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

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A complete theory for the rotation-vibration energies of tetrahedrally pentatomic molecules has been derived to second degree of approximation for certain vibration states. In this discussion the elements of the matrix H are given 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 $\nu_2+\nu_4$. The selection rules governing what transitions may take place have been determined with relations for the intensities.

I. INTRODUCTION

THE band spectra of tetrahedrally symmetric molecules, of which methane is a typical example, have long been known to possess anomalies in their rotational structure. Not only does the value of the moment of inertia A_0, computed from the rotational line separation $\Delta\nu$ by the relation $A_0=(h/4\pi^2\Delta\nu)$, vary from band to band, but recent measurements[1] have shown that the rotation lines themselves are not single lines, but show multiplet structure. The first effect has been explained in a theory originally proposed by Teller[2] and subsequently enlarged upon by Johnston and Dennison[3] which shows that the Coriolis interactions between rotation and the threefold degenerate oscillations yield corrections to the energies of these states so significant that the relation for A_0 becomes $(\zeta h/4\pi^2\Delta\nu)$ where ζ is a constant, varying from band to band, which depends upon the nature of the normal vibration and may be substantially different from unity. The second effect has, for the frequency ν_4, been accounted for by Jahn[4] who attributes this splitting principally to a Coriolis interaction between the optically active frequency ν_4 and the optically inactive vibration ν_2. The work of Jahn does not, however, take into account any of the other kinds of interactions which may be present, such as the centrifugal expansion of the molecule, the Coriolis interactions between more remotely separated vibration frequencies and the effects of the anharmonicity of the oscillational motion, all of which are indicated by experiment to be of considerable importance. Jahn's work serves essentially to emphasize the importance of obtaining a complete theory for the energies of such polyatomic models where all second-order effects are taken into account.

In a recent paper[5] we have made just such calculations for non-linear triatomic molecules and have given explicit expressions for the elements of the energy matrix for the general rotation-vibration state. In principle it is possible to make such calculations also for the tetrahedrally symmetric model, but in practice it is not feasible to do so and it becomes necessary to treat each vibration state as a separate case. We have determined the elements of the energy matrix accurately to second order of approximation for the states $V_1\nu_1$, ν_2, $V_1\nu_1+\nu_3$, $V_1\nu_1+\nu_4$, $\nu_2+\nu_3$, $\nu_2+\nu_4$, $2\nu_3$, $2\nu_4$ and $\nu_3+\nu_4$. In this paper we desire to set down our results for the first six of the above states, leaving for a Part II the discussion of the states $2\nu_3$, $2\nu_4$ and the combination states between ν_3 and ν_4.

II. DERIVATION OF THE SCHRÖDINGER EQUATION

The orientation is a system of body-fixed coordinates x, y, z of the model which we shall refer to herein is illustrated in Fig. 1. In their equilibrium positions, the four identical Y

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[1] W. B. Steward and H. H. Nielsen, Phys. Rev. **47**, 878 (1935); W. B. Steward and H. H. Nielsen, Phys. Rev. **48**, 862 (1935); A. H. Nielsen and H. H. Nielsen, Phys. Rev. **48**, 864 (1935).

[2] E. Teller, *Hand und Jahrbuch Chem. Phys.* **9**, II, 43 (1934).

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

[4] H. A. Jahn, Proc. Roy. Soc. **A168**, 469 (1938).

[5] W. H. Shaffer and H. H. Nielsen, Phys Rev. **56**, 188 (1939).

particles of masses m_1 lie at the corners of a regular tetrahedron, of which the edges have a length $2(2)^{\frac{1}{2}}a$, and the X particle of mass m_5 is situated at the center of mass of the Y particles. From Fig. 1 the equilibrium positions of the five particles will be seen to be the following: 1, $(a, -a, -a)$; 2, $(-a, a, -a)$; 3, $(-a, -a, a)$; 4, (a, a, a); 5, $(0, 0, 0)$.

The kinetic energy of the molecule expressed in the coordinates x, y and z will be:

$$T=\tfrac{1}{2}\{\sum_{s=1}^{5}m_s(\dot{x}_s^2+\dot{y}_s^2+\dot{z}_s^2)+\sum_{\alpha}A_\alpha\omega_\alpha^2 -\sum_{\alpha\beta}{}'D_{\alpha\beta}\omega_\alpha\omega_\beta+2\sum_{\alpha}\Omega_\alpha\omega_\alpha\}, \quad (1)$$

α and β being summed over the values x, y and z and the prime associated with the summation $\alpha\beta$ meaning that $\alpha\neq\beta$. In the above the x_s, y_s and z_s are the instantaneous values of the coordinates of the particles; A_α and D_α are respectively the moments and products of inertia; Ω_α are the internal angular momenta, their values being:

$$A_\alpha=\sum_{s=1}^{5}m_s(\beta_s^2+\dot{\gamma}_s^2), \quad D_{\alpha\beta}=\sum_{s=1}^{5}m_s\alpha_s\beta_s, \quad \Omega_\alpha=\sum_{s=1}^{5}m(\dot{\beta}_s\delta\gamma_s-\dot{\gamma}_s\delta\beta_s). \quad (2)$$

The ω_α are the components of the angular velocities along the axes x, y and z and the $\delta\alpha$ in the above are the displacements of the atoms from their rest positions in the x, y and z directions.

