altering the lattice structure of the precipitate. The precipitate may possibly be face-centered cubic gamma-iron containing copper, or iron atoms in great concentration on the lattice points of the copper lattice.

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The Rotation-Vibration Energies of Tetrahedrally Symmetric Pentatomic Molecules. II

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A general discussion of a method which may be used to obtain the first-order Coriolis splitting of the harmonic and combination states of ν_3 and ν_4 is presented. The method is applied to obtain these splittings of $2\nu_3$, $2\nu_4$ and $\nu_3+\nu_4$ and to derive the stabilized wave functions for these states. With these functions the selection rules and the elements of the matrix of the second-order Hamiltonian $H^{(2)\prime}$ have been calculated for these states.

I. Introduction

In Part I of this paper[1] we have given the quantum-mechanical Hamiltonian for the investigation of the vibration-rotation energies of the XY_4 type molecules, including all terms which may contribute to the energy to second order of approximation. In addition to the harmonic oscillator and rigid spherical top terms of the zeroth order, the Hamiltonian includes cubic and quartic anharmonic terms, centrifugal expansion terms, all possible types of Coriolis and other interactions between rotation and oscillation. The Hamiltonian was transformed by a contact transformation into $H^{(0)}+\lambda H^{(1)\prime}+\lambda^2 H^{(2)\prime}$ so that to second approximation only the Coriolis interaction terms between rotation and the threefold degenerate oscillations ν_3 and ν_4 are contained in $H^{(1)\prime}$. This facilitates the calculation of the energies to second approximation which otherwise would be very difficult because of the high degree of degeneracy of the zeroth-order energies. In Part I we have calculated and set down the elements of the matrix H accurate to second order of approximation for the states $V_1\nu_1$, ν_2, $V_1\nu_1+\nu_3$, $V_1\nu_1+\nu_4$, $\nu_2+\nu_3$ and $\nu_2+\nu_4$.

Part II deals with the energies of the states $2\nu_3$ (or $2\nu_4$) and $\nu_3+\nu_4$, which are, respectively, six- and ninefold degenerate because of the degeneracy of ν_3 and ν_4. The manner in which this degeneracy is removed by the first-order Coriolis terms $H^{(1)\prime}$ is discussed and calculations are made on the selection rules and the second-order energies.

[1] W. H. Shaffer, H. H. Nielsen and L. H. Thomas, Phys. Rev. **56**, 895 (1939).

II. The First-Order Coriolis Interaction Energies

We shall discuss first a general method of treating the first-order Coriolis interaction terms $H^{(1)\prime}$ which can be written in the form:

$$H^{(1)\prime}=-(\zeta_3/A_0)(\mathbf{J}_3\cdot\mathbf{J})-(\zeta_4/A_0)(\mathbf{J}_4\cdot\mathbf{J}), \quad (1)$$

where $\mathbf{J}_3$ and $\mathbf{J}_4$ are the internal angular momenta associated with ν_3 and ν_4, respectively, and $\mathbf{J}$ is the total angular momentum of the molecule. It is readily shown from a study in spherical polar coordinates of the threefold degenerate modes ν_3 and ν_4 as isotropic three-dimensional oscillators that the quantum number J_3 may assume the values V_3, V_3-2, V_3-4, $\cdots 0$ or 1 (and J_4 the values V_4, V_4-2, etc.) where V_3 and V_4 are the vibrational quantum numbers associated with ν_3 and ν_4, respectively. The total internal angular momentum of the molecule is thus:

$$\mathbf{J}_2=\mathbf{J}_3+\mathbf{J}_4, \quad (2)$$

where $\mathbf{J}_2$ may evidently take the values:

$$J_2=J_3+J_4, \quad J_3+J_4-1, \quad \cdots|J_3-J_4|. \quad (3)$$

Thus the total angular momentum of the molecule, $\mathbf{J}$, becomes

$$\mathbf{J}=\mathbf{J}_1+\mathbf{J}_2, \tag{4}$$

$\mathbf{J}_1$ being the angular momentum of the rotation of the molecular framework. J_1 may take the values:

$$J_1=J+J_2,\quad J+J_2-1,\quad \cdots |J-J_2|. \tag{5}$$

When only one of the vibrational quantum numbers V_k ($k=3$, 4), is different from zero it follows that $\mathbf{J}_k\equiv\mathbf{J}_2$ so that

$$H^{(1)\prime}=(-\zeta_k/A_0)(\mathbf{J}_2\cdot\mathbf{J})=(-\zeta_k/A_0)(\mathbf{J}_k\cdot\mathbf{J}).$$

It is readily shown with the aid of (4) that:

$$H^{(1)\prime}=(-\zeta_k/A_0)\{(\mathbf{J}_2\cdot\mathbf{J}_2)+(\mathbf{J}\cdot\mathbf{J})-(\mathbf{J}_1\cdot\mathbf{J}_1)\}, \tag{6}$$

which when $V_k=1$ leads directly to the eigenvalues of $H^{(1)\prime}$ given in Part I and elsewhere. When V_3 and V_4 both are different from zero, the substitution of (2) and (4) into (1) yields:

$$\begin{aligned}H^{(1)\prime}=-(1/2A_0)\{&(\zeta_3+\zeta_4)(\mathbf{J}_2\cdot\mathbf{J}_2)\\&+2\zeta_3(\mathbf{J}_3\cdot\mathbf{J}_1)+2\zeta_4(\mathbf{J}_4\cdot\mathbf{J}_1)\\&+(\zeta_3-\zeta_4)(\mathbf{J}_3\cdot\mathbf{J}_3)+(\zeta_4-\zeta_3)(\mathbf{J}_4\cdot\mathbf{J}_4)\}.\end{aligned} \tag{7}$$

The only nonvanishing matrix elements of the quantities $(J_i\cdot J_i)$ are diagonal in all the quantum numbers and have the values:

$$J_i(J_i+1)\hbar^2\quad (J_i \text{ denoting } J,\ J_3,\ J_4,\ J_1, \text{ or } J_2). \tag{8}$$

A method similar to that of Condon and Shortley[2] yields the following nonvanishing matrix elements of $(\mathbf{J}_3\cdot\mathbf{J}_1)$ and $(\mathbf{J}_4\cdot\mathbf{J}_1)$:

$$\begin{aligned}&\left.\begin{matrix}(J_2|(\mathbf{J}_3\cdot\mathbf{J}_1)|J_2)\\(J_2|(\mathbf{J}_4\cdot\mathbf{J}_1)|J_2)\end{matrix}\right\}\\&=[\pm J_3(J_3+1)\mp J_4(J_4+1)+J_2(J_2+1)]\\&\times[J(J+1)-J_1(J_1+1)-J_2(J_2+1)]\\&\qquad\times\hbar^2/4J_2(J_2+1),\end{aligned} \tag{9}$$

$$\begin{aligned}&\left.\begin{matrix}(J_2|(\mathbf{J}_3\cdot\mathbf{J}_1)|J_2-1)\\-(J_2|(\mathbf{J}_4\cdot\mathbf{J}_1)|J_2-1)\end{matrix}\right\}\\&=[(J_2-J_3+J_4)(J_2+J_3-J_4)(J_2+J_3+J_4+1)\\&\times(J_3+J_4-J_2+1)(J+J_2-J_1)]^{\frac{1}{2}}\\&\times[(J+J_1-J_2+1)(J+J_1+J_2+1)\\&\quad\times(J_1+J_2-J)/4J_2^2(4J_2^2-1)]^{\frac{1}{2}}(\hbar^2/2).\end{aligned} \tag{10}$$

The matrix elements in (9) and (10) are diagonal in the quantum numbers J, J_1, J_3 and J_4.

III. The Eigenfunctions and Eigenvalues of H for $2\nu_3$, $2\nu_4$ and $\nu_3+\nu_4$

A. The state $2\nu_3$ (and $2\nu_4$)

For the state $2\nu_3$, $V_3=2$ and $V_1=V_2=V_4=0$. The zeroth-order energy for this state is:

$$E^{(0)}=\tfrac{1}{2}h(\nu_1+2\nu_2+7\nu_3+3\nu_4)+J(J+1)(\hbar^2/2A_0). \tag{11}$$

From the foregoing it is evident that $J_2(=J_3)$ may take the values: (a), $J_2=2$ and (b), $J_2=0$. It follows from (5) that the corresponding values of J_1 are: (a) $J_2=J\pm2$, $J\pm1$, J and (b) $J_1=J$. Eq. (6) together with (8) leads at once to the following eigenvalues $E_i^{(1)}=\epsilon_i(\zeta_3\hbar^2/A_0)$:

(a) $J_1=J$: $\epsilon_0=0$;
(b) $J_1=J+2$: $\epsilon_{\text{I}}=2J$; $J_1=J+1$: $\epsilon_{\text{II}}=J-2$; $J_1=J$: $\epsilon_{\text{III}}=-3$;
$J_1=J-1$: $\epsilon_{\text{IV}}=-(J+3)$; $J_1=J-2$: $\epsilon_{\text{V}}=-2(J+1)$. (12)

Thus the sixfold vibrational degeneracy of the state $2\nu_3$ is removed by $H^{(1)\prime}$. There remains, however, a $(2J+1)$ degeneracy in the quantum number K which can be removed only by terms of second and higher orders in H, and a $(2J+1)$-fold degeneracy in the magnetic quantum number M.

