac{1}{2}) + (\delta_{\varepsilon t}^\prime \pm i \delta_{\varepsilon t}^\prime) m |g(J, K)q_{tt'} ,$$

$$|Km2| = \frac{1}{2} \sum_{t'} |k_{tt'} q_{tt'} - \frac{1}{2} \mu_{tt'} (q_{tt'} q_{tt'})^{-1} | + i \hbar^2 (\delta_{\varepsilon t}^\prime K + \delta_{\varepsilon t}^\prime) m (q_{tt'} q_{tt'})^{-1},$$

$$|K \pm 1m2| = \frac{1}{2} \hbar^2 \sum_{t'} (\delta_{\varepsilon t}^\prime \pm i \delta_{\varepsilon t}^\prime) g(J, K) (q_{tt'} q_{tt'})^{-1}.$$  

The elements off-diagonal in $m$ are:

$$|Km \pm 3sv| = -\frac{1}{4} V_0^{3s}.$$  

Finally, the elements off-diagonal in both $v$ and $m$ are

$$|Km \pm 3s'| = \mp \frac{1}{2} \hbar \sum_{t} k_{tt'} q_{tt'}.$$  

The summations over $s$ and $s'$ are from one to infinity, the summations over $t$ are from one to five, and the summations over $tt'$ are for $t \neq t'.$

**VIII. DIAGONALIZATION OF SECULAR DETERMINANT**

We outline here the diagonalization of the secular determinant. As in the rigid rotor case, there exist only $(m \mid m \pm 3s)$ elements off-diagonal in $m$, hence the secular determinant of the Hamiltonian (94) factors immediately into three subdeterminants, two of which are degenerate. Each subdeterminant can be divided into torsional $m$ blocks labeled with the values $\cdots, m_0 - 6, m_0 - 3, m_0, m_0 + 3, m_0 + 6, \cdots$ where the $m_0$ block includes the desired root. The diagonal $m$ blocks contain elements that are described below; the $m$ blocks one off-diagonal (labeled $m, m \pm 3$) contain elements $H'$ which are not restricted to being small; and the blocks two and more off-diagonal contain small terms independent of $J$ and $K.$

Each $m$ block is divided into vibrational $v$ blocks, in which we need only the ground and first two excited states of $v.$ (The second excited state is necessary for terms of the type $q_{tt'}$, which are each off-diagonal by one in $v.$) Each $mv$ block is simultaneously a particular rotational $J$ block, since we are able to consider one value of $J$ at a time in view of the absence of elements off-diagonal in $J$, and each $Jmv$ block is divided into $2J + 1$ blocks labeled with $K(-J \leq K \leq J).$

It is of value now to notice some general properties of the diagonalization procedure in order to save unnecessary work. In the process of clearing rows and columns (for example, in order to obtain a $J = 1, K = 0, v = 0$ root to second order) we find that the only matrix elements that appear in the expression for
the desired root are: All diagonal elements, those which appear in the row and column of the root in question, and those which appear in all other rows and columns whose diagonal element is a \( K = 0 \) element, for all values of \( v \) and \( m \). Thus we can regard as zeros all elements that appear in other rows and columns when we are solving for a \( K = 0 \) root, and need only consider

\[
(K | K') = (0 | 0, \pm 1)
\]
elements (and their complex conjugates) of the Hamiltonian. This property, incidentally, removes the usual procedure of symmetrizing the Hamiltonian in order to eliminate the \( K \) degeneracy, since the degenerate diagonal values and the elements connecting them do not appear in the expression for the \( K = 0 \) root. (For the \( K = \pm 1 \) case, a symmetrizing transformation must be applied. We restrict ourselves to finding a \( K = 0 \) level, although the method is perfectly general and can be extended to the calculation of any desired element.)

A second property that is of value, is that any \((JKmv | JK'm'v')\) element independent of \( J \) vanishes in the expression for \( \Delta \nu^m \), which is the difference between the \( J = 0 \) and \( J = 1 \) diagonalized roots. Thus, we can disregard any term of the Hamiltonian that contributes these elements unless another term contributes a \( J \) dependence to that same matrix element, in which case both must be retained. Among others, the terms two or more off-diagonal in \( m \) are of this type, and so they will be discarded.

We abbreviate the diagonal elements of the original Hamiltonian, suppressing the \( J \) designation, as

\[
(JKmv | H | JKmv) = H_K(v)^n,
\]
and use the further abbreviation

\[
H_K(0)^n = H_K^n
\]
for the ground vibrational state. For the small off-diagonal elements needed for the \( K = 0 \) root, we abbreviate

\[
(J0m0 | H | JKmv) = h_K(v)^n
\]
and

\[
(J0mv | H | J0m \pm 3v) = H'.
\]

Since we seek a particular \( K = 0 \) root, we subtract the eigenvalue \( E_0^{m_0} \) from the diagonal elements, and, working from both ends toward the middle, we eliminate rows and columns from the secular determinant and retain terms to second order, until we arrive at the root in question. This process, although it is tedious, is perfectly straightforward and results in the continued fraction

\[
E_0^{m_0} = H_0^{m_0} + \Delta H_0^{m_0} - H^2/H^{m_0+2} + \Delta H_0^{m_0+2} - E_0^{m_0} - \ldots
- H^2/H^{m_0+3} + \Delta H_0^{m_0+3} - E_0^{m_0} - \ldots.
\]

(98)
We shall give the $H_0^n$ explicitly later, noting, at this point, only that they are second-order quantities.