To be useful in deriving the Schrödinger equation Eq. (1) must be expressed in terms of the normal coordinates. To obtain these it will be necessary briefly to consider the problem of the oscillation of the molecule in the body-fixed coordinates. There are in all nine degrees of oscillational freedom for this type of molecule so that the above coordinates are not all independent. It is convenient, therefore, to introduce the nine intermediate coordinates which are related to the x_s, y_s and z_s by the relations:

$$\begin{aligned}
x_1&=a+\tfrac{1}{2}(\mu_1/m_1)\xi_1+\tfrac{1}{2}\zeta_1-\tfrac{1}{2}\eta_3-\tfrac{1}{2}\eta_2,\\
x_2&=-a+\tfrac{1}{2}(\mu_1/m_1)\xi_1-\tfrac{1}{2}\zeta_1+\tfrac{1}{2}\eta_3-\tfrac{1}{2}\eta_2,\\
x_3&=-a+\tfrac{1}{2}(\mu_1/m_1)\xi_1-\tfrac{1}{2}\zeta_1+\tfrac{1}{2}\eta_3+\tfrac{1}{2}\eta_2, \qquad (3)\\
x_4&=a+\tfrac{1}{2}(\mu_1/m_1)\xi_1+\tfrac{1}{2}\zeta_1-\tfrac{1}{2}\eta_3+\tfrac{1}{2}\eta_2,\\
x_5&=-2(\mu_1/m_5)\xi_1.
\end{aligned}$$

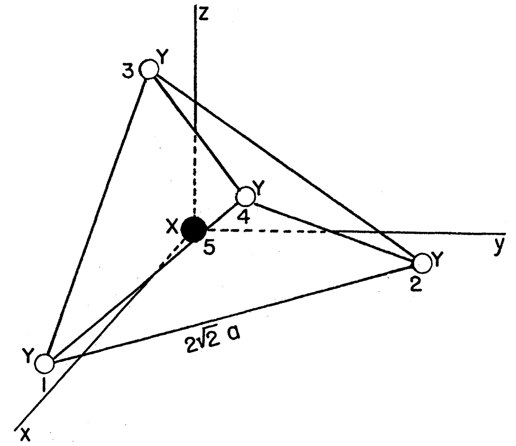

FIG. 1. The orientation in a system of body-fixed coordinates x, y, z of the pentatomic molecule.

The corresponding y_s and z_s are obtained from (3) simply by replacing the coordinates $(\xi_1, \zeta_1, \eta_3, \eta_2)$ by $(\xi_2, \eta_3, \zeta_2, \eta_1)$ and $(\xi_3, \eta_2, \eta_1, \zeta_3)$, respectively, with appropriate changes in the equilibrium coordinates. In the above μ_1 is substituted for $m_1m_5/(4m_1+m_5)$. It may readily be verified that these conform to the usual requirements that the centroid shall remain fixed and that to zeroth approximation the angular momentum in the coordinates x, y and z shall be zero.

We must next select a function for the harmonic portion of the potential energy. To do so we proceed as follows: We denote by S_{ij} the distance between two particles i and j and by δ_{ij} their relative displacements from their positions of equilibrium so that $S_{ij}=S_{ij}^0+\delta_{ij}$. We shall adopt the perfectly general quadratic function of the displacement coordinates δ_{ij}

$$\begin{aligned}
V_0=\tfrac{1}{2}\{&\tfrac{1}{2}K_1\sum_{i=1}^{4}\sum_{j=1}^{4}{}'\delta_{ij}^2+K_2\sum_{k=1}^{4}\delta_{k5}^2\\
&+\tfrac{1}{4}K_3\sum_{i=1}^{4}\sum_{j=1}^{4}{}'\sum_{k=1}^{4}{}''\delta_{ij}(\delta_{ik}+\delta_{jk})\\
&+\tfrac{1}{2}K_4\sum_{j=1}^{4}\sum_{k=1}^{4}{}'\delta_{j5}\delta_{k5}+\tfrac{1}{2}K_5\sum_{i=1}^{4}\sum_{j=1}^{4}{}'\delta_{ij}(\delta_{j5}+\delta_{i5})\\
&+\tfrac{1}{4}K_6\sum_{i=1}^{4}{}'\sum_{j=1}^{4}{}''\sum_{k=1}^{4}{}'''\sum_{l=1}^{4}{}''''\delta_{ij}\delta_{kl}\\
&+\tfrac{1}{2}K_7\sum_{i=1}^{4}\sum_{j=1}^{4}{}'\sum_{k=1}^{4}{}''\delta_{ij}\delta_{k5}\} \qquad (4)
\end{aligned}$$

as the one suitable for our problem. In (4) the single and double primes are used to indicate that no two indices may simultaneously take the same values. The K's are the force constant factors. When δ_{ij} are expressed in the intermediate coordinates one obtains for (4):

$$V_0=\tfrac{1}{2}\{k_1\sum_{i=1}^{3}\xi_i^2+2k_2\sum_{i=1}^{3}\eta_i\xi_i+k_3\sum_{i=1}^{3}\eta_i^2+k_4\sum_{i=1}^{3}\zeta_i^2+k_5\sum_{\substack{i=1\\j=1}}^{3}{}'\zeta_i\zeta_j\},\quad(5)$$

where the constants

$$\begin{aligned}k_1&=(K_2/3)-(K_4/6),\\ 2k_2&=(4K_2/3)-(2K_4/3)+(4K_5/6^{\frac12})-(4K_7/6^{\frac12}),\\ k_3&=4K_1+(4K_2/3)-2K_3-(2K_4/3)\\&\quad+(8K_5/6^{\frac12})-2K_6-(8K_7/6^{\frac12}),\quad(6)\\ k_4&=2K_1+(K_2/3)+3K_3+\tfrac12K_4\\&\quad+(4K_5/6^{\frac12})+K_6+(4K_7/6^{\frac12}),\\ 2k_5&=2K_1+7K_3+K_4+(8K_5/6^{\frac12})\\&\quad+K_6+(8K_7/6^{\frac12}).\end{aligned}$$