The wave functions required for our further work are the functions which will diagonalize $H^{(0)}+\lambda H^{(1)\prime}$. Treated in spherical polar coordinates, the wave functions characteristic of the state $2\nu_3$, which to zeroth approximation is sixfold degenerate, are the following:

$$\begin{aligned}&\text{(a)}\quad \chi_0(JK'M)=3^{-\frac{1}{2}}\{\phi(200)+\phi(020)+\phi(002)\}R(JK'M),\\&\text{(b)}\quad \chi_1(JK'M)=2^{-1}\{\phi(200)-\phi(020)+2^{\frac{1}{2}}i\phi(110)\}R(JK'M),\\&\qquad \chi_2(JK'M)=2^{-\frac{1}{2}}\{\phi(101)+i\phi(011)\}R(JK'M),\\&\qquad \chi_3(JK'M)=6^{-\frac{1}{2}}\{2\phi(002)-\phi(200)-\phi(020)\}R(JK'M),\\&\qquad \chi_4(JK'M)=-2^{-\frac{1}{2}}\{\phi(101)-i\phi(011)\}R(JK'M),\\&\qquad \chi_5(JK'M)=2^{-1}\{\phi(200)-\phi(020)-2^{\frac{1}{2}}i\phi(110)\}R(JK'M),\end{aligned} \tag{13}$$

where $R(JK'M)$ denotes a wave function of the spherical top and $\phi(n_1n_2n_3)=\phi(n_1)\phi(n_2)\phi(n_3)$, $\phi(n_i)$ being the wave function of a linear harmonic oscillator associated with the coordinate q_i. As

[2] E. U. Condon and G. H. Shortley, *Introduction to Atomic Spectra* (Cambridge University Press, 1935), Section 12[3].

in Part I, $n_1+n_2+n_3=V_3$. It is readily shown that the wave functions we require are the following linear combinations of the functions (13); for case (a), $\Psi_0(JK'M)=\chi_0(JK'M)$; for case (b), $\Psi_s(JKM)=a_s\chi_1(JK+2M)+b_s\chi_2(JK+1M)+c_s\chi_3(JKM)+d_s\chi_4(JK-1M)+e_s\chi_i(JK-2M)$. In matrix notation we may write:

$$\|\Psi\|=\|A\|\cdot\|\chi\|=\begin{Vmatrix}\Psi_{\mathrm{I}}\\ \Psi_{\mathrm{II}}\\ \Psi_{\mathrm{III}}\\ \Psi_{\mathrm{IV}}\\ \Psi_{\mathrm{V}}\end{Vmatrix}=\begin{Vmatrix}e_1 & d_1 & c_1 & b_1 & a_1\\ e_2 & d_2 & c_2 & b_2 & a_2\\ e_3 & d_3 & c_3 & b_3 & a_3\\ e_4 & d_4 & c_4 & b_4 & a_4\\ e_5 & d_5 & c_5 & b_5 & a_5\end{Vmatrix}\cdot\begin{Vmatrix}\chi_5\\ \chi_4\\ \chi_3\\ \chi_2\\ \chi_1\end{Vmatrix}. \tag{14}$$

The matrix A of (14) is identical, element for element, with the matrix in Table 2[3] of reference 2 where j_1 and m are replaced by J and K, respectively.

The selection rules have been determined by investigating the nonvanishing elements of the electric moment. This has been done by two different methods: first, by use of the quadratic terms in the electric moment together with the eigenfunctions (14); second, by use of the linear terms in the electric moment together with wave functions corrected by taking into account cubic terms in the potential energy. The two methods yield identical results for both selection rules and the quantum-mechanical amplitudes.

The selection rules governing transitions between rotation levels in the normal state and the Coriolis components of the state $2\nu_3$ are the following: (a) Transitions to ϵ_0 from the normal state are forbidden; (b) $\Delta J=0,\ -1$ to ϵ_{I}; $\Delta J=0,\ \pm1$ to ϵ_{II}, ϵ_{III}, ϵ_{IV}; $\Delta J=0,\ +1$ to ϵ_{V}. The selection rules for K and M are the same as in the case of transitions to $V_1\nu_1+\nu_3$, *viz.*, $\Delta K=0$, $\Delta M=0,\ \pm1$.

The actual relative intensities of the lines are proportional to the quantities $B(J'K',\ JK)$ which denote the squares of the absolute values of the amplitudes for transitions $(J'K')$ to (JK). The values of $B(J'K',\ JK)$ for the state $2\nu_3$ are given below:

$$\begin{aligned}
&\text{(a)}\quad J_2=2,\ J_1=J+2:\\
&\quad B(J-1K,\ JK)=0,\\
&\qquad B(JK,\ JK)=J[(J+2)^2-K^2][(J+1)^2-K^2]/(J+1)^2(J+2)(2J+1)(2J+3),\\
&\quad B(J+1K,\ JK)=(2J+1)K^2[(J+2)^2-K^2]/(J+1)^2(J+2)(2J+3)^2;\\
&\text{(b)}\quad J_2=2,\ J_1=J-2:\\
&\quad B(J-1K,\ JK)=(2J+1)K^2[(J-1)^2-K^2]/J^2(J-1)(2J-1)^2,\\
&\qquad B(JK,\ JK)=(J+1)(J^2-K^2)[(J-1)^2-K^2]/J^2(J-1)(4J^2-1),\\
&\quad B(J+1K,\ JK)=0;\\
&\text{(c)}\quad J_2=2,\ J_1=J+1:\\
&\quad B(J-1K,\ JK)=(J+2)[J^2-K^2][(J+1)^2-K^2]/2J^2(J+1)(4J^2-1),\\
&\qquad B(JK,\ JK)=(J-2)^2K^2[(J+1)^2-K^2]/2J^2(J+1)^2(J+2)(2J+1),\\
&\quad B(J+1K,\ JK)=J[3K^2-(J+1)(J+2)]^2/2(J+1)^2(J+2)(2J+3)(2J+1);\\
&\text{(d)}\quad J_2=2,\ J_1=J-1:\\
&\quad B(J-1K,\ JK)=(J+1)[3K^2-J(J-1)]^2/2J^2(J-1)(4J^2-1),\\
&\qquad B(JK,\ JK)=(J+3)^2K^2(J^2-K^2)/2J^2(J+1)^2(J-1)(2J+1),\\
&\quad B(J+1K,\ JK)=(J-1)(J^2-K^2)[(J+1)^2-K^2]/2(J+1)^2J(2J+1)(2J+3);\\
&\text{(e)}\quad J_2=2,\ J_1=1:\\
&\quad B(J-1K,\ JK)=3(2J+3)K^2(J^2-K^2)/2J^2(J+1)(2J-1)^2,\\
&\qquad B(JK,\ JK)=3[3K^2-J(J+1)]^2/2J^2(J+1)^2(2J-1)(2J+3),\\
&\quad B(J+1K,\ JK)=3(2J-1)K^2[(J+1)^2-K^2]/2(J+1)^2J(2J+3)^2.
\end{aligned} \tag{15}$$

As a further check on the reliability of these amplitudes we have verified that they are consistent with the principle of spectroscopic stability.

The second-order energy corrections are obtained by solving for the roots of the secular determinant $|(K|H^{(2)\prime}|K')-E^{(2)}\delta_{K'}{}^{K}|$, the elements of which are obtained after the manner of Part I. These are listed below, the quantities a, b, c, d, and e being the elements of the matrix A given in (15).

$$
\begin{aligned}
(K|H^{(2)\prime}|K)=&(\hbar^2/2A_0)\{R_0+fR_1+f^2R_2+(b_i^2-c_i^2+d_i^2)R_3+(a_i^2+e_i^2)fR_4+(b_i^2+d_i^2)fR_5\\
&+[a_i^2(K+2)^2+e_i^2(K-2)^2]R_6+c_i^2K^2R_7+[b_i^2(K+1)^2+d_i^2(K-1)^2]R_8+[a_i^2(6f(K+2)^2\\
&-5(K+2)^2-7(K+2)^4)+b_i^2(6f(K+1)^2-5(K+1)^2-7(K+1)^4)+c_i^2(6fK^2-5K^2-7K^4)\\
&+d_i^2(6f(K-1)^2-5(K-1)^2-7(K-1)^4)+e_i^2(6f(K-2)^2-5(K-2)^2-7(K-2)^4)]R_9\\
&+(a_ib_i(2K+3)[f-(K+1)(K+2)]^{\frac12}+b_ic_i(2K+1)[f-K(K+1)]^{\frac12}/6^{\frac12}+c_id_i(2K-1)\\
&\times[f-K(K-1)]^{\frac12}/6^{\frac12}+d_ie_i(2K-3)[f-(K-1)(K-2)]^{\frac12})R_{10}+(a_ib_i(2f-6K^2-18K-15)\\
&\times[f-(K+1)(K+2)]^{\frac12}+3b_ic_i(2f-6K^2-6K-3)[f-K(K+1)]^{\frac12}/6^{\frac12}+3b_ic_i(2f-6K^2+6K-3)\\
&\times[f-K(K-1)]^{\frac12}/6^{\frac12}+d_ie_i(2f-6K^2+18K-15)[f-(K-1)(K-2))^{\frac12})R_{11}+(2a_i^2[8(K+2)^3\\
&+(K+2)-4f(K+2)]+b_i^2[8(K+1)^3+(K+1)-4f(K+1)]-d_i^2[8(K-1)^3+(K-1)\\
&-4f(K-1)]-2e_i^2[8(K-2)^3+(K-2)-4f(K-2)])(R_{11}/2)+(6^{-\frac12}a_ic_i[f-K(K+1)]^{\frac12}\\
&\times[f-(K+1)(K+2)]^{\frac12}-\tfrac12 b_id_i[f-K(K-1)]^{\frac12}[f-K(K+1)]^{\frac12}\\
&+6^{-\frac12}c_ie_i[f-K(K-1)]^{\frac12}[f-(K-1)(K-2)]^{\frac12})R_{12}\},\qquad(16)
\end{aligned}
$$