We adopt the following procedure for modifying the diagonal elements $H_K(v)^m$. Define the continued fraction

$$X_m = H_0^m - H/2/H_0^{m+2} - \cdots$$

Then calculate modified diagonal elements by use of the recurrence formula

$$H_K(v)^m = H_K(v)^m - \lambda^m - H/2/H_K(v)^{m+2}$$

where the parenthetical expression means that plus or minus is to be used when $m$ is greater than or less than $m_0$. Thus, the modified elements $H_0^m = H_0(0)^m$ are those that appear in the calculation of $\lambda^m$, and the remaining modified elements are calculated with $\lambda^m$.

Comparison of Eqs. (98) and (99) shows that $\lambda^m$ is very nearly equal to $E_0^m$. Thus, we can rewrite Eq. (98) as

$$E_0^m = H_0^m + \Delta H_0^m$$

and, after we remove the second-order quantities from their positions in the continued fraction, we obtain

$$E_0^m = \lambda^m + \Delta H_0^m$$

in which we introduce the abbreviations

$$r_K(v)^m = H/2/H_K(0)^m$$

and, for convenience,

$$r_K(0)^m = r_K^m.$$
INTERACTIONS IN MOLECULES

These quantities are defined for every value of \( m' \) greater than (or less than) \( m \), where \( m \) is greater than (or less than) \( m_0 \), and where

\[
R_k(v)^{mn} = 1
\]  
(104b)

for all \( m \) including \( m_0 \).

It is then possible to rewrite Eq. (102) in the form

\[
(E_{\phi}^{m_0} - \lambda^{m_0}) \sum_m R_\phi(0)^{m_0 m} = \sum_m R_\phi(0)^{m_0 m} \Delta H_0^m,
\]  
(105)

where the summation is over all values of \( m \) from \(-\infty\) to \(+\infty\) in steps of three, including \( m_0 \). It is obvious that the formal summations in all of this work will be greatly reduced when the convergence of the various quantities is considered. For example, for methyl alcohol, we needed the \( R_k(v)^{mn} \) only to \( m' = m \pm 9 \), at the most.

The second-order quantities \( \Delta H_0^m \), as they appeared after the original diagonalization or in (105), are rather cumbersome functions of the original elements \( h_k(v)^m \). However, when the summation on the right-hand side of Eq. (105) is carried out, the terms regroup into the expressions

\[
\sum_m R_\phi(0)^{m_0 m} \Delta H_0^m = - \sum_m R_\phi(0)^{m_0 m} \sum_{m',k} [h_k(v)^m]^2 / R_k(v)^m, \]
(106)

where the \( R_k(v)^m \) are given by (100), and the modified elements \( h_k(v)^m \) are given by the recurrence formulas,

\[
h_k(v)^m = \sum_m R_k(v)^{mn} h_k(v)^{m'},
\]  
(107)

where

\[
(m' = m, m \pm 3, m \pm 6, \ldots)(m \geq m_0)
\]

\[
= \ldots, m_0 - 6, m_0 - 3, m_0, m_0 + 3, m_0 + 6, \ldots(m = m_0)
\]

The small off-diagonal elements \( h_k(v)^m \) are of the form

\[
h_k(v)^m = h_k(v) + m h'_k(v) + m^2 h''_k(v),
\]  
(108)

where any one or two of the terms can be zero for a particular element. Therefore, we write the modified elements in the form

\[
h_k(v)^m = h_k(v)S_k(v)^m + h'_k(v)T_k(v)^m + h''_k(v)U_k(v)^m
\]  
(109)

in which we have written

\[
S_k(v)^m = \sum_{m'} R_k(v)^{mm'},
\]

\[
T_k(v)^m = \sum_{m'} m'R_k(v)^{mm'},
\]  
(110)

\[
U_k(v)^m = \sum_{m'} (m')^2 R_k(v)^{mm'},
\]

with the same limits on the summation as those given for Eq. (107). It is con-
venient to define the ratio,

\[ N^m = \frac{R_0(0)^m}{S_0(0)^m}, \]

and rewrite Eq. (105) in the form

\[ E_0^m = \lambda^m - \sum_m N^m \sum_{K, v} \frac{[h_K(v)S_K(v)^m + h_K'(v)T_K(v)^m + h_K''(v)U_K(v)^m]^2}{R_K(v)^m} \]  

We have now obtained the eigenvalue for \( K = 0, v = 0, m = m_0 \) for any value of \( J \). We can show that, under certain conditions, the only quantities on the right-hand side of Eq. (112) that are dependent upon \( J \) are the \( h_K(v) \) and \( \lambda \).