The actual normal coordinates, which we shall designate by $q_1, q_2, \cdots q_9$, are simple linear combinations of the intermediate coordinates (3). In fact it is readily verified that oscillational kinetic and potential energies take the following simple form

$$T_v+V_0=\tfrac12\{\sum_{i=1}^{3}(\dot q_i^2/\omega_3+\omega_3q_i^2)+\sum_{j=4}^{6}(\dot q_j^2/\omega_4+\omega_4q_j^2)+\sum_{k=7}^{8}(\dot q_k^2/\omega_2+\omega_2q_k^2)+(\dot q_9^2/\omega_1+\omega_1q_9^2),\quad(7)$$

where the intermediate coordinates ξ_i, η_i and ζ_i are taken to be the following linear combinations of q_i:

$$\begin{aligned}\xi_l&=(\mu_1)^{-\frac12}(q_l\cos\gamma/\omega_3^{\frac12}+q_{l+3}\sin\gamma/\omega_4^{\frac12}),\\ \eta_l&=(2m_5)^{-\frac12}(-q_l\sin\gamma/\omega_3^{\frac12}+q_{l+3}\cos\gamma/\omega_4^{\frac12}),\quad(7)\\ \zeta_l&=(3m_5)^{-\frac12}(u_\alpha(2)^{\frac12}+q_9/\omega_1^{\frac12}),\end{aligned}$$

where the index l takes the values 1, 2 and 3 and α takes, respectively, the values x, y and z. For the sake of brevity the following notation has been adopted: $u_\alpha=\omega_2^{-\frac12}(q_7\cos\epsilon_l+q_8\sin\epsilon_l)$, $\epsilon_l=\epsilon_1+2\pi(l-1)/3$ where ϵ_1 is arbitrary;

$$\left.\begin{matrix}\sin\gamma\\ \cos\gamma\end{matrix}\right\}=\mp(2)^{-\frac12}\{1\mp[(2m_5k_1-\mu_1k_3)^2/(8\mu_1m_5k_2^2-(2m_5k_1-\mu_1k_3)^2)]^{\frac12}\}^{\frac12},$$

$$\omega_{1,\,2}=2\pi\nu_{1,\,2}=\{[k_4+(k_5/2)(1\pm3)]/m_5\}^{\frac12},$$

$$\omega_{3,\,4}=2\pi\nu_{3,\,4}=\{((\mu_1k_3+2m_5k_1)\pm[(\mu_1k_3-2m_5k_1)^2+8\mu_1m_5k_2^2]^{\frac12})/4\mu_1m_5\}^{\frac12}.$$

To carry our calculations to the desired approximation, contributions to the energy from the anharmonic terms in the potential energy, cubic and quartic in the coordinates must be taken into account. These have also been chosen as perfectly general functions of the coordinates which are tetrahedrally symmetric. They have been designated by V_1 and V_2 and are the following:

TABLE I. *Basic transformation functions S_ρ required to remove the types of terms occurring in $H^{(1)\prime}$ together with the corresponding values of $i(H^0S_\rho-S_\rho H^{(0)})$.*

ρ	S_ρ	$i(H^{(0)}S_\rho-S_\rho H^{(0)})$
1	$(-p_k/h\nu_k)$	q_k
2	$(q_k/h\nu_k)$	p_k
3	$(-2/h\nu_k)(p_k^3/3+\frac12q_kp_kq_k)$	q_k^3
4	$(1/h)(\nu_sq_rq_s+\nu_rp_rp_s)/(\nu_r^2-\nu_s^2)$[1]	q_rp_s
5	$-\{(2\nu_r^2-\nu_s^2)q_r^2p_s+\nu_r\nu_s(q_rp_r+p_rq_r)q_s+2\nu_r^2p_r^2p_s\}/h\nu_s(4\nu_r^2-\nu_s^2)$	$q_r^2q_s$
6	$-\{\nu_r(\nu_r^2-\nu_s^2-\nu_t^2)p_rq_sq_t+\nu_s(\nu_s^2-\nu_r^2-\nu_t^2)q_rp_sq_t-2\nu_r\nu_s\nu_tp_rp_sp_t+\nu_t(\nu_t^2-\nu_r^2-\nu_s^2)q_rq_sq_t\}h^{-1}(\nu_r^4+\nu_s^4+\nu_t^4-2\nu_r^2\nu_s^2-2\nu_t^2\nu_s^2-2\nu_r^2\nu_t^2)^{-1}$	$q_rq_sq_t$
7	$(q_rq_s+p_rp_s)/h(\nu_r-\nu_s)$	$q_rp_s-p_rq_s$

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[1] S_4 is the function which removes from $H^{(1)}$ the Coriolis interaction terms which are of the type $(q_rp_s-p_rq_s)P_\alpha$. When these terms originate with degenerate oscillations the difference $\nu_r-\nu_s$ occurring in the denominator vanishes. Obviously such terms cannot be removed from $H^{(1)}$ by this method.