in which the parameters R_s are the following quantities:

$$
\begin{aligned}
R_0(2\nu_3)=&(A_0/2)\{39d_1+7d_3+9d_5+12d_6+3d_{10}+14d_{11}+7d_{18}+3d_{20}+7d_{21}+14d_{22}-7d_{23}/2+3d_{27}\\
&+6d_{28}-3d_{29}/2+3d_{30}+3d_{31}+9d_{33}\}-(9/4)+9\zeta_3^2/2+(7/2)[(\omega_4/\omega_3)+(\omega_3/\omega_4)]\zeta_{34}^2\\
&+(7/4)[(\omega_2/\omega_3)+(\omega_3/\omega_2)]\zeta_{23}^2+(3/4)[(\omega_2/\omega_4)+(\omega_4/\omega_2)]\zeta_{24}^2-3\zeta_{34}^2-(A_0/4)\{10c_1^2/3\omega_3\\
&+c_2^2(14\omega_3\omega_4+18\omega_3^2-12\omega_4^2)/\omega_4(4\omega_3^2-\omega_4^2)+c_3^2(14\omega_4-3\omega_3)/(4\omega_4^2-\omega_3^2)+c_4^2/3\omega_4\\
&+42c_5(c_7+c_{11}+c_{12})/\omega_1+c_5^2(188\omega_3^2-63\omega_1^2+28\omega_1\omega_3)/\omega_1(4\omega_3^2-\omega_1^2)+(c_6^2/(\omega_1^4+\omega_3^4+\omega_4^4\\
&-2\omega_1^2\omega_3^2-2\omega_1^2\omega_4^2-2\omega_3^2\omega_4^2))[3\omega_3(\omega_3^2-\omega_4^2-\omega_1^2)+7\omega_4(\omega_4^2-\omega_3^2-\omega_1^2)+7\omega_1(\omega_1^2-\omega_3^2-\omega_4^2)\\
&+6\omega_1\omega_3\omega_4]+3c_7^2(6\omega_4+5\omega_1)/(2\omega_4+\omega_1)+18c_7(c_{11}+c_{12})/\omega_1+c_8^2(44\omega_3^2+28\omega_2\omega_3\\
&-27\omega_2^2)/\omega_2(4\omega_3^2-\omega_2^2)+(c_9^2/(\omega_2^4+\omega_3^4+\omega_4^4-2\omega_2^2\omega_3^2-2\omega_2^2\omega_4^2-2\omega_3^2\omega_4^2))[6\omega_2\omega_3\omega_4\\
&+3\omega_3(\omega_3^2-\omega_4^2-\omega_2^2)+7\omega_4(\omega_4^2-\omega_3^2-\omega_2^2)+7(\omega_2^2-\omega_3^2-\omega_4^2)]+6c_{10}^2/(\omega_2+2\omega_4)\\
&+18c_{11}c_{12}/\omega_1+11c_{11}^2/\omega_1+36c_{12}^2(\omega_1+\omega_2)/\omega_1(\omega_1+2\omega_2)+5c_{13}^2/16\},\\
R_1(2\nu_3)=&(\hbar/2A_0)\{3\zeta_{23}^2/\omega_3+3\zeta_{24}^2/2\omega_4+1/\omega_2+2/\omega_1+2\zeta_{34}^2[3\omega_3(\omega_3^2+3\omega_4^2)-8\omega_4(\omega_4^2+3\omega_3^2)]\\
&\times(3\omega_3\omega_4(\omega_3^2-\omega_4^2))^{-1}+\zeta_{23}^2(5\omega_2^3+15\omega_2\omega_3^2-9\omega_2^2\omega_3-3\omega_3^3)/3\omega_2\omega_3(\omega_2^2-\omega_3^2)\\
&+\zeta_{24}^2(\omega_3-\omega_4)^2/\omega_2\omega_4(\omega_2+\omega_4)\}+(\hbar^2/2A_0^2\omega_2^2)+(\hbar/A_0)(A_0/6\omega_1^3)^{\frac12}(7c_5+3c_7+3c_{11}+3c_{12}),\\
R_2(2\nu_3)=&-(\hbar^2/6A_0^2)\{5/2\omega_2^2+8/\omega_1^2+(3/4)(\zeta_{23}^2/\omega_3^2+\zeta_{24}^2/\omega_4^2)\},\\
R_3(2\nu_3)=&(A_0/2)(-6d_1+3d_6)+3\zeta_3^2/2+(A_0/4)\{3(2\omega_3^2-\omega_4^2)c_2^2/\omega_4(\omega_4^2-4\omega_3^2)-8\omega_3^2c_5^2/\omega_1(4\omega_3^2-\omega_1^2)\\
&-(9\omega_2^2-28\omega_3^2)c_8^2/\omega_2(4\omega_3^2-\omega_2^2)\},\\
R_4(2\nu_3)=&(\hbar/2A_0)\{\zeta_{23}^2/\omega_3+2a_1/\omega_2+(4/3)(3\omega_3^2+\omega_4^2)\zeta_{34}^2/\omega_3(\omega_3^2-\omega_4^2)\\
&+(4/3)(\omega_2^2+3\omega_3^2)\zeta_{23}^2/\omega_3(\omega_2^2-\omega_3^2)\},\\
R_5(2\nu_3)=&R_4/4,\quad R_6=-3R_4/2,\quad R_7=3R_4/4,\quad R_8=3R_4/4,\quad R_9=(\hbar^2/4A_0^2)(1/\omega_2^2-\tfrac12\zeta_{23}^2/\omega_3^2),\\
R_{10}(2\nu_3)=&(\hbar/A_0)\{3\zeta_{23}^2/4\omega_3+c_1\zeta_{23}A_0^{\frac12}/\omega_3^{\frac32}-c_2\zeta_{24}A_0^{\frac12}/\omega_4^{\frac32}+(\omega_4^2+3\omega_3^2)\zeta_{34}^2/\omega_3(\omega_3^2-\omega_4^2)\},\\
R_{11}(2\nu_3)=&(\hbar^2\zeta_{23}^2/2A_0^2\omega_3^2),\quad R_{12}(2\nu_3)=-3R_4(2\nu_3)/2-R_{10}(2\nu_3).
\end{aligned}
$$

$$
\begin{aligned}
(K|H^{(2)\prime}|K+2)=&(K+2|H^{(2)\prime}|K)=(\hbar^2/2A_0)\{-2c_ie_i(+2)6^{-\frac12}(f-3K^2)+b_id_i(+2)[f-3(K+1)^2]\\
&-2a_ic_i(+2)6^{-\frac12}[f-3(K+2)^2]-a_ia_i(+2)[f-(K+2)(K+3)]^{\frac12}[f-(K+3)(K+4)]^{\frac12}\\
&+b_ib_i(+2)[f-(K+1)(K+2)]^{\frac12}[f-(K+2)(K+3)]^{\frac12}+c_ic_i(+2)[f-K(K+1)]^{\frac12}\\
&\times[f-(K+1)(K+2)]^{\frac12}+d_id_i(+2)[f-K(K-1)]^{\frac12}[f-K(K+1)]^{\frac12}\\
&-e_ie_i(+2)[f-(K-1)(K-2)]^{\frac12}[f-K(K-1)]^{\frac12}\}R_{13},\qquad(17)
\end{aligned}
$$

where $R_{13}=(A_0\omega_3/2\hbar)R_{11}$.