We need only assume that the same \( Kmv \) diagonal elements, for two different values of \( J \), differ by a small term, say \( \delta\lambda_{jj'} \). That is, that

\[ (J'Kmv | H | J'Kmv) = (JKmv | H | JKmv) + \delta\lambda_{jj'} \]  

For convenience, we consider the two levels \( J = 0 \) and \( J = 1 \), and extend our earlier symbols by adding this quantum number as a subscript. Then, if our earlier work was for \( J = 0 \), we have, for \( J = 1 \),

\[ E_{J_1}^m = E_0^m = (H_0^m + \delta\lambda) + \Delta H_0^m \]

\[ - \frac{H^2}{H_0} \frac{H_{0^m}}{m+3} + \delta\lambda + \Delta H_{10}^m - E_0^m - \cdots \]  

Following the same procedure, we regroup the \( m \)th term of this equation into the form

\[ H_{0^m} + (\Delta H_{10}^m + \lambda^m + \delta\lambda - E_0^m) - \lambda^m - \cdots \]

It is obvious that we shall obtain an equation that corresponds to Eq. (105), of the form

\[ [E_0^m - (\lambda^m + \delta\lambda)] \sum_m R_0(0)^m = \sum_m \frac{R_0(0)^m \Delta H_{10}^m}{m}, \]

where \( \lambda^m \) and the \( R_0(0)^m \) are calculated from \( J = 0 \) matrix elements; thus they are identical to those in (105). The same procedure can be easily followed through with the quantities \( H_{10}^m \), and finally we write

\[ E_{J_0}^m = \lambda^m + \delta\lambda_{0J} - \sum_m N^m \sum_{K, v} \frac{[h_{J_0}(v)]^2}{R_K(v)^m} \]  

where we originally solved for the \( J = 0 \) root, and where we used (109) to define

\[ h_{J_0}(v)^m = h_{J_0}(v)S(v)^m + h_{J_0}'(v)T(v)^m + h_{J_0''}(v)U(v)^m. \]

**IX. THE J = 0 → 1, \( \Delta K = 0 \) TRANSITION**

From the zero-order rigid rotor Hamiltonian (89), we see that the transition \( J = 0 \to 1, \Delta K = 0 \) has a single frequency.
\[ v_0 \text{ (cycles/sec)} = \frac{h}{2\pi} \beta_+ , \]  

(118)

where \( \beta_+ \) is in \((g \text{ cm}^2)^{-1}\) units. Owing to the perturbations from \( H^{(1)} \) of (80b), this frequency is different for different torsional levels in the ground vibrational state. We denote these frequencies by

\[ v^m = v_0 + \Delta v^m. \]  

(119)

The method of obtaining these frequency differences \( \Delta v^m \), and hence the \( J = 0 \rightarrow 1 \) spectrum, is as follows. By the methods of Section VIII, we obtain the eigenvalues \( E_{\nu m}^{(v)} \) of Eq. (116). The \( \delta \lambda_{ij} \) of (116) is just our \( v_0 \) given above and the difference of the two eigenvalues gives

\[ v^m = v_0 + \sum_n N^{m} \sum_{K,v_0} \frac{[h_{1K}(v)^m]^2 - [h_{0K}(v)^m]^2}{H_{K}(v)^m}, \]  

(120)

The various terms in this equation have been defined in terms of the original matrix elements. Among these, we can obtain explicitly the off-diagonal elements \( h_{jk}(v)^m \) from the Hamiltonian (94). The elements \( h_{22}(v)^m \) and the small elements \( (m \mid m + 3s) \) are independent of \( J \); thus they will vanish in (120). The remaining elements of interest are:

\[ h_{\pm 1}(0)^m = \left( \frac{h^2}{2} \right) \{ (\delta \gamma_{\nu}^{(0)} \pm i \delta \gamma_{\nu}^{(0)}) \sum\} \frac{1}{2} (\delta \beta_{\nu}^{(0)} \pm i \delta \beta_{\nu}^{(0)}) \}, \]

\[ h_{00}(0)^m = \left( \frac{h^2}{2} \right) \{ (\delta \gamma_{\nu}^{(0)} \pm i \delta \gamma_{\nu}^{(0)}) \sum\} \frac{1}{2} (\delta \beta_{\nu}^{(0)} \pm i \delta \beta_{\nu}^{(0)}) \}, \]

\[ h_{\pm 1}(1)^m = \left( \frac{h^2}{2} \right) \{ (\delta \gamma_{\nu}^{(0)} \pm i \delta \gamma_{\nu}^{(0)}) \sum\} \frac{1}{2} (\delta \beta_{\nu}^{(0)} \pm i \delta \beta_{\nu}^{(0)}) \}, \]

\[ h_{\pm 1}(2)^m = \left( \frac{h^2}{2} \right) \{ (\delta \gamma_{\nu}^{(0)} \pm i \delta \gamma_{\nu}^{(0)}) \sum\} \frac{1}{2} (\delta \beta_{\nu}^{(0)} \pm i \delta \beta_{\nu}^{(0)}) \}, \]  

(121)

Insertion of these terms in (120) gives

\[ \Delta v^m \text{ (cycles/sec)} = - \frac{1}{2} \left( \frac{h^2}{2\pi} \right)^3 \sum t (q_{0t})^2 \sum_s N^{m} \sum_{X^m} \left\{ \left[ \delta \beta_{\nu} \cdot S_{0}(t)^m \right]^2 + \left[ \delta \beta_{\nu} \cdot S_{0}(t)^m \cdot U_{0}(t)^m \right]^2 \right\} \]

\[ + \frac{1}{2} \sum_{K=1}^{2} \frac{1}{H_{K}(t)^m} \left\{ \frac{1}{2} \left[ (\delta \beta_{\nu}^{(0)} \pm i \delta \beta_{\nu}^{(0)}) \right]^2 + (\delta \beta_{\nu}^{(0)} \pm i \delta \beta_{\nu}^{(0)}) \right\} \]