$$
\begin{aligned}
V_1 = {} & C_1 q_1 q_2 q_3 + C_2(q_1q_2q_6 + q_1q_3q_5 + q_2q_3q_4) + C_3(q_1q_5q_6 + q_2q_4q_6 + q_3q_4q_5) + C_4 q_4q_5q_6 + C_5(q_1^2+q_2^2+q_3^2)q_9 \\
& + C_6(q_1q_4+q_2q_5+q_3q_6)q_9 + C_7(q_4^2+q_5^2+q_6^2)q_9 + C_8(u_xq_1^2+u_yq_2^2+u_zq_3^2) \\
& + C_9(u_xq_1q_4+u_yq_2q_5+u_zq_3q_6) + C_{10}(u_xq_4^2+u_yq_5^2+u_zq_6^2) + C_{11}q_9^3 \\
& + C_{12}(u_x^2+u_y^2+u_z^2)q_9 + C_{13}u_xu_yu_z, \\
V_2 = {} & d_1(q_1^4+q_2^4+q_3^4) + d_2(q_1^3q_4+q_2^3q_5+q_3^3q_6) + d_3(q_1^2q_4^2+q_2^2q_5^2+q_3^2q_6^2) + d_4(q_1q_4^3+q_2q_5^3+q_3q_6^3) \\
& + d_5(q_4^4+q_5^4+q_6^4) + d_6(q_1^2q_2^2+q_2^2q_3^2+q_1^2q_3^2) + d_7(q_1q_4q_2^2+q_1^2q_2q_5+q_2q_5q_3^2+q_2^2q_3q_6 \\
& + q_3q_6q_1^2+q_3^2q_1q_4) + d_8(q_1q_2q_4q_5+q_2q_3q_5q_6+q_3q_1q_4q_6) + d_9(q_4^2q_2q_5+q_1q_4q_5^2+q_2q_5q_6^2+q_3q_5^2q_6 \\
& + q_3q_6q_4^2+q_6^2q_1q_4) + d_{10}(q_4^2q_5^2+q_5^2q_6^2+q_4^2q_6^2) + d_{11}(q_1^2q_5^2+q_1^2q_6^2+q_2^2q_6^2+q_2^2q_4^2+q_3^2q_4^2+q_3^2q_5^2) \\
& + d_{12}q_9(q_1q_2q_3) + d_{13}(q_2q_3q_4+q_1q_3q_5+q_1q_2q_6)q_9 + d_{14}(q_3q_4q_5+q_2q_4q_6+q_1q_5q_6)q_9 + d_{15}q_4q_5q_6q_9 \\
& + d_{16}(u_xq_2q_3q_4+u_yq_1q_3q_5+u_zq_1q_2q_6) + d_{17}(u_xq_1q_5q_6+u_yq_2q_4q_6+u_zq_3q_4q_5) + d_{18}q_9^2(q_1^2+q_2^2+q_3^2) \\
& + d_{19}q_9^2(q_1q_4+q_2q_5+q_3q_6) + d_{20}q_9^2(q_4^2+q_5^2+q_6^2) + d_{21}(u_x^2q_1^2+u_y^2q_2^2+u_z^2q_3^2) \\
& + d_{22}[u_x^2(q_2^2+q_3^2)+u_y^2(q_1^2+q_3^2)+u_z^2(q_1^2+q_2^2)] + d_{23}(u_xu_yq_3^2+u_xu_zq_2^2+u_yu_zq_1^2) \\
& + d_{24}(u_x^2q_1q_4+u_y^2q_2q_5+u_z^2q_3q_6) + d_{25}[u_x^2(q_1q_5+q_3q_6)+u_y^2(q_3q_6+q_1q_4)+u_z^2(q_1q_4+q_2q_5)] \\
& d_{26}(u_xu_yq_3q_6+u_xu_zq_2q_5+u_yu_zq_1q_4) + d_{27}(u_x^2q_4^2+u_y^2q_5^2+u_z^2q_6^2) + d_{29}(u_xu_yq_6^2+u_xu_zq_5^2+u_yu_zq_4^2) \\
& + d_{28}(u_x^2(q_5^2+q_6^2)+u_y^2(q_4^2+q_6^2)+u_z^2(q_4^2+q_5^2)) + d_{30}q_9^4 + d_{31}q_9^2(u_x^2+u_y^2+u_z^2) \\
& + d_{32}u_xu_yu_zq_9 + d_{33}(u_x^4+u_y^4+u_z^4).
\end{aligned}
\tag{8}
$$

When the complete kinetic and potential energies have been written down in terms of the normal coordinates and expressed in the Hamiltonian form, one may proceed directly to obtain the Schrödinger equation. We have made use of the method of Wilson and Howard[6] and later verified the results by the variational method of Schrödinger. We shall give none of the intermediate details here, but set down directly the appropriate quantum mechanical Hamiltonian expressed in orders of magnitude. It is the following:

$$H^0 = (P^2/2A_0) + \pi\nu_3\sum_{i=1}^{3}(p_i^2+q_i^2) + \pi\nu_4\sum_{j=4}^{6}(p_j^2+q_j^2) + \pi\nu_2\sum_{k=7}^{8}(p_k^2+q_k^2) + \pi\nu_1(p_9^2+q_9^2), \tag{9a}$$

where p_s is the differential operator $-i\hbar(\partial/\partial q_s)$, P, the total angular momentum operator and A_0 the constant part of the moments of inertia.

$$H^{(1)} = -(\sum_\alpha p_\alpha P_\alpha/A_0) + \sum_\alpha E_\alpha P_\alpha^2 + \tfrac{1}{2}\sum_{\alpha\beta}{}' F_{\alpha\beta}(P_\alpha P_\beta) - i\hbar(3\pi\nu_1/A_0)^{\frac{1}{2}}p_9 + V_1. \tag{9b}$$

The summation α and β is over x, y, z, and the prime indicating that no two indices may at the same time take the same value. In the above $E_\alpha = (3A_0^3)^{-\frac{1}{2}}[\omega_2^{-\frac{1}{2}}u_\alpha - 2(2\omega_1)^{-\frac{1}{2}}q_9]$ and $F_{\alpha\beta} = F_{\beta\alpha} = (m_5/2A_0^3)^{\frac{1}{2}}\eta_r$, r taking the values 1, 2 and 3 with $\alpha\beta$ equal to yz, xz and xy, respectively. The quantity p_x is equal to:

$$
\begin{aligned}
p_x = {} & \zeta_3(q_2p_3 - q_3p_2) + \zeta_4(q_5p_6 - q_6p_5) + \zeta_{34}[(\nu_4/\nu_3)^{\frac{1}{2}}(q_2p_6 - q_6p_2) + (\nu_3/\nu_4)^{\frac{1}{2}}(q_5p_3 - q_6p_2)] \\
& + \zeta_{23}[(\nu_3/\nu_2)^{\frac{1}{2}}v_xp_1 - (\nu_2/\nu_3)^{\frac{1}{2}}q_1p_{v_x}] - \zeta_{24}[(\nu_4/\nu_2)^{\frac{1}{2}}v_xp_4 - (\nu_2/\nu_4)^{\frac{1}{2}}q_4p_{v_x}],
\end{aligned}
$$

p_y and p_z being, respectively, obtained by cyclicly rotating the coordinates q_1, q_2, q_3; the coordinates q_4, q_5, q_6; the momenta p_1, p_2, p_3 and p_4, p_5, p_6 in the relation p_x. For the sake of brevity the notation

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[6] E. Bright Wilson and J. B. Howard, J. Chem. Phys. **4**, 260 (1936).