$$
\begin{aligned}
(K|H^{(2)\prime}|K+4)=&(K+4|H^{(2)\prime}|K)=(\hbar^2/2A_0)\{[a_ic_i(+4)6^{-\frac12}(f-(K+2)(K+3))^{\frac12}(f-(K+3)\\
&\times(K+4))^{\frac12}-\tfrac12 b_id_i(+4)(f-(K+1)(K+2))^{\frac12}(f-(K+2)(K+3))^{\frac12}+c_ie_i(+4)6^{-\frac12}(f-K(K+1))^{\frac12}\\
&\times(f-(K+1)(K+2))^{\frac12}]R_{14}-[a_ia_i(+4)(f-(K+2)(K+3))^{\frac12}(f-(K+3)(K+4))^{\frac12}\\
&\times(f-(K+4)(K+5))^{\frac12}(f-(K+5)(K+6))^{\frac12}+b_ib_i(+4)(f-(K+1)(K+2))^{\frac12}(f-(K+2)(K+3))^{\frac12}\\
&\times(f-(K+3)(K+4))^{\frac12}(f-(K+4)(K+5))^{\frac12}+c_ic_i(+4)(f-K(K+1))^{\frac12}(f-(K+1)(K+2))^{\frac12}\\
&\times(f-(K+2)(K+3))^{\frac12}(f-(K+3)(K+4))^{\frac12}+d_id_i(+4)(f-K(K-1))^{\frac12}(f-K(K+1))^{\frac12}\\
&\times(f-(K+1)(K+2))^{\frac12}(f-(K+2)(K+3))^{\frac12}+e_ie_i(+4)(f-(K-1)(K-2))^{\frac12}(f-K(K-1))^{\frac12}\\
&\times(f-K(K+1))^{\frac12}(f-(K+1)(K+2))^{\frac12}](R_4/2)+[a_ib_i(+4)(f-(K+2)(K+3))^{\frac12}(f-(K+3)\\
&\times(K+4))^{\frac12}(f-(K+4)(K+5))^{\frac12}+(3b_ic_i(+4)/6^{\frac12})(f-(K+1)(K+2))^{\frac12}(f-(K-2)(K+3))^{\frac12}\\
&\times(f-(K+3)(K+4))^{\frac12}+(3c_id_i(+4)/6^{\frac12})(f-K(K+1))^{\frac12}(f-(K+1)(K+2))^{\frac12}(f-(K+2)(K+3))^{\frac12}\\
&+d_ie_i(+4)(f-K(K-1))^{\frac12}(f-K(K+1))^{\frac12}(f-(K+1)(K+2))^{\frac12}]R_{11}\},\qquad(18)
\end{aligned}
$$

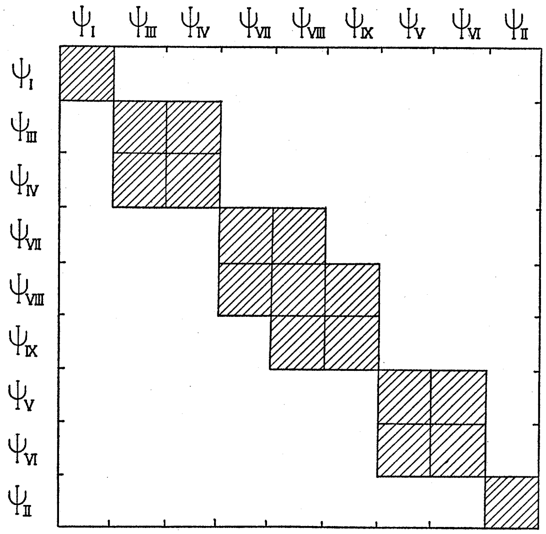

FIG. 1. Matrix of H_1 for the state $\nu_3+\nu_4$.

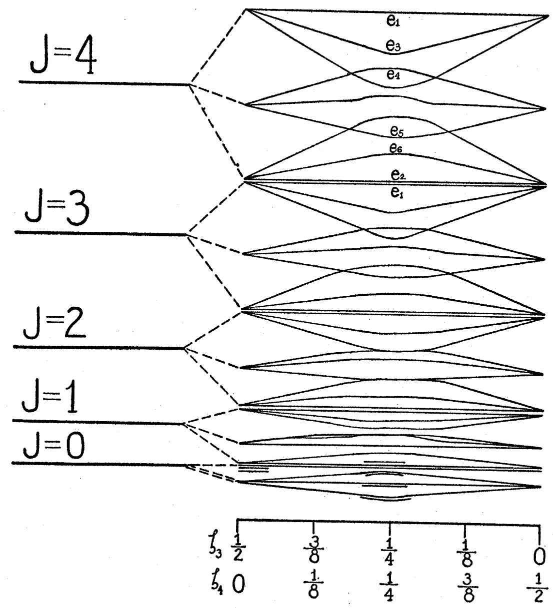

FIG. 2. Coriolis levels for state $\nu_3+\nu_4$ of XY_4.

where $R_{14}(2\nu_3)=-3R_4(2\nu_3)/4+R_{10}(2\nu_3)/2$.

Since the state $2\nu_4$ is entirely similar to the state $2\nu_3$ the above discussion is directly applicable to it. The elements of the matrix $H^{(2)\prime}$ for that state may be obtained from (16), (17) and (18) simply by interchanging ζ_3 and ζ_4 and, as well, those other quantities (discussed in Part I) which there must be interchanged to obtain the matrix elements of $V_1\nu_1+\nu_4$ from those of $V_1\nu_1+\nu_3$.

B. The state $\nu_3+\nu_4$

In the state $\nu_3+\nu_4$ the vibration quantum numbers take the following values: $V_3=V_4=1$, $V_1=V_2=0$ so that the zeroth-order energy becomes:

$$E^{(0)}{}_{\nu_3+\nu_4}=(h/2)(\nu_1+2\nu_2+5\nu_3+5\nu_4)+J(J+1)(\hbar^2/2A_0). \tag{19}$$

From (2), it follows that $J_3=J_4=1$ and from (3) that J_2 may be (a) $J_2=2$, (b) $J_2=1$ and (c) $J_2=0$. The corresponding values of J_1 are (a) $J_1=J\pm 2$, $J\pm 1$, J (b) $J_1=J\pm 1$, J and (c) $J_1=J$. With the aid of (7),(8), (9) and (10) it is possible to set up the matrix of $H^{(1)\prime}$ for the state $\nu_3+\nu_4$. It will be a step matrix and will have the appearance of the Fig. 1. In the figure the symbols I, II, etc., represent the following combinations of quantum numbers: I: $J_1=J+2$, $J_2=2$; II: $J_1=J-2$, $J_2=2$; III: $J_1=J+1$, $J_2=2$; IV: $J_1=J+1$, $J_2=1$; V: $J_1=J-1$, $J_2=2$; VI: $J_1=J-1$, $J_2=1$; VII: $J_1=J$, $J_2=2$; VIII: $J_1=$J, $J_2=1$; IX: $J_1=J$, $J_2=0$. Solution of the secular determinant of Fig. 1 yields for the state $\nu_3+\nu_4$ the following nine Coriolis components into which the zeroth-order levels (19) are split by $H^{(1)\prime}$. Denoting these by $E_i^{(1)}$ which is set equal to $(e_i\hbar^2/A_0)$ we have:[3]

$$\begin{aligned}
&J_1=J+2: \quad e_1=J(\zeta_3+\zeta_4); \quad J_1=J-2: e_2=-(J+1)(\zeta_3+\zeta_4);\\
&J_1=J+1: e_{3,\,4}=\tfrac{1}{2}\{(J-1)(\zeta_3+\zeta_4)\pm[(J+1)^2(\zeta_3-\zeta_4)^2+4\zeta_3\zeta_4]^{\frac{1}{2}}\};\\
&J_1=J-1: e_{5,\,6}=-\tfrac{1}{2}\{(J+2)(\zeta_3+\zeta_4)\mp[J^2(\zeta_3-\zeta_4)^2+4\zeta_3\zeta_4]^{\frac{1}{2}}\}.
\end{aligned} \tag{20}$$

$J_1=J$: $e_{7,\,8,\,9}$ are the roots of the cubic equation:

$$e^3+2(\zeta_3+\zeta_4)e^2+[(3/4)(\zeta_3+\zeta_4)^2-(1/4)(4J^2+4J-1)(\zeta_3-\zeta_4)^2]e-J(J+1)(\zeta_3+\zeta_4)(\zeta_3-\zeta_4)^2=0.$$

[3] An independent method not based on the vector addition of angular momenta has been used to check the above results.

The manner in which the Coriolis levels depend on the values of ζ_3 and ζ_4 ($\zeta_3+\zeta_4=\frac{1}{2}$) is illustrated in Fig. 2 where the parent rotational levels are indicated by $J=0$, 1, 2, etc. In the diagram the Coriolis levels e_1 of J and e_2 of $J+1$ are shown separated in order simply to clarify the illustration. It is interesting to note that the nine Coriolis levels associated with a given value of J become three levels for the case $\zeta_3=0$, $\zeta_4=\frac{1}{2}$, each of which is threefold degenerate. Under these conditions the Coriolis pattern is entirely like that for the state ν_4 where $\zeta_4=\frac{1}{2}$, a result which is quite natural since setting $\zeta_3=0$ corresponds effectively to reducing the internal angular momentum associated with ν_3 to zero. The values ζ_3 and ζ_4 for methane have been determined by Johnston and Dennison[4] to be equal to 0.0345 and 0.4655, respectively. This indicates that the first-order Coriolis levels of $\nu_3+\nu_4$ should in that case fall into three sets of three nearly coincident levels.