\[ + \frac{1}{2} \sum_{K=1}^{2} \sum_{t=1}^{2} \frac{1}{H_{K}(t)^m} \left\{ \delta \beta_{\nu} \cdot S_{0}(t)^m \right\} \]

\[ + \frac{1}{2} \sum_{K=1}^{2} \sum_{t=1}^{2} \frac{1}{H_{K}(t)^m} \left\{ \delta \beta_{\nu} \cdot S_{0}(t)^m \right\} \]

\[ + \frac{1}{2} \sum_{K=1}^{2} \sum_{t=1}^{2} \frac{1}{H_{K}(t)^m} \left\{ \delta \beta_{\nu} \cdot S_{0}(t)^m \right\} \]

\[ + \frac{1}{2} \sum_{K=1}^{2} \sum_{t=1}^{2} \frac{1}{H_{K}(t)^m} \left\{ \delta \beta_{\nu} \cdot S_{0}(t)^m \right\} \]

(122)

where we use \( t = 0 \) to indicate the ground state \( v = 0 \); \( t = 1, 2, 3, 4, 5 \) to indi-
cate the set \( v \), that comprises the first excited vibrational state \( v = 1 \); and \( t' \) to indicate the state \( v = 2 \). Note that, from (121), the only nonzero coefficients for \( t = 0 \) are the terms with \( \delta \beta_{\alpha^2}^{(0)} \) and \( \delta \gamma_{\theta \phi}^{(0)} \).

It will be recognized that the terms contributing to \( \Delta \nu^{m_0} \) have originated from the terms in the kinetic energy,

\[
\delta \beta_{\alpha^2}^{(0)} q_i (P_x^2 + P_y^2), \quad \delta \beta_{\alpha^2}^{(0)} q_i (P_x^2 + P_y^2) P',
\]

\[
\delta \beta_{\alpha^2}^{(0)} q_i P_x P', \quad \delta \gamma_{\theta \phi}^{(0)} q_i P' P', \quad \delta \gamma_{\theta \phi}^{(0)} q_i P' P
\]

in the order of (122).

Equation (122) will be applied to the case of methyl alcohol in Appendix 2.

X. METHYL ALCOHOL: RESULTS AND GENERAL CONCLUSIONS

The numerical calculations for the \( J = 0 \rightarrow 1 \) spectrum are outlined in Appendix 2, and the contributions to the splittings \( \Delta \nu^{m_0} \) are listed in Table VI. Upon examination of these results, we note first the appearance of a few major terms. The contributions from \( (\delta \beta_{\alpha^2}^{(0)}, \delta \gamma_{\theta \phi}^{(0)}) \) for \( t = 1 \) and 2 make up the primary contribution to \( \Delta \nu^{m_0} \) in each case. Indeed, we find that other terms of magnitude up to 30 Mc/sec cancel within a few megacycles for each \( m_0 \). Therefore, our first conclusion with regard to our model is that the \( J = 0 \rightarrow 1 \) spectrum arises primarily from the kinetic energy terms

\[
(\delta \beta_{\alpha^2}^{(0)} P_x + \delta \gamma_{\theta \phi}^{(0)} P') q_i q_t
\]

for \( q_t \) and \( q_x \), which are the coordinates of the inplane rocking motions of the OH bar and the CH\(_3\) symmetric top, respectively.

The second point, which arises from the inspection of the breakdown of each \( \Delta \nu^{m_0} \), is the relative constancy of the \( I_{\alpha^2}^{(0)} \) contributions. Except for the ground state \( m_0 = 0 \), the term varies less than half a megacycle; hence it does not contribute to the spectrum. For the ground state (\( m_0 = 0 \) and 1), the difference is about 2.22 Mc/sec but it is in the wrong direction. That is, it tends to move

<table>
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<tr>
<th>( n )</th>
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<th>( m_0 )</th>
<th>( \Delta \nu^{m_0} )</th>
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</tr>
<tr>
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<td>4</td>
<td>-198.69</td>
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INTERACTIONS IN MOLECULES

TABLE VI

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<th>$m_0 = 1$</th>
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<tr>
<td></td>
<td>$-0.121$</td>
</tr>
</tbody>
</table>

$\Delta \nu^{m_0}$ contributions to $\Delta \nu$

In Table V we list the calculated results of the $\Delta \nu^{m_0}$ splittings for the purpose of comparing them with the experimental spectrum that has been modified by choosing the $m_0 = 1$ line as a zero reference point. We see immediately that, although a qualitative picture has been obtained, the quantitative fit is not as pleasing. The ground-state splitting is very poor. Inspection of the $m_0 = +3$ computations leading to the tabulated values show it to be strongly coupled to the $m_0 = -3$ line.

The fairly good match at $m_0 = 4$, however, is more meaningful. The computations show that it is not coupled to other levels, to any great extent. Specifically, the summation over $m$ of (122) can be approximated with an error of less than two percent by its leading term $m_0$. This, combined with the fact that $\Delta \nu^4$ consists primarily of only two terms (123), indicates that a comparatively simple expression suffices for $\Delta \nu^4$. Nevertheless, this does not enable us to inves-
tigate the accuracy of our chosen parameters, since the ground state (only frequency differences are significant) is a complicated function of several levels. The most that can be obtained from the simplicity of $\Delta \nu^4$ is an indication of the relative sensitivity of its value to changes in various parameters.