$v_\alpha = q_7 \sin \epsilon_r - q_8 \cos \epsilon_r$ and $p_{v_\alpha} = p_7 \sin \epsilon_r - p_8 \cos \epsilon_r$, $\zeta_3 = (1-(3/2)\sin^2\gamma)$, $\zeta_4 = (1-(3/2)\cos^2\gamma)$, $\zeta_{23} = \sin\gamma$, $\zeta_{24} = \cos\gamma$ and $\zeta_{34} = (3/2)\zeta_{23}\zeta_{24}$ is introduced.

$$H^{(2)} = C + \sum_\alpha G_\alpha P_\alpha{}^2 + \tfrac{1}{2}\sum_{\alpha\beta}{}' H_{\alpha\beta} P_\alpha P_\beta + \sum_\alpha I_\alpha P_\alpha + \sum_\alpha (p_\alpha{}^2/2A_0) + V_2, \tag{9c}$$

where

$$\begin{aligned} C = (i\hbar/4A_0)\{ &(q_1p_1+q_2p_2+q_3p_3)\zeta_{23}{}^2 + (q_4p_4+q_5p_5+q_6p_6)\zeta_{24}{}^2 - (4/3)\zeta_{34}[(\nu_3/\nu_4)^{\frac{1}{2}}(q_4p_1+q_5p_2+q_6p_3) \\ &+ (\nu_4/\nu_3)^{\frac{1}{2}}(q_1p_4+q_2p_5+q_3p_6)] + q_7p_7+q_8p_8+4q_9p_9\}, \end{aligned}$$

$$\begin{aligned} G_x = (4\pi A_0{}^2)^{-1}\{ &(\zeta_{23}{}^2/\nu_3)(q_1{}^2-(q_2{}^2/4)+(3q_3{}^2/4)) + (\zeta_{24}{}^2/\nu_4)(q_4{}^2-(q_5{}^2/4)+(3q_6{}^2/4)) + (u_x{}^2/\nu_2) \\ &+ (2/\nu_1)q_9{}^2 + (4/3)(\nu_3\nu_4)^{-\frac{1}{2}}\zeta_{34}(-q_1q_4+(1/4)q_2q_5-(3/4)q_3q_6) - 2(2/\nu_1\nu_2)^{\frac{1}{2}}u_xq_9\}, \end{aligned}$$

$$\begin{aligned} H_{xy} = (4\pi A_0{}^2)^{-1}\{ &(-\zeta_{34}/2)(\nu_3\nu_4)^{-\frac{1}{2}}(q_1q_5+q_2q_4) + (3\zeta_{23}{}^2/4\nu_3)q_1q_2 + (3\zeta_{24}/4\nu_4)q_4q_5 \\ &- [(\zeta_{24}{}^2/\nu_4)^{\frac{1}{2}}q_6 - (\zeta_{23}/\nu_3)^{\frac{1}{2}}q_3][(6/\nu_1)^{\frac{1}{2}}q_9 + (3/4\nu_2)^{\frac{1}{2}}u_z]\}, \end{aligned}$$

$$\begin{aligned} I_x = -(2\pi A_0{}^3)^{-\frac{1}{2}}\{ &[(4/3\nu_2)^{\frac{1}{2}}u_x - (8/3\nu_1)^{\frac{1}{2}}q_9]p_x + [(\zeta_{24}{}^2/\nu_4)^{\frac{1}{2}}q_6 - (\zeta_{23}{}^2/\nu_3)^{\frac{1}{2}}q_3]p_y \\ &+ [(\zeta_{24}{}^2/\nu_4)^{\frac{1}{2}}q_5 - (\zeta_{23}{}^2/\nu_3)^{\frac{1}{2}}q_2]p_z\}. \end{aligned}$$

The quantities G_y, G_z, H_{yz}, H_{xz}, I_y and I_z may be obtained from the above by cyclically rotating u_x, u_y, u_z; p_x, p_y, p_z; q_1, q_2, q_3; q_4, q_5, q_6.

III. Determination of the Eigenfunctions and Eigenvalues

The Schrödinger equation corresponding to (9a) is separable in the coordinates and has the eigenfunction:

$$\Psi^0(n_1,n_2,\text{—}n_9,\ J,K,M) = N\ R(J,K,M)\Phi(n_1,n_2,n_3) \times \Phi(n_4,n_5,n_6)\Phi(n_7,n_8)\Phi(n_9) \tag{10}$$

where $R(J, K, M)$ is the wave function of the spherical top, $\Phi(n_1, n_2, n_3)$ and $\Phi(n_4, n_5, n_6)$ the eigenfunctions of two three-dimensionally isotropic oscillators of frequencies ν_3 and ν_4, respectively; $\Phi(n_7, n_8)$, the wave function of a two-dimensionally isotropic oscillator of frequency ν_2 and $\Phi(n_9)$ is the wave function of a linear oscillator. The n_s are all integers and may be regarded as the vibration quantum numbers associated with the coordinates q_s. N is a normalization factor. The zeroth order eigenvalues become:

$$\begin{aligned} E^0(V_1, V_2, V_3, V_4, J) = &(V_1+\tfrac{1}{2})h\nu_1 \\ &+ (V_2+1)h\nu_2 + (V_3+\tfrac{3}{2})h\nu_3 \\ &+ (V_4+\tfrac{3}{2})h\nu_4 + J(J+1)h^2/8\pi^2A_0, \end{aligned} \tag{11}$$

where for convenience the substitution $V_1 = n_9$, $V_2 = n_7+n_8$, $V_3 = n_1+n_2+n_3$ and $V_4 = n_4+n_5+n_6$ is made.