The basic wave functions $\Psi_{\mathrm{I}}, \Psi_{\mathrm{II}}, \cdots, \Psi_{\mathrm{IX}}$ used in setting up the matrix $H^{(1)\prime}$ in the form of Fig. 1 fall into three sets corresponding to $J_2=2$, $J_2=1$ and $J_2=0$. They are linear combinations of the following preliminary functions

$$\begin{aligned}
&\chi_0=-3^{-\frac{1}{2}}\{F(\nu_3)H(\nu_4)+G(\nu_3)G(\nu_4)+H(\nu_3)H(\nu_4)\}R(JKM);\\
&\chi_1=F(\nu_3)F(\nu_4)R(JK+2M);\quad \chi_2=2^{-\frac{1}{2}}\{F(\nu_3)G(\nu_4)+G(\nu_3)F(\nu_4)\}R(JK+1M);\\
&\chi_3=-6^{-\frac{1}{2}}\{F(\nu_3)H(\nu_4)-2G(\nu_3)G(\nu_4)+H(\nu_3)F(\nu_4)\}R(JKM);\\
&\chi_4=-2^{-\frac{1}{2}}\{H(\nu_3)G(\nu_4)+G(\nu_3)H(\nu_4)\}R(JK-1M);\quad \chi_5=H(\nu_3)H(\nu_4)R(JK-2M);\\
&\chi_6=2^{-\frac{1}{2}}\{F(\nu_3)G(\nu_4)-G(\nu_3)F(\nu_4)\}R(JK+1M);\quad \chi_7=2^{-\frac{1}{2}}\{H(\nu_3)F(\nu_4)-F(\nu_3)H_4)\}R(JKM);\\
&\chi_8=2^{-\frac{1}{2}}\{H(\nu_3)G(\nu_4)-G(\nu_3)H(\nu_4)\}R(JK-1M),
\end{aligned}\tag{21}$$

where $F(\nu_3)$, $G(\nu_3)$ and $H(\nu_3)$ are the basic wave functions for ν_3 defined in Part I and where $F(\nu_4)$, $G(\nu_4)$ and $H(\nu_4)$ are the corresponding functions for the state ν_4. It is not difficult to show that the required combinations are the following ones:

$$\|\Psi\|_{(J_2=2)}=\|A\|\cdot\|\chi\|_{(J_2=2)},\tag{22a}$$

where $\|\Psi\|_{(J_2=2)}=\|\Psi_{\mathrm{I}}\Psi_{\mathrm{II}}\Psi_{\mathrm{III}}\Psi_{\mathrm{IV}}\Psi_{\mathrm{V}}\|$, $\|\chi\|_{(J_2=2)}=\|\chi_5\chi_4\chi_3\chi_2\chi_1\|$ and A is identically the same transformation matrix which occurs in (14);

$$\left\|\begin{matrix}\Psi_{\mathrm{VI}}\\ \Psi_{\mathrm{VII}}\\ \Psi_{\mathrm{VIII}}\end{matrix}\right\|_{(J_2=1)}=\left\|\begin{matrix}\gamma_1 & \beta_1 & \alpha_1\\ \gamma_2 & \beta_2 & \alpha_2\\ \gamma_3 & \beta_3 & \alpha_3\end{matrix}\right\|\cdot\left\|\begin{matrix}\chi_8\\ \chi_7\\ \chi_6\end{matrix}\right\|=\|B\|\cdot\|\chi\|_{(J_2=1)},\tag{22b}$$

in which the matrix B is identical with the one in Table 2[3] of reference 2 when j_1 and m have been replaced, respectively, by J and K; and

$$\Psi_{\mathrm{IX}}=\chi_0.\tag{22c}$$

The actual eigenfunctions of $H^{(1)\prime}$ corresponding to the eigenvalues $E_i^{(1)}$ of (20) will once more be linear combinations of the functions $\Psi(J_2=2)$, $\Psi(J_2=1)$, and $\Psi(J_2=0)$ and may be written:

$$\Psi(E_i^{(1)})=A_i\Psi(J_2=2)+B_i\Psi(J_2=1)+C_i\Psi(J_2=0),\tag{23}$$

where the A_i, B_i and C_i are the normalized first minors of the secular determinant of the matrix in Fig. 1. These may readily be obtained for special values of ζ_3 and ζ_4.

Using the wave functions (23), the selection rules governing the transitions between the normal vibration state and the Coriolis component levels $E_i^{(1)}$ of the state $\nu_3+\nu_4$ have been determined in the same manner as for the state $2\nu_3$ and are found to be the following:

$$\Delta J=0,\ -1 \text{ to } E_1^{(1)};\quad \Delta J=0,\ +1 \text{ to } E_2^{(1)};\quad \Delta J=0,\ \pm1 \text{ to } E_s^{(1)}\quad \text{where } s=3,4,\cdots 9.$$

As before the selection rules for K and M are $\Delta K=0$, $\Delta M=0$, ±1. It is found in evaluating the nonvanishing elements of the electric moment, that only that part of the wave function (23) will contribute which depends upon $J_2=2$. These elements are again proportional to the quantities

[4] M. Johnston and D. M. Dennison, Phys. Rev. **48**, 868 (1935).

$B(J'K', JK)$ obtained in connection with $2\nu_3$, the proportionality constants being the squares of the A_i which occur as coefficients of $\Psi(J_2=2)$ in (23). For the limiting cases $\zeta_3=0$, $\zeta_4=\frac{1}{2}$ (and $\zeta_3=\frac{1}{2}$, $\zeta_4=0$) it has again been verified that the principle of spectroscopic stability is obeyed.

The matrix of $H^{(2)'}$ may now be set up using as the stabilized wave functions, the functions $\Psi(E_i^{(1)})$ of (23). There are no matrix elements of $H^{(2)'}$ which involve different values of J_2, i.e., all such integrals as $\int \bar{\Psi}(J_2=2)H^{(2)'}\Psi(J_2=1)dv$, etc., vanish, The $(K|K')$ matrix elements of $H^{(2)'}$ thus take the form

$$(K|H^{(2)'}|K')=A_iA_i'(K|H^{(2)'}|K')_{J_2=2}+B_iB_i'(K|H^{(2)'}|K')_{J_2=1}+C_iC_i'(K|H^{(2)'}|K')_{J_2=0},$$

where $(K|H^{(2)'}|K')_{J_2}=\int\bar{\Psi}(J_2JKM)H^{(2)'}\Psi(J_2JK'M)dv$, J_2 taking the values 2, 1, 0. The elements $(K|H^{(2)'}|K')_{J_2}$ are given below:

$$\begin{aligned}(K|H^{(2)'}|K)_{J_2=2}=&(\hbar^2/2A_0)\{R_0+R_1f+R_2f^2+(b_i^2-c_i^2+d_i^2)R_3+(a_i^2+e_i^2)fR_4+(1/4)(b_i^2+d_i^2)fR_4\\
&-(3/2)[a_i^2(K+2)^2+e_i^2(K-2)^2]R_4+3c_i^2K^2R_4/2+(3/4)[b_i^2(K+1)^2+d_i^2(K-1)^2]R_4\\
&-[6^{-\frac{1}{2}}a_ic_i(f-(K+1)(K+2))^{\frac{1}{2}}(f-K(K+1))^{\frac{1}{2}}+\tfrac{1}{2}b_id_i(f-K(K+1))^{\frac{1}{2}}(f-K(K-1))^{\frac{1}{2}}\\
&+6^{-\frac{1}{2}}c_ie_i(f-K(K-1))^{\frac{1}{2}}(f-(K-1)(K-2))^{\frac{1}{2}}](R_5+3R_4/2)+[a_ib_i(2K+3)(f-(K+1)(K+2))^{\frac{1}{2}}\\
&+6^{-\frac{1}{2}}b_ic_i(2K+1)(f-K(K+1))^{\frac{1}{2}}-6^{-\frac{1}{2}}c_id_i(2K-1)(f-K(K-1))^{\frac{1}{2}}-d_ie_i(2K-3)(f-(K-1)\\
&\times(K-2))^{\frac{1}{2}}]R_5+[a_ib_i(2f-6K^2-18K-15)(f-(K+1)(K+2))^{\frac{1}{2}}+(3b_ic_i/6^{\frac{1}{2}})(2f-6K^2-6K-3)\\
&\times(f-K(K+1))^{\frac{1}{2}}+(3c_id_i/6^{\frac{1}{2}})(2f-6K^2+6K-3)(f-K(K-1))^{\frac{1}{2}}+d_ie_i(2f-6K^2+18K-15)\\
&\times(f-(K-1)(K-2))^{\frac{1}{2}}]R_6+[a_i^2(8(K+2)^3+(K+2)-4f(K+2))+(b_i^2/2)(8(K+1)^3+(K+1)\\
&-4f(K+1))-(d_i^2/2)(8(K-1)^3+(K-1)-4f(K-1))-e_i^2(8(K-2)^3+(K-2)-4f(K-2))]\\
&\times(-R_6/2)+[a_i^2(6f(K+2)^2-5(K+2)^2-7(K+2)^4)+b_i^2(6f(K+1)^2-5(K+1)^2-7(K+1)^4)\\
&+c_i^2(6fK^2-5K^2-7K^4)+d_i^2(6f(K-1)^2-5(K-1)^2-7(K-1)^4)+e_i^2(6f(K-2)^2-5(K-2)^2\\
&-7(K-2)^4]R_7. \qquad (24)\end{aligned}$$