Altogether, the interactions among various states $m_0$ (for a given $r$) are strong; in general, no simple expression suffices for the spectrum in this formulation.

**Possible Sources of Discrepancies**

There are several possible explanations of the rather poor quantitative fit between our calculated and observed spectrum. First, the parameters used may be sufficiently in error to explain the differences. The interatomic distances and bond angles are probably not critical enough to explain terms like $m_0 = -2$, but the barrier height $V^3$ enters rather strongly into the interaction terms. Thus, changes of a few wave numbers in the terms entering into the denominators (actually, the $H(x,t)$) of the perturbation terms are sometimes significant because of the nearness of two levels.

The second possible explanation may lie in the treatment of the vibrational Hamilton. The use of observed infrared frequencies for normal frequencies is admittedly an approximation, but the possibility of a large discrepancy lies in the assignment of the frequencies themselves. For instance, Davies (9) notes disagreement among authors, the assignment of the frequency $1340 \text{ cm}^{-1}$ as the planar OH vibration being questioned by several. A possible change to $1110 \text{ cm}^{-1}$ would change the numerical results to a rather large extent, since we have noted that the second largest contributions to the spectrum arise from it.

The final point to be mentioned is our choice of model, that is, two rigid groups vibrating relative to each other. While the qualitative success of the theory is to some extent a justification of the model, which is obviously an improvement over the rigid internal rotor, significant contributions from internal vibrational motions of the methyl group are still possible. From the results of this work, we might expect the symmetrical distortions of the top to contribute most strongly, in analogy to the major contributions from symmetrical in-plane bendings of the two rigid groups. It is obvious that a small addition to each $\Delta \nu^6$ would change the relative spacings of the spectrum, but the changes that would be necessary to fit the experimentally observed spectrum are not similar in form (that is, in dependence on $m_0$) to the major terms already obtained.

**Extension and Improvements of the Theory**

The questions already raised make it inadvisable to attempt an extensive variation of the parameters in order to get a close fit to the observed spectrum. The remaining seven internal vibration coordinates and changes in the vibrational

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3 For note added in proof, see p. 379.
assignments of the coordinates could quite conceivably contribute as much or more to the spectrum as changes in geometric parameters and barrier height.

If we utilize the basic ideas developed in the separation of the internal-rotation dependent portion of the kinetic energy of our model, we should be able to extend the development to a model that retains all of the possible vibrations. With this separation and the separation of the potential energy given in Section VI, we would have a standard normal-coordinate analysis problem. With additional experimental data, a complete analysis of the vibrational spectrum of methyl alcohol might be practical.

On such a basis, it would be more in order to carry out a perturbation calculation of the $J = 0 \rightarrow 1$ spectrum and, if necessary, a variation of the barrier height or of other parameters to fit the observed spectrum. The perturbation calculations for obtaining the $\Delta \nu^{m_0}$ would be in no wise more complicated than those we have performed, in spite of the fact that the number of terms contributing to each $\Delta \nu^{m_0}$ would be greatly multiplied. Thus, the main opportunities for further work lie in the extension of the treatment of the classical kinetic energy and a complete normal-coordinate analysis of the vibrational spectrum.1

APPENDIX 1. INTERNAL COORDINATES FOR METHYL ALCOHOL

We derive here the inverse of (56) following the method of Wilson's $s$-vectors (8). Our auxiliary coordinates for methyl alcohol give us a planar model of the form shown in Fig. 1, where the vectors $R_i$ are from the center of mass of the molecule which is in the plane of the figure. With the equilibrium axis $z_0$ parallel to $R_{32} = R_3 - R_2$, and with $y_0$ in the plane of the figure, we have

\[
\begin{align*}
Y_{02} - Y_{01} &= r_0 \sin \theta_0', \\
Z_{02} - Z_{01} &= r_0 \cos \theta_0', \\
Y_{01} - Y_{04} &= s \sin (\theta_0' - \theta_0), \\
Z_{01} - Z_{04} &= s \cos (\theta_0' - \theta_0), \\
Y_{03} - Y_{02} &= 0, \\
X_{01} &= X_{02} = X_{03} = X_{04} = 0
\end{align*}
\]

(124)

where $s$ and $t$ are constants because of the rigidity of each group.

![Fig. 1. Auxiliary coordinates for methyl alcohol.](image)
Define unit vectors $\mathbf{e}_{ij}$ along the bond directions, which then have the equilibrium components

$$
\begin{bmatrix}
0 \\
\sin \theta_0' \\
\cos \theta_0'
\end{bmatrix}
\begin{bmatrix}
0 \\
0 \\
1
\end{bmatrix}
\begin{bmatrix}
0 \\
\sin(\theta_0' - \theta_0) \\
\cos(\theta_0' - \theta_0)
\end{bmatrix}
$$

(125)

Since the framework group is linear, there must be four internal coordinates to specify. We choose them as follows:

- $q_1 = \delta \theta$ is a small increase in the angle $\theta$ at $R_1$,
- $q_2 = \delta \theta'$ is a small increase in the angle $\theta'$ at $R_2$,
- $q_3 = \delta \theta''$ is a small angle formed by the bond $R_{23}$ that bends out (126)
  of the plane formed by $R_{12}$ and $R_{14}$,
- $q_4 = \delta r/r_0$ is a small relative increase in the bond $R_{12}$.