The evaluation of the corrections to the energy contributed by $H^{(1)}$ and $H^{(2)}$ may be effected by perturbation methods, but is a formidable undertaking when one considers the large number of terms included in $H^{(1)}$ and $H^{(2)}$ and the high degree of degeneracy of the zeroth order energies. The only terms in $H^{(1)}$ which can contribute in first approximation are the Coriolis terms arising from the oscillations ν_3 and ν_4 and a linear combination of the functions (10) can always be found such that the matrix of these will have elements only along the principal diagonal. This suggests the effectiveness of transforming H by a contact transformation[7] THT^{-1} into $H^{(0)\prime} + H^{(1)\prime} + H^{(2)\prime}$ so that $H^{(1)\prime}$ will, to second approximation, contain only the above Coriolis terms. The evaluation of the second-order energies will thus, in principle, be reduced to a first-order perturbation calculation where the wave functions to be used are the stabilized wave functions of $H^{(0)\prime}$, i.e., the linear combination of the functions (10) which diagonalize $H^{(0)\prime} + H^{(1)\prime}$.

We shall denote by $T(\lambda)$ the transformation function $e^{i\lambda S}$ (and by $T^{-1}(\lambda) = e^{-i\lambda S}$ its inverse)

---

[7] See for example, J. H. Van Vleck, Phys. Rev. **33**, 467 (1929); O. M. Johrdahl, Phys. Rev. **45**, 87 (1934).

which to second approximation may be written:

$$T=1+i\lambda S-\tfrac{1}{2}\lambda^2S^2-(i/6)\lambda^3S^3+\cdots. \quad (12)$$

The transformed Hamiltonian will become to second approximation $THT^{-1}=H'=H^{(0)\prime}+\lambda H^{(1)\prime}+\lambda^2H^{(2)\prime}$ where $H=H^{(0)}+\lambda H^{(1)}+\lambda^2H^{(2)}$. When (12) is used for T (and T^{-1}) in the above indicated transformation one obtains by equating together like powers of λ:

$$\begin{aligned}
&H^{(0)\prime}=H^{(0)},\\
&H^{(1)\prime}=H^{(1)}-i(H^{(0)}S-SH^{(0)}), \qquad (13)\\
&H^{(2)\prime}=H^{(2)}+(i/2)[S(H^{(1)}+H^{(1)\prime})\\
&\qquad\qquad -(H^{(1)}+H^{(1)\prime})S].
\end{aligned}$$

The portion of $H^{(1)}$ which we wish to remove consists of terms each of which is a function of the normal coordinates q_k (or the conjugate momenta p_k) multiplied by a coefficient which is either a constant or a function of the angular momentum operators P_α, for example ap_k and $q_kP_x^2$. When, as in the latter case, the coefficients are functions of P_α they may still be treated merely as constants since the rotational part of $H^{(0)}$ is proportional directly to the square of P, which commutes with all functions of P_α so that $(H^{(0)}P_\alpha-P_\alpha H^{(0)})=0$. In Table I is given the basic transformation functions S_ρ required to remove the types of terms occurring in $H^{(1)\prime}$ together with the corresponding values of $i(H^0S_\rho-S_\rho H^{(0)})$. The complete S function will be a sum of terms, each of which will be a basic S_ρ multiplied by an appropriate coefficient. It will contain as many elements as there are terms to be removed; each element in S being chosen to remove a single term in $H^{(1)}$.

The transformed Hamiltonian H' written in orders of magnitude becomes:

$$H^{(0)\prime}=H^{(0)}, \qquad (14a)$$

$$\begin{aligned}
H^{(1)\prime}=&-(\zeta_3/A_0)[(q_2p_3-q_3p_2)P_x+(q_3p_1-q_1p_3)P_y+(q_1p_2-q_2p_1)P_z]\\
&-(\zeta_4/A_0)[(q_5p_6-q_6p_5)P_x+(q_6p_4-q_4p_6)P_y+(q_4p_5-q_5p_4)P_z], \qquad (14b)
\end{aligned}$$

$$H^{(2)\prime}=H^{(2)}+(i/2)[S(H^{(1)}+H^{(1)\prime})-(H^{(1)}+H^{(1)\prime})S], \qquad (14c)$$

where

$$\begin{aligned}
(i/2)[S(H^{(1)}+H^{(1)\prime})-(H^{(1)}+H^{(1)\prime})S]=&\bar{V}_2+\sum_{\alpha}G'_\alpha P_\alpha{}^2+\sum_{\alpha\beta}{}'H'_{\alpha\beta}P_\alpha P_\beta+\tau_{\alpha\alpha\alpha\alpha}\sum_{\alpha}P_\alpha{}^4\\
&+\tau_{\alpha\alpha\beta\beta}\sum_{\alpha\beta}{}'(P_\alpha{}^2P_\beta{}^2)+\tau_{\alpha\beta\alpha\beta}\sum_{\alpha\beta}{}'(P_\alpha P_\beta+P_\beta P_\alpha)^2+\sum_{\alpha\beta\gamma\beta}\tau_{\alpha\beta\gamma\beta}[(P_\alpha P_\beta+P_\beta P_\alpha)(P_\gamma P_\beta+P_\beta P_\gamma)\\
&-(P_\gamma P_\beta+P_\beta P_\gamma)(P_\alpha P_\beta+P_\beta P_\alpha)]+\tau_0P^2. \qquad (14c')
\end{aligned}$$