where

$$\begin{aligned}R_0(\nu_3+\nu_4)=&(A_0/2)\{21(d_1+d_5)+9d_3+7(d_6+d_{10})+16d_{11}+5(d_{18}+d_{21}+d_{27})+10(d_{22}+d_{28})\\
&+3(d_{30}+d_{31}+3d_{33})-(5/2)(d_{23}+d_{29})\}+2(\zeta_3-\zeta_4)^2+6\zeta_3\zeta_4+4[(\omega_4/\omega_3)+(\omega_3/\omega_4)]\zeta_{34}^2\\
&+(45/16)[(\omega_2/\omega_3)+(\omega_3/\omega_2)]\zeta_{23}^2+(45/16)[(\omega_2/\omega_4)+(\omega_4/\omega_2)]\zeta_{24}^2-(9/4)-2\zeta_{34}^2-(A_0/4)\\
&\times\{(5/3)(c_1^2/\omega_3+c_4^2/\omega_4)+(4\omega_3+7\omega_4)c_2^2/\omega_4(2\omega_3+\omega_4)+(4\omega_4+7\omega_3)c_3^2/\omega_3(2\omega_4+\omega_3)\\
&+6\omega_3c_2^2/(4\omega_3^2-\omega_4^2)+6\omega_4c_3^2/(4\omega_4^2-\omega_3^2)+5(10\omega_3+7\omega_1)c_5^2/\omega_1(2\omega_3+\omega_1)\\
&+5(10\omega_4+7\omega_1)c_7^2/\omega_1(2\omega_4+\omega_1)+50c_5c_7/\omega_1+15(c_5+c_7)(c_{11}/\omega_1+c_{12}/\omega_1)\\
&+(c_6^2/(\omega_1^4+\omega_3^4+\omega_4^4-2\omega_1^2\omega_3^2-2\omega_1^2\omega_4^2-2\omega_3^2\omega_4^2))[6\omega_1\omega_3\omega_4+5\omega_3(\omega_3^2-\omega_4^2-\omega_1^2)\\
&+5\omega_4(\omega_4^2-\omega_3^2-\omega_1^2)+9\omega_1(\omega_1^2-\omega_3^2-\omega_4^2)]+2(4\omega_3+7\omega_2)c_8^2/\omega_2(2\omega_3+\omega_2)+2c_8c_{10}/\omega_2\\
&+2(4\omega_4+7\omega_2)c_{10}^2/\omega_2(2\omega_4+\omega_2)+11c_{11}^2/\omega_1+18c_{11}c_{12}/\omega_1+36(\omega_1+\omega_2)c_{12}^2/\omega_1(2\omega_2+\omega_1)\\
&+5c_{13}^2/16\omega_2+(c_9^2/(\omega_2^4+\omega_3^4+\omega_4^4-2\omega_2^2\omega_3^2-2\omega_2^2\omega_4^2-2\omega_3^2\omega_4^2))[5\omega_3(\omega_3^2-\omega_4^2-\omega_2^2)\\
&+5\omega_4(\omega_4^2-\omega_3^2-\omega_2^2)+9\omega_2(\omega_2^2-\omega_3^2-\omega_4^2)+6\omega_2\omega_3\omega_4]\},\\
R_1(\nu_3+\nu_4)=&(\hbar/2A_0)\{(9/4)(\zeta_{23}^2/\omega_3+\zeta_{24}^2/\omega_4)+1/\omega_2+2/\omega_1-(a_1+a_2)/2\omega_2\\
&+11\zeta_{34}^2(\omega_3-\omega_4)^2/3\omega_3\omega_4(\omega_3+\omega_4)+(\zeta_{23}^2/3\omega_2\omega_3)(4\omega_2^3-9\omega_2^2\omega_3+12\omega_2\omega_3^2-3\omega_3^3)/(\omega_2^2-\omega_3^2)\\
&+(\zeta_{24}^2/3\omega_2\omega_4)(4\omega_2^3+12\omega_2\omega_4^2-9\omega_2^2\omega_4-3\omega_4^3)/(\omega_2^2-\omega_4^2)+(\hbar/A_0\omega_2^2)\\
&+(2A_0/3\omega_1^3)^{\frac{1}{2}}(5c_5+5c_7+3c_{11}+3c_{12})\},\\
R_2(\nu_3+\nu_4)=&-(\hbar^2/6A_0^2)[8/\omega_1^2+5/2\omega_2^2+(3/4)(\zeta_{23}^2/\omega_3^2+\zeta_{24}^2/\omega_4^2)],\\
R_3(\nu_3+\nu_4)=&(A_0/2)(d_8-2d_3+2d_{11})+(A_0/4)[-2c_1c_3/\omega_3-2c_2c_4/\omega_4-4\omega_3c_2^2/(4\omega_3^2-\omega_4^2)\\
&-4\omega_4c_3^2/(4\omega_4^2-\omega_3^2)+4c_6^2\omega_1\omega_3\omega_4/(\omega_1^4+\omega_3^4+\omega_4^4-2\omega_1^2\omega_3^2-2\omega_1^2\omega_4^2-2\omega_3^2\omega_4^2)\\
&+6c_8c_{10}/\omega_2+3\omega_2(\omega_2^2-\omega_3^2-\omega_4^2)c_9^2/(\omega_2^4+\omega_3^4+\omega_4^4-2\omega_2^2\omega_3^2-2\omega_2^2\omega_4^2-2\omega_3^2\omega_4^2)],\\
R_4(\nu_3+\nu_4)=&(\hbar/2A_0)\{\tfrac{1}{2}(\zeta_{23}^2/\omega_3+\zeta_{24}^2/\omega_4)+(a_1+a_2)/\omega_2+2\zeta_{34}^2(\omega_3-\omega_4)^2/3\omega_3\omega_4(\omega_3+\omega_4)\\
&+2\zeta_{23}^2(\omega_2^2+3\omega_3^2)/3\omega_3(\omega_2^2-\omega_3^2)+2\zeta_{24}^2(\omega_2^2+3\omega_4^2)/3\omega_4(\omega_2^2-\omega_4^2)\},\\
R_5(\nu_3+\nu_4)=&(\hbar/2A_0)\{(3/4)(\zeta_{23}^2/\omega_3+\zeta_{24}^2/\omega_4)+(c_1+c_3)(\zeta_{23}/\omega_3)(A_0/\omega_3)^{\frac{1}{2}}-(c_2+c_4)(\zeta_{24}/\omega_4)(A_0/\omega_4)^{\frac{1}{2}}\\
&-\zeta_{34}^2(\omega_3-\omega_4)^2/\omega_3\omega_4(\omega_3+\omega_4)\},\\
R_6(\nu_3+\nu_4)=&(\hbar^2/2A_0)(\zeta_{23}^2/\omega_3^2+\zeta_{24}^2/\omega_4^2),\\
R_7(\nu_3+\nu_4)=&(\hbar^2/4A_0^2)[1/\omega_2^2-\tfrac{1}{2}(\zeta_{23}^2/\omega_3^2+\zeta_{24}^2/\omega_4^2)].\end{aligned}$$

In the above $a_1=-c_8(A_0/3\omega_2)^{\frac{1}{2}}$ and $a_2=-c_{10}(A_0/3\omega_2)^{\frac{1}{2}}$.

$$\begin{aligned}
&(K|H^{(2)\prime}|K+2)_{J_2=2}=(K+2|H^{(2)\prime}|K)_{J_2=2}=(\hbar^2/2A_0)\{-a_ia_i(+2)(f-(K+2)(K+3))^{\frac12}\\
&\quad\times(f-(K+3)(K+4))^{\frac12}+\tfrac12 b_ib_i(+2)(f-(K+1)(K+2))^{\frac12}(f-(K+2)(K+3))^{\frac12}\\
&\quad+c_ic_i(f-K(K+1))^{\frac12}(f-(K+1)(K+2))^{\frac12}+\tfrac12 d_id_i(+2)(f-K(K-1))^{\frac12}(f-K(K+1))^{\frac12}\\
&\quad-e_ie_i(+2)(f-(K-1)(K-2))^{\frac12}(f-K(K-1))^{\frac12}-(2/6^{\frac12})a_ic_i(+2)(f-3(K+2)^2)\\
&\qquad\qquad-b_id_i(+2)(f-3(K+1)^2)-(2/6^{\frac12})c_ie_i(+2)(f-3(K-2)^2)\}R_8, \qquad (25)
\end{aligned}$$

where: $R_8(\nu_3+\nu_4)=(1/4)R_6$.