With the use of (125), we relate the $q_i$ to the Cartesian coordinates $\delta G_i$. First, we treat $q_4$. Consider

$$
\delta R_{12} = \delta (r_{12}) = r_0 \delta e_{12} + \epsilon_{012} \delta r,
$$

$$
\delta e_{12} = \delta (R_{12}/r) = \frac{1}{r_0} (\delta R_{12} - \epsilon_{012} \cdot \delta R_{12})
$$

so that

$$
\delta r = \epsilon_{012} \cdot \delta R_{12} = \epsilon_{012} \cdot (\delta e_{12} - \delta R_{12})
$$

and

$$
q_4 = \frac{1}{r_0} [(\delta Y_2 - \delta Y_1) \sin \theta_0' - (\delta Z_2 - \delta Z_1) \cos \theta_0'].
$$

(127)

Next, we treat $q_1$, defining $\theta$ by the relation

$$
\cos \theta = \epsilon_{21} \cdot \epsilon_{14}.
$$

Then, differentiating, we have

$$
- \sin \theta \delta \theta = \epsilon_{012} \cdot \delta e_{14} + \delta e_{21} \cdot \epsilon_{004},
$$

and treating the $\delta e$ as before, we obtain

$$
\delta \theta = \frac{1}{s \sin \theta_0} (\epsilon_{012} - \cos \theta_0 \epsilon_{004}) \cdot (\delta R_{14}) + \frac{1}{r \sin \theta_0} (\epsilon_{004} - \cos \theta_0 \epsilon_{002}) \cdot (\delta R_{12})
$$

.$$
and

\[ q_1 = \left[ \cos \theta'_0 \frac{r}{s} + \cos(\theta'_0 - \theta_0) \delta Y_1 + \left[ \sin \theta'_0 \frac{r}{s} - \sin(\theta'_0 - \theta_0) \right] \delta Z_1 \right. \]

\[ + \left. \left[ \cos \theta'_0 \frac{r}{s} \delta Y_2 + \left[ \sin \theta'_0 \frac{r}{s} \right] \delta Z_2 - \left[ \cos(\theta'_0 - \theta_0) \right] \delta Y_4 \right. \]

\[ + \left. \left[ \sin(\theta'_0 - \theta_0) \right] \delta Z_4 \right]. \tag{128} \]

For the coordinate \( q_2 \), we similarly define

\[ \cos \theta' = \varepsilon_{12} \cdot \varepsilon_{23} \]

and obtain

\[ \delta \theta = -\frac{1}{l \sin \theta'} \left( \varepsilon_{01} + \cos \theta'_0 \varepsilon_{023} \right) \cdot (\delta \mathbf{R}_{23}) - \frac{1}{r \sin \theta'} \left( \varepsilon_{023} + \cos \theta'_0 \varepsilon_{012} \right) \cdot (\delta \mathbf{R}_{12}) \]

and

\[ q_2 = \left( \cos \theta'_0 \right) \delta Y_1 - \left( \cos \theta'_0 - \frac{1}{l} \right) \delta Y_2 = \left( \frac{1}{l} \right) \delta Y_3 + \left( \sin \theta'_0 \right) \delta Z_1 \]

\[ - \left( \sin \theta'_0 \right) \delta Z_2. \tag{129} \]

For the coordinate \( q_4 \), a unit vector normal to the plane of \( \mathbf{R}_{12} \) and \( \mathbf{R}_{14} \) is given by

\[ \left( \frac{1}{\sin \theta} \right) \left( \varepsilon_{12} \times \varepsilon_{14} \right) \]

This vector forms an angle \( \left( \frac{\pi}{2} - \theta'' \right) \) with \( \mathbf{R}_{23} \). Therefore we can write

\[ \cos \left( \frac{\pi}{2} - \theta'' \right) = \sin \theta'' = \varepsilon_{23} \cdot \left( \frac{\varepsilon_{21} \times \varepsilon_{14}}{\sin \theta} \right). \]

We use \( \theta'' = 0 \) and differentiate as before and, after considerable simplification, we obtain

\[ q_0 = \left[ \sin \theta'_0 \left( \cos \theta'_0 - \frac{1}{l} \right) \right] \delta X_1 \]

\[ + \left[ \left( \cos \theta'_0 - \frac{1}{l} \right) - \sin \theta'_0 \left( \cos \theta_0 \right) \right] \delta X_2 \]

\[ + \left( \frac{1}{l} \right) \delta X_3 + \left[ \frac{\sin \theta'_0}{\sin \theta_0} \right] \delta X_4. \tag{130} \]

These equations can be obtained directly from Wilson's work, but considerable care must be taken in transcribing notation, and an error in sign appears in his work. A second danger involved in choosing these internal coordinates lies in the definition of \( q_3 \). It is not too obvious that this motion is not a torsional motion of the \( R_2 R_3 \) bond about the direction of the \( R_2 R_3 \) bond. However, if this description is adopted, we find that the coordinate varies as \((\sin \theta')^{-1}\), which goes to infinity in the limit of \( \theta' \) going to zero. It can be verified that in this limit, \( q_2 \) and \( q_3 \), if chosen correctly, become perpendicular vibrations of the type

\[
\frac{1}{r} (\delta Y_2 - \delta Y_1) + \frac{1}{l} (\delta Y_3 - \delta Y_2)
\]

and

\[
\frac{1}{r} (\delta X_2 - \delta X_1) + \frac{1}{l} (\delta X_3 - \delta X_2)
\]

as we would expect for parallel bonds \( R_{12} \) and \( R_{23} \).