In the above:

$$\begin{aligned}
\bar{V}_2=&(3\hbar^2/4A_0)+B(\nu_3)+B(\nu_4)+C(\nu_3)+C(\nu_4)+J(\nu_3)+J(\nu_4)+K(\nu_3)+K(\nu_4)\\
&-(c_6{}^2/4\pi)(\nu_1{}^4+\nu_3{}^4+\nu_4{}^4-2\nu_1{}^2\nu_3{}^2-2\nu_1{}^2\nu_4{}^2-2\nu_3{}^2\nu_4{}^2)^{-1}\{\nu_3(\nu_3{}^2-\nu_4{}^2-\nu_1{}^2)q_9{}^2(q_4{}^2+q_5{}^2+q_6{}^2)\\
&+\nu_4(\nu_4{}^2-\nu_3{}^2-\nu_1{}^2)q_9{}^2(q_1{}^2+q_2{}^2+q_3{}^2)+\nu_1(\nu_1{}^2-\nu_3{}^2-\nu_4{}^2)(q_1q_4+q_2q_5+q_3q_6)^2+\tfrac{3}{2}i\hbar\nu_1\nu_3\nu_4\\
&-2\nu_1\nu_3\nu_4[p_1p_4(q_2q_5+q_3q_6)+p_2p_5(q_1q_4+q_3q_6)+p_3p_6(q_1q_4+q_2q_5)]\}-(c_9{}^2/4\pi)(\nu_2{}^4+\nu_3{}^4+\nu_4{}^4\\
&-2\nu_3{}^2\nu_2{}^2-2\nu_2{}^2\nu_4{}^2-2\nu_3{}^2\nu_4{}^2)^{-1}\{\nu_3(\nu_3{}^2-\nu_4{}^2-\nu_2{}^2)(u_x{}^2q_4{}^2+u_y{}^2q_5{}^2+u_z{}^2q_6{}^2)\\
&+\nu_4(\nu_4{}^2-\nu_3{}^2-\nu_2{}^2)(u_x{}^2q_1{}^2+u_y{}^2q_2{}^2+u_z{}^2q_3{}^2)+\nu_2(\nu_2{}^2-\nu_4{}^2-\nu_3{}^2)(q_1{}^2q_4{}^2+q_2{}^2q_5{}^2+q_3{}^2q_6{}^2-q_1q_2q_4q_5\\
&-q_1q_3q_4q_6-q_2q_3q_5q_6)+\tfrac{3}{2}i\hbar\nu_2\nu_3\nu_4+\nu_2\nu_3\nu_4[p_1p_4(q_2q_5+q_3q_6)+p_1p_5(q_1q_4+q_3q_6)\\
&+p_3p_6(q_1q_4+q_2q_5)]\}-(ic_{11}{}^2/\hbar\nu_1)\{(1/3)(p_9{}^3q_9{}^3-q_9{}^3p_9{}^3)+\tfrac{1}{2}(q_9p_9q_9{}^4-q_9{}^4p_9q_8)\}\\
&-(9c_{12}{}^2/8\pi\nu_1(4\nu_2{}^2-\nu_1{}^2))\{(2\nu_2{}^2-\nu_1{}^2)(q_7{}^2+q_8{}^2)^2+2\nu_2{}^2(p_7{}^2q_8{}^2+q_7{}^2p_8{}^2)+4\nu_1\nu_2q_9{}^2(q_7{}^2+q_8{}^2)
\end{aligned}$$

Formula continued on following page

$$
\begin{aligned}
&+\nu_2^2(p_7^2q_7^2+q_7^2p_7^2+p_8^2q_8^2+q_8^2p_8^2)\}-(c_{13}^2/4\pi\nu_2)\{(i/48\hbar)(p_7^3q_7^3-q_7^3p_7^3+p_8^3q_8^3-q_8^3p_8^3)\\
&+(3/8)q_7^2q_8^2+(3/32)(q_7^4+q_8^4)-(3/16)[p_8(p_7q_7^2+q_7^2p_7)+p_7(p_8q_8^2+q_8^2p_8)+p_7^2q_8^2+p_8^2q_7^2]\\
&+(3i/16\hbar)[p_7^2q_7^2p_8q_8-q_8p_8q_7^2p_7^2+p_7^2q_7p_8q_8^2-q_8^2p_8q_7p_7^2+p_8^2q_8p_7q_7^2-q_7^2p_7q_8p_8^2+p_7q_7p_8^2q_8^2\\
&-q_8^2p_8^2q_7p_7]\}-((c_1c_3/2\pi\nu_3)+(c_2c_4/2\pi\nu_4))(q_1q_2q_4q_5+q_1q_3q_4q_6+q_2q_3q_5q_6)-(c_5c_7/2\pi\nu_1)(q_1^2+q_2^2+q_3^2)\\
&\times(q_4^2+q_5^2+q_6^2)-((3c_5c_{11}/2\pi\nu_1)q_9^2+(3c_5c_{12}/4\pi\nu_1)(q_7^2+q_8^2))(q_1^2+q_2^2+q_3^2)-((3c_7c_{11}/2\pi\nu_1)q_9^2\\
&+(3c_7c_{12}/2\pi\nu_1)(q_7^2+q_8^2))(q_4^2+q_5^2+q_6^2)-(c_8c_{10}/2\pi\nu_2)[q_4^2(q_1^2-\tfrac{1}{2}q_2^2-\tfrac{1}{2}q_3^2)+q_5^2(q_2^2-\tfrac{1}{2}q_1^2-\tfrac{1}{2}q_3^2)\\
&\qquad\qquad+q_6^2(q_3^2-\tfrac{1}{2}q_1^2-\tfrac{1}{2}q_2^2)]-(9c_{11}c_{12}/4\pi\nu_1)q_9^2(q_7^2+q_8^2),
\end{aligned}
$$

where

$$
B(\nu_3)=(-c_1^2/12\pi\nu_3)\{q_1^2q_2^2+q_1^2q_3^2+q_2^2q_3^2+(2i/\hbar)(p_1q_1p_2q_2p_3q_3-q_1p_1q_2p_2q_3p_3)\},
$$

$$
\begin{aligned}
C(\nu_3)=(c_2^2/4\pi\nu_4)(\nu_4^2-4\nu_3^2)^{-1}\{&[(q_2q_6+q_3q_5)^2+(q_1q_6+q_3q_4)^2+(q_1q_5+q_2q_4)^2]\nu_3\nu_4\\
&-(q_1^2q_2^2+q_2^2q_3^2+q_1^2q_3^2)(\nu_4^2-2\nu_3^2)+(2i\nu_3^2/\hbar)(p_1q_1p_3q_3p_5q_5+p_1q_1p_2q_2p_6q_6+p_2q_2p_3q_3p_4q_4\\
&-q_1p_1q_3p_3q_5p_5-q_1p_1q_2p_2q_6p_6-q_2p_2q_3p_3q_4p_4)\},
\end{aligned}
$$