$$\begin{aligned}
&(K|H^{(2)\prime}|K+4)_{J_2=2}=(K+4|H^{(2)\prime}|K)_{J_2=2}=(\hbar^2/2A_0)\{[6^{-\frac12}a_ic_i(+4)(f-(K+2)(K+3))^{\frac12}\\
&\quad\times(f-(K+3)(K+4))^{\frac12}+6^{-\frac12}c_ie_i(+4)(f-K(K+1))^{\frac12}(f-(K+1)(K+2))^{\frac12}+\tfrac12 b_id_i(+4)\\
&\quad\times(f-(K+1)(K+2))^{\frac12}(f-(K+2)(K+3))^{\frac12}](-3R_4/4+\tfrac12R_5)+[a_ia_i(+4)(f-(K+2)(K+3))^{\frac12}\\
&\quad\times(f-(K+3)(K+4))^{\frac12}(f-(K+4)(K+5))^{\frac12}(f-(K+5)(K+6))^{\frac12}+b_ib_i(+4)(f-(K+1)\\
&\quad\times(K+2))^{\frac12}(f-(K+2)(K+3))^{\frac12}(f-(K+3)(K+4))^{\frac12}(f-(K+4)(K+5))^{\frac12}+c_ic_i(+4)\\
&\quad\times(f-K(K+1))^{\frac12}(f-(K+1)(K+2))^{\frac12}(f-(K+2)(K+3))^{\frac12}(f-(K+3)(K+4))^{\frac12}\\
&\quad+d_id_i(+4)(f-K(K-1))^{\frac12}(f-K(K+1))^{\frac12}(f-(K+1)(K+2))^{\frac12}(f-(K+2)(K+3))^{\frac12}\\
&\quad+e_ie_i(+4)(f-(K-1)(K-2))^{\frac12}(f-K(K-1))^{\frac12}(f-K(K+1))^{\frac12}(f-(K+1)(K-2))^{\frac12}](R_7/2)\\
&\quad\times[a_ib_i(+4)(f-(K+2)(K+3))^{\frac12}(f-(K+3)(K+4))^{\frac12}(f-(K+4)(K+5))^{\frac12}\\
&\quad+(3/6^{\frac12})b_ic_i(+4)(f-(K+1)(K+2))^{\frac12}(f-(K+2)(K+3))^{\frac12}(f-(K+3)(K+4))^{\frac12}\\
&\quad+(3/6^{\frac12})c_id_i(+4)(f-K(K+1))^{\frac12}(f-(K+1)(K+2))^{\frac12}(f-(K+2)(K+3))^{\frac12}\\
&\qquad\qquad+d_ie_i(+4)(f-K(K-1))^{\frac12}(f-K(K+1))^{\frac12}(f-(K+1)(K+2))^{\frac12}](R_6/2)\}, \qquad (26)
\end{aligned}$$

$$\begin{aligned}
&(K|H^{(2)\prime}|K)_{J_2=1}=(\hbar^2/2A_0)\{R_0'+fR_1'+f^2R_2'+[(\alpha_i^2+\gamma_i^2)f-\alpha_i^2(K+1)^2+2\beta_i^2K^2\\
&\quad-\gamma_i^2(K-1)^2]R_3'-\alpha_i\gamma_i(f-K(K-1))^{\frac12}(f-K(K+1))^{\frac12}(R_3'+R_4'/2)+2^{-\frac12}\beta_i[\alpha_i(f-K(K+1))^{\frac12}\\
&\quad\times(2K+1)-\gamma_i(f-K(K-1))^{\frac12}(2K-1)]R_4'+[\alpha_i^2(6f(K+1)^2-5(K+1)^2-7(K+1)^4)\\
&\quad+\beta_i^2(6fK^2-5K^2-7K^4)+\gamma_i^2(6f(K-1)^2-5(K-1)^2-7(K-1)^4)R_5'\\
&\quad+2^{\frac12}\beta_i[\alpha_i(2f-6K^2-6K-3)(f-K(K+1))^{\frac12}+\gamma_i(2f-6K^2+6K-3)(f-K(K-1))^{\frac12}]R_6'\\
&\qquad\qquad+[-\alpha_i^2(8(K+1)^3+(K+1)-4f(K+1))+\gamma_i^2(8(K-1)^3+(K-1)-4f(K-1))]R_6', \qquad (27)
\end{aligned}$$

where

$$\begin{aligned}
R_0'(\nu_3+\nu_4)=&(A_0/2)\{21(d_1+d_5)+7(d_3+d_6+d_{10})-d_8+18d_{11}+10(d_{18}+d_{20}+d_{21}+d_{27})\\
&+20(d_{22}+d_{28})-(5/2)(d_{23}+d_{29})+3(d_{30}+d_{31}+3d_{33})\}-(9/4)+2(\zeta_3-\zeta_4)^2\\
&+5[(\omega_3/\omega_4)+(\omega_4/\omega_3)]\zeta_{34}^2+(5/2)[(\omega_2/\omega_3)+(\omega_3/\omega_2)]\zeta_{23}^2+(5/2)[(\omega_2/\omega_4)\\
&+(\omega_4/\omega_2)]\zeta_{24}^2-4\zeta_{34}^2+(A_0/4)\{(-5/3)(c_1^2/\omega_3+c_4^2/\omega_4)+2c_1c_3/\omega_3+2c_2c_4/\omega_4\\
&-(4\omega_3+7\omega_4)c_2^2/\omega_4(\omega_4+2\omega_3)-(4\omega_4+7\omega_3)c_3^2/\omega_3(\omega_3+2\omega_4)-6\omega_3c_2^2/(4\omega_3^2-\omega_4^2)\\
&-6\omega_4c_3^2/(4\omega_4^2-\omega_3^2)-5(10\omega_3+7\omega_1)c_5^2/\omega_1(\omega_1+2\omega_3)-5(10\omega_4+7\omega_1)c_7^2/\omega_1(2\omega_4+\omega_1)\\
&-50c_5c_7/\omega_1-30c_5(c_{11}+c_{12})/\omega_1-30c_7(c_{11}+c_{12})/\omega_1+4c_8c_{10}/\omega_2-18c_{11}c_{12}/\omega_1\\
&-2(4\omega_3+7\omega_2)c_8^2/\omega_2(2\omega_3+\omega_2)-5c_6^2[\omega_3(\omega_3^2-\omega_4^2-\omega_1^2)+\omega_4(\omega_4^2-\omega_3^2-\omega_1^2)\\
&+\omega_1(\omega_1^2-\omega_3^2-\omega_4^2)+2\omega_1\omega_3\omega_4]/(\omega_1^4+\omega_3^4+\omega_4^4-2\omega_1^2\omega_3^2-2\omega_1^2\omega_4^2-2\omega_3^2\omega_4^2)\\
&-c_9^2[5\omega_3(\omega_3^2-\omega_4^2-\omega_2^2)+5\omega_4(\omega_4^2-\omega_3^2-\omega_2^2)+8\omega_2(\omega_2^2-\omega_3^2-\omega_4^2)\\
&+\omega_2\omega_3\omega_4]/(\omega_2^4+\omega_3^4+\omega_4^4-2\omega_2^2\omega_3^2-2\omega_2^2\omega_4^2-2\omega_3^2\omega_4^2)-2c_{10}^2(4\omega_4+7\omega_2)/\omega_2(2\omega_4+\omega_2)\\
&\qquad-11c_{11}^2/\omega_1-36(\omega_1+\omega_2)c_{12}^2/\omega_1(\omega_1+2\omega_2)-(5/16)(c_{13}^2/\omega_2)\},
\end{aligned}$$

$$\begin{aligned}
R_1'(\nu_3+\nu_4)=&(\hbar/2A_0)\{(11/4)(\zeta_{23}^2/\omega_3+\zeta_{24}^2/\omega_4)+1/\omega_2+2/\omega_1+(a_1+a_2)/2\omega_2+(\hbar/A_0\omega_2^2)\\
&+3(\omega_3-\omega_4)^2\zeta_{34}^2/\omega_3\omega_4(\omega_3+\omega_4)+[(2\omega_2^3+6\omega_2\omega_3^2-3\omega_2^2\omega_3-\omega_3^3)\zeta_{23}^2/\omega_2\omega_3(\omega_2^2-\omega_3^2)]\\
&+(8A_0/3\omega_1^3)^{\frac12}(5c_5+5c_7+3c_{11}+3c_{12})+[(2\omega_2^3+6\omega_2\omega_4^2-3\omega_2^2\omega_4-\omega_4^3)\zeta_{24}^2/\omega_2\omega_4(\omega_2^2-\omega_4^2)]\},
\end{aligned}$$

$$R_2'(\nu_3+\nu_4)=R_2(\nu_3+\nu_4),$$

$$\begin{aligned}
R_3'(\nu_3+\nu_4)=&(-\hbar/2A_0)\{(3/8)(\zeta_{23}^2/\omega_3+\zeta_{24}^2/\omega_4)+(3/4\omega_2)(a_1+a_2)-\tfrac12(\omega_3-\omega_4)^2\zeta_{34}^2/\omega_3\omega_4(\omega_3+\omega_4)\\
&+(\omega_2^2+3\omega_3^2)\zeta_{23}^2/2\omega_3(\omega_2^2-\omega_3^2)+\tfrac12(\omega_2^2+3\omega_4^2)\zeta_{24}^2/\omega_4(\omega_2^2-\omega_4^2)\},
\end{aligned}$$

$$\begin{aligned}
R_4'(\nu_3+\nu_4)=&(-\hbar/2A_0)\{(3/4)(\zeta_{23}^2/\omega_3+\zeta_{24}^2/\omega_4)+(c_1+c_3)(\zeta_{23}/\omega_3)(A_0/\omega_3)^{\frac12}\\
&-(c_2+c_4)(\zeta_{24}/\omega_4)(A_0/\omega_4)^{\frac12}-(\omega_3-\omega_4)^2\zeta_{34}^2/\omega_3\omega_4(\omega_3+\omega_4)\},
\end{aligned}$$

$$R_5'(\nu_3+\nu_4)=(\hbar^2/4A_0^2)[1/\omega_2^2-\tfrac12(\zeta_{23}^2/\omega_3^2+\zeta_{24}^2/\omega_4^2)],\quad R_6'(\nu_3+\nu_4)=R_6(\nu_3+\nu_4)/4;$$

$$\begin{aligned}
&(K|H^{(2)\prime}|K+2)_{J_2=1}=(K+2|H^{(2)\prime}|K)_{J_2=1}=(\hbar^2/2A_0)\{\alpha_i\gamma_i(+2)(2f-6(K+1)^2)+\alpha_i\alpha_i(+2)\\
&\quad\times(f-(K+1)(K+2))^{\frac12}(f-(K+2)(K+3))^{\frac12}-2\beta_i\beta_i(+2)(f-K(K+1))^{\frac12}(f-(K+1)(K+2))^{\frac12}\\
&\qquad\qquad+\gamma_i\gamma_i(+2)(f-K(K-1))^{\frac12}(f-K(K+1))^{\frac12}\}R_7', \qquad (28)
\end{aligned}$$

where $R_7(\nu_3+\nu_4)=(\hbar/16A_0)(\zeta_{23}^2/\omega_3+\zeta_{24}^2/\omega_4)$.

$$
\begin{aligned}
(K|H^{(2)\prime}|K+4)_{J_2=1}&=(K+4|H^{(2)\prime}|K)_{J_2=1}=(\hbar^2/2A_0)\{(f-(K+1)(K+2))^{\frac{1}{2}}(f-(K+2)(K+3))^{\frac{1}{2}}\}\\
&\times\{\alpha_i\gamma_i(+4)(-\tfrac{1}{2}R_3'+R_4'/4)+2^{\frac{1}{2}}[\alpha_i\beta_i(+4)(f-(K+3)(K+4))^{\frac{1}{2}}+\beta_i\gamma_i(+4)\\
&\times(f-K(K+1))^{\frac{1}{2}}]R_6'-[\alpha_i\alpha_i(+4)(f-(K+3)(K+4))^{\frac{1}{2}}(f-(K+4)(K+5))^{\frac{1}{2}}+\beta_i\beta_i(+4)\\
&\times(f-K(K+1))^{\frac{1}{2}}(f-(K+3)(K+4))^{\frac{1}{2}}+\gamma_i\gamma_i(+4)(f-K(K+1))^{\frac{1}{2}}(f-K(K-1))^{\frac{1}{2}}](R_5'/2)\},
\end{aligned}
\tag{29}
$$

$$
(K|H^{(2)\prime}|K)_{J_2=0}=(\hbar^2/2A_0)\{R_0''+fR_1''+f^2R_2''+(6fK^2-5K^2-7K^4)R_3''\},
\tag{30}
$$

where:

$$
\begin{aligned}
R_0''(\nu_3+\nu_4)=&(A_0/2)\{21(d_1+d_5)+7(d_6+d_{10})+11d_3+2d_8+14d_{11}+5(d_{18}+d_{20}+d_{21}+d_{27})\\
&+10(d_{22}+d_{28})-(5/2)(d_{23}+d_{29})+3(d_{30}+d_{31}+3d_{33})\}-9/4+2(\zeta_3-\zeta_4)^2-\zeta_{34}^2\\
&+(5/2)[(\omega_3/\omega_4)+(\omega_4/\omega_3)]\zeta_{34}^2(5/4)[(\omega_2/\omega_3)+(\omega_3/\omega_2)]\zeta_{23}^2+(5/4)[(\omega_2/\omega_4)\\
&+(\omega_4/\omega_2)]\zeta_{24}^2\}-(A_0/4)\{(5/3)(c_1^2/\omega_3+c_4^2/\omega_4)+c_1c_3/3\omega_3+c_2c_4/3\omega_4\\
&+(4\omega_3+7\omega_4)c_2^2/\omega_4(2\omega_3+\omega_4)+(4\omega_4+7\omega_3)c_3^2/\omega_3(2\omega_4+\omega_3)+5(10\omega_3+7\omega_1)c_5^2/(2\omega_3+\omega_1)\omega_1\\
&+5(10\omega_4+7\omega_1)c_7^2/\omega_1(2\omega_4+\omega_1)+50c_5c_7/\omega_1 30(c_{11}+c_{12})(c_5+c_7)/\omega_1+5c_6^2[2\omega_1\omega_3\omega_4\\
&+\omega_3^3(\omega_3^2-\omega_4^2-\omega_1^2)+\omega_4(\omega_4^2-\omega_3^2-\omega_1^2)+\omega_1(\omega_1^2-\omega_3^2-\omega_4^2)]/(\omega_1^4+\omega_3^4+\omega_4^4\\
&-2\omega_1^2\omega_3^2-2\omega_1^2\omega_4^2-2\omega_3\omega_4)+c_9^2[5\omega_3(\omega_3^2-\omega_4^2-\omega_2^2)+5\omega_4(\omega_4^2-\omega_3^2-\omega_2^2)\\
&+9\omega_2(\omega_2^2-\omega_3^2-\omega_4^2)+2\omega_2\omega_3\omega_4]/(\omega_2^4+\omega_3^4+\omega_4^4-2\omega_2^2\omega_3^2-2\omega_2^2\omega_4^2-2\omega_3^2\omega_4^2)\\
&+2(4\omega_3+7\omega_2)c_8^2/\omega_2(2\omega_3+\omega_2)+2(4\omega_4+7\omega_2)c_{10}^2/\omega_2(2\omega_4+\omega_2)-8\omega_3c_2^2/(\omega_4^2-4\omega_3^2)\\
&-8\omega_4c_3^2/(\omega_3^2-4\omega_4^2)+8c_8c_{10}/\omega_2+9c_{11}c_{12}/\omega_1+11c_{11}/\omega_1\\
&\qquad\qquad+36(\omega_1+\omega_2)c_{12}^2/\omega_1(2\omega_2+\omega_1)+5c_{13}^2/16\omega_2\},\\
R_1''(\nu_3+\nu_4)=&(\hbar/2A_0)\{(5/2)(\zeta_{23}^2/\omega_3+\zeta_{24}^2/\omega_4)+1/\omega_2+2/\omega_1+(10/3)(\omega_3-\omega_4)^2\zeta_{34}^2/\omega_3\omega_4(\omega_3+\omega_4)\\
&+(\hbar/A_0\omega_2^2)+[(5\omega_2^3+15\omega_2\omega_3^2-9\omega_2^2\omega_3-3\omega_3^3)\zeta_{23}^2/3\omega_2\omega_3(\omega_2^2-\omega_3^2)]\\
&+(2A_0/3\omega_1^3)^{\frac{1}{2}}(c_5+c_7+3c_{11}+3c_{12})+[(5\omega_2^3+15\omega_2\omega_4^2-9\omega_2^2\omega_4-3\omega_4^3)\zeta_{24}^2/3\omega_2\omega_4(\omega_2^2-\omega_4^2)]\},
\end{aligned}
$$

$R_2''(\nu_3+\nu_4)=R_2'(\nu_3+\nu_4)$; $R_3''(\nu_3+\nu_4)=R_5'(\nu_3+\nu_4)$.

$$
(K|H^{(2)\prime}|K+2)_{J_2=0}=(K+2|H^{(2)\prime}|K)_{J_2=0}=0.
\tag{31}
$$

$$
\begin{aligned}
(K|H^{(2)\prime}|K+4)_{J_2=0}&=(K+4|H^{(2)\prime}|K)_{J_2=0}=-(\hbar^2/2A_0)(f-K(K+1))^{\frac{1}{2}}\\
&\times(f-(K+1)(K+2))^{\frac{1}{2}}(f-(K+2)(K+3))^{\frac{1}{2}}(f-(K+3)(K+4))^{\frac{1}{2}}(R_3''/2).
\end{aligned}
\tag{32}
$$

IV. Conclusions

The discussion which has here been given in general and applied to the overtones $2\nu_3$ and $2\nu_4$ and the combination frequency $\nu_3+\nu_4$ may readily be applied also to higher overtones and combination bands also. From the formulae in Section II the first-order Coriolis splittings may at once be evaluated. Also the wave functions are obtainable since the elements of the additional transformation matrices required to set up the basic wave functions may be calculated from the formula (5) of Section 14[3] given in reference 2. The calculation of the elements of the matrix $H^{(2)\prime}$, however, becomes an increasingly laborious and tedious task.

It is interesting to note that the Coriolis resonance interaction becomes of increasing importance as one goes to higher vibration states so that the fine structure of the rotation lines may be expected to become increasingly prominent in the higher harmonics and combination bands.