**APPENDIX 2. NUMERICAL CALCULATIONS FOR METHYL ALCOHOL**

The molecular parameters of methyl alcohol determined by Ivash and Dennison (1) were chosen to give a comparison of the results of this theory with the observed spectrum of methyl alcohol given in Table II. Several adjustments to their values have been made by other authors (13), but the approximations that were used have raised serious questions about any improvement in the parameters. For example, the equilibrium product of inertia was varied in order to obtain rigid rotor fits to the ground-state splitting of the spectrum in question. We shall find that the product-of-inertia terms, although they are strongly varying functions of the COH bond angle, contribute only about half of the ground-state splitting.

We digress for the purpose of calling attention to the fact that, with the parameters adopted below, we can express the equilibrium product of inertia as a function of the COH bond angle \( \theta' \),

\[
I_{yy}^{(0)} = 0.86886 - 16.879 \sin \theta' - 1.6905 \sin^2 \theta' + 8.0156 \sin^3 \theta',
\]

in units of amu \( \cdot A^2 \). For Dennison's value of \( \theta' = 3^\circ9.5' \), this gives

\[
I_{yy}^{(0)} = -0.06484 \text{ amu} \cdot A^2 \\
= -0.1076 \text{ g cm}^2,
\]

and, for a value of \( \theta' = 2^\circ56.5' \), the term vanishes. Thus, with a change of less than a quarter of a degree, the equilibrium model coincides with the molecule principal axes.

The following values of the parameters, as defined in Appendix 1, will be
adopted:

\[ r = 1.434 \text{ Å}, \quad \theta = 74^24' \quad M_R = 1.00813 \text{ amu}, \]
\[ s = 0.937, \quad \theta' = 3^09.5', \quad M_C = 12.010, \]  \[ t = 1.093, \quad M_O = 16.000. \]

First, the equilibrium conditions (55) locate the coordinates \( R_{0i} \) relative to the origin, and give, in angstrom units,

\[ R_{01} = (0, -0.064920, -0.696559), \]
\[ R_{02} = (0, +0.014069, +0.735261), \]
\[ R_{03} = (0, +0.014069, +1.82826), \]
\[ R_{04} = (0, +0.820543, -1.00302). \]  \[ (133) \]

We can now put numerical values into the \( 3N_1 + 6 = 12 \) equations (a) through (d) listed below Eq. (56) and invert them to obtain the coefficients \( l_i^x \). In practice, we find it convenient to insert the last two conditions in the others analytically, eliminate two degrees of freedom, and then place the remaining coefficients in a matrix for routine inversion. Owing to the planar symmetry of the molecule, this matrix factors immediately into two submatrices, each of which can be inverted independently.

We list here only the results of this procedure, namely, the coefficients \( l_i^x \). For convenience, we list them as vectors \( L_i^x \) with coefficients corresponding to \( i = 1, 2, 3, 4 \). Thus, in angstrom units, we have:

\[
L_1^x = \begin{bmatrix}
-0.0437597 \\
0.026370 \\
0.079904 \\
0.247696 \\
\end{bmatrix}, \quad L_2^x = \begin{bmatrix}
-0.0246797 \\
-0.0285481 \\
-0.028548 \\
0.817417 \\
\end{bmatrix}, \quad L_3^x = \begin{bmatrix}
-0.0578277 \\
0.131728 \\
-0.816573 \\
-0.998399 \\
\end{bmatrix}, \quad L_4^x = \begin{bmatrix}
0.0085957 \\
-0.001862 \\
-0.001862 \\
-0.108629 \\
\end{bmatrix}.
\]  \[ (134) \]
These vectors are interesting because their components give the motion of the coordinates $\delta G_i$ ($i = 1, 2, 3, 4$) for the four internal motions $q_t$ ($t = 1, 2, 3, 4$).

With these coefficients, the many terms that enter into the kinetic energy can be calculated, computational simplicity being achieved by placing the various terms in appropriate matrices and utilizing matrix multiplication procedures.

We list only the results in the form of matrices with entries $\beta_{ff}^{(0)}$ of (65) and entries $\delta\beta_{ff}^{(0)}$ and $\delta\beta_{ff}^{(1)}$ of (70), (71), and (72). In units of $(\text{amu} - \text{A}^2)^{-1}$, they are:

$$\beta_{ff}^{(0)} = \begin{bmatrix}
0.046988 \\
0.048703 \\
1.3348 & -1.3348 \\
-1.3348 & 1.6462 \\
1.2465 & & 0.57438 \\
& & & 0.52830 \\
& & & & 0.064049
\end{bmatrix}, \quad (135)$$

corresponding to (65), and

$$\delta\beta_{ff}^{(0)} = \begin{bmatrix}
0 & 0 & 0 & 0 \\
0 & 0 & -4.2147 & +4.2147 \\
0 & -4.2147 & 0 & 0 \\
0 & +4.2147 & 0 & 0
\end{bmatrix} \times 10^{-3}$$