$$
\begin{aligned}
J(\nu_3)=(-c_5^2/4\pi\nu_1)(4\nu_3^2-\nu_1^2)^{-1}\{&(2\nu_3^2-\nu_1^2)(q_1^2+q_2^2+q_3^2)^2+4\nu_1\nu_3q_9^2(q_1^2+q_2^2+q_3^2)\\
&+2\nu_3^2[p_1^2(q_2^2+q_3^2)+p_2^2(q_1^2+q_3^2)+p_3^2(q_1^2+q_2^2)]+(2i\nu_3^2/\hbar)[(p_1^2q_1^2+p_2^2q_2^2+p_3^2q_3^2)p_9q_9\\
&-q_9p_9(q_1^2p_1^2+q_2^2p_2^2+q_3^2p_3^2)]\},
\end{aligned}
$$

$$
\begin{aligned}
K(\nu_3)=(-c_8^2/4\pi\nu_2)(4\nu_3^2-\nu_2^2)^{-1}\{&(2\nu_3^2-\nu_2^2)(q_1^4+q_2^4+q_3^4-q_1^2q_2^2-q_1^2q_3^2-q_2^2q_3^2)\\
&+4\nu_2\nu_3(u_x^2q_1^2+u_y^2q_2^2+u_z^2q_3^2)-\nu_3^2[p_1(q_2^2+q_3^2)+p_2(q_1^2+q_3^2)+p_3(q_1^2+q_2^2)]\\
&+\nu_3^2[p_1^2q_1^2-q_1^2p_1^2+p_2^2q_2^2-q_2^2p_2^2]\}.
\end{aligned}
$$

The corresponding quantities for ν_4 are obtained, respectively, by replacing c_1^2 by c_4^2; c_2^2 by c_3^2; c_5^2 by c_7^2 and c_8^2 by c_{10}^2 and in addition by interchanging ν_3 by ν_4 and the coordinates and momenta q_1, q_2, q_3, p_1, p_2, p_3, respectively, by q_4, q_5, q_6, p_4, p_5, p_6. Other quantities which occur in (14c′) are

$$
\tau_{\alpha\alpha\alpha\alpha}=(-12\pi^2A_0^3)^{-1}(1/\nu_2^2+2/\nu_1^2),\quad \tau_{\alpha\alpha\beta\beta}=(2/\nu_1^2-1/2\nu_2^2),\quad \tau_{\alpha\beta\alpha\beta}=(-1/32\pi^2A_0^3)(\zeta_{24}^2/\nu_4^2+\zeta_{23}^2/\nu_3^2),
$$

$$
\begin{aligned}
\tau_{xyxz}=(-i/16\pi hA_0^3)\{&(\zeta_{24}p_6/\nu_4^{\frac{3}{2}}-\zeta_{23}p_3/\nu_3^{\frac{3}{2}})(\zeta_{24}q_5/\nu_4^{\frac{1}{2}}-\zeta_{23}q_2/v_3^{\frac{1}{2}})-(\zeta_{24}p_5/\nu_4^{\frac{3}{2}}-\zeta_{23}p_2/\nu_3^{\frac{3}{2}})\\
&\times(\zeta_{24}q_6/\nu_4^{\frac{1}{2}}-\zeta_{23}q_3/\nu_3^{\frac{1}{2}})\};
\end{aligned}
$$

$$
\tau_0=\{2c_5(q_1^2+q_2^2+q_3^2)+2c_7(q_4^2+q_5^2+q_6^2)+6c_{11}q_9^2+3c_{12}(q_7^2+q_8^2)\}(4\pi A_0^{\frac{3}{2}}(3\pi\nu_1)^{\frac{1}{2}})^{-1},
$$

$$
\begin{aligned}
G_x'=\{&(a_1/\nu_2)(q_1^2-\tfrac{1}{2}q_2^2-\tfrac{1}{2}q_3^2)+(a_2/\nu_2)(q_4^2-\tfrac{1}{2}q_5^2-\tfrac{1}{2}q_6^2)+(\zeta_{34}^2/(\nu_3^2-\nu_4^2))[(\nu_4^2+\nu_3^2)((q_5^2+q_6^2)/\nu_4\\
&-(q_2^2+q_3^2)/\nu_3)+2\nu_4(p_5^2+p_6^2)-2\nu_3(p_2^2+p_3^2)]+(\zeta_{23}^2/(\nu_2^2-\nu_3^2))[(\nu_3^2+\nu_4^2)(q_1^2/\nu_3-v_x/\nu_2)\\
&-2\nu_2p_{v_x}^2+2\nu_3p_1^2]+(\zeta_{24}^2/(\nu_2^2-\nu_4^2))[(\nu_2^2+\nu_4^2)(q_4^2/\nu_3-v_x^2/\nu_2)-2\nu_2p_{v_x}+2\nu_4p_4^2],
\end{aligned}
$$

$$
\begin{aligned}
H_{xy}'=\{&(3a_6/\nu_3)-(a_7/\nu_4)+a_{10}/(\nu_3\nu_4)^{\frac{1}{2}}+(\zeta_{34}^2/(\nu_3^2-\nu_4^2))(\nu_4^2+3\nu_3^2)/\nu_3\}q_1q_2+\{(3a_9/\nu_4)+(a_8/\nu_3)\\
&+a_{11}/(\nu_3\nu_4)^{\frac{1}{2}}-(\zeta_{34}^2/(\nu_3^2-\nu_4^2)(3\nu_4^2+\nu_3^2)/\nu_4\}q_4q_5,
\end{aligned}
$$

where for the sake of brevity the substitutions have been made:

$$
a_1=-c_8(A_0/6\pi\nu_2)^{\frac{1}{2}},\qquad a_2=-c_{10}(A_0/6\pi\nu_2)^{\frac{1}{2}},\qquad a_6=(c_1\zeta_{23}/6)(A_0/2\pi\nu_