$$\delta\beta_{ff}^{(1)} = \begin{bmatrix}
2.83433 & 0 & 0 & 0 & 0 & 1.4444 & 0 & 1.9833 \\
0 & -4.2626 & -90.459 & 92.844 & 0 & 0 & 2.4128 & 0 \\
0 & -90.459 & 914.70 & -914.70 & 0 & 0 & -88.469 & 0 \\
0 & 92.844 & -914.70 & 914.70 & 0 & 0 & 115.98 & 0
\end{bmatrix} \times 10^{-3}$$

$$\delta\beta_{ff}^{(2)} = \begin{bmatrix}
-0.068436 & 0 & 0 & 0 & -3.1344 & 0 & 0 & 4.4196 \\
0 & -0.040712 & 164.32 & -206.58 & 0 & 0 & 0 & 0 \\
0 & 164.32 & -24.645 & 24.645 & 0 & 0 & 2383.3 & 0 \\
0 & -206.58 & 24.645 & -24.645 & 0 & 0 & -2870.8 & 0
\end{bmatrix} \times 10^{-3}$$
\[ \delta \beta_{J'}^{(3)} = 10^{-3} \times 
\begin{bmatrix}
0 & 0 & 0 & 40.537 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & -5.2004 & 0 & 0 & 4.8441 \\
0 & 0 & 0 & 0 & 190.68 & -2104.67 & 0 & -11.905 \\
40.537 & 0 & 0 & -249.99 & 2588.7 & 0 & 13.827 \\
\end{bmatrix} \]

and

\[ \delta \beta_{J'}^{(4)} = 10^{-3} \times 
\begin{bmatrix}
76.931 & 0 & 0 & 0 & -38.598 & -39.634 & 0 & 0 \\
0 & 82.578 & -42.383 & 40.879 & 0 & 0 & -43.737 & 0 \\
0 & -42.383 & 52.397 & -52.397 & 0 & 0 & 107.49 & 0 \\
0 & 40.879 & -52.397 & 52.397 & 0 & 0 & 124.84 & 0 \\
\end{bmatrix} \]  \hspace{1cm} (136)

corresponding to (70) after expansion, as given by (71) and (72). The \[ \mu_{J''}(t' \neq t'') \] are not listed, since they do not enter into the calculation of the \[ J = 0 \rightarrow 1 \] spectrum.

We next use the frequencies \( \nu_i \) taken from Table III, as defined by (126),

\[ \nu_1 = 1340 \text{ cm}^{-1}, \quad \nu_3 = 1171 \text{ cm}^{-1}, \]
\[ \nu_2 = 1056 \text{ cm}^{-1}, \quad \nu_4 = 1034 \text{ cm}^{-1}, \]  \hspace{1cm} (137)

the values \( \mu_{Ji} \) calculated above, and the definitions (85) in order to calculate the dimensionless quantities \( q_{0t} \),

\[ q_1 = 0.12524, \quad q_3 = 0.09125, \]
\[ q_2 = 0.09577, \quad q_4 = 0.03240, \]  \hspace{1cm} (138)

which are the "amplitudes" of the quantum mechanical vibrations \( q_i \).

Finally, we adopt the Ivash and Dennison value \( (l) \) for the potential barrier

\[ V_0^2 = 374.821 \text{ cm}^{-1}. \]  \hspace{1cm} (139)

We now go directly to the expression for the \( J = 0 \rightarrow 1 \) splitting \( \Delta \nu^{m_0} \), as given by (122), utilizing, of course, the definitions of the various terms appearing there. Since we are interested in the contributions from the various terms described after (122), we list these contributions to \( \Delta \nu^{m_0} \) for each \( m_0 \). In a preliminary calculation by somewhat different, but equivalent, methods, the contributions arising from the terms \( q_i P_{P'} \) were in the range 6.55 to 6.59 Mc/sec for the various terms \( \Delta \nu^{m_0} \). Since we are interested in differences in terms of the order of 10 or 100 megacycles per second, these virtually constant terms have been discarded in the calculations described below.
In KTn notation, we list in Table VI the torsional levels \( m_0 \) in the following order:

<table>
<thead>
<tr>
<th>( n )</th>
<th>( r = 1 )</th>
<th>( r = 2, 3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>( m_0 = 0 )</td>
<td>( m_0 = 1 )</td>
</tr>
<tr>
<td>1</td>
<td>( m_1 = 3 )</td>
<td>( m_1 = -2 )</td>
</tr>
<tr>
<td>2</td>
<td>( m_2 = -3 )</td>
<td>( m_2 = 4 )</td>
</tr>
</tbody>
</table>

and we use below the coefficients \( \delta_{ij}^{\gamma} \) to illustrate the tabulations of contributions to each \( \Delta \nu^{\gamma} \). Note that, from symmetry considerations, \( x \) and \( y \) terms do not mix for a given vibration \( t \).

\[
\begin{align*}
\langle \delta_{xy}^0, \delta_{yy}^0 \rangle & \quad \text{Total from } L_x^{(0)} \\
\langle \delta_{xy}^1, \delta_{yy}^1 \rangle & \quad \text{Total from } q_1 \\
\langle \delta_{xy}^2, \delta_{yy}^2 \rangle & \quad \text{Total from } q_2 \\
\langle \delta_{xy}^1, \delta_{yy}^2 \rangle & \quad \text{Total from } q_3 \\
\langle \delta_{xy}^1, \delta_{yy}^1 \rangle & \quad \text{Total from } q_4 \\
\end{align*}
\]

In this form, we list our numerical results in Table VI in megacycles per second.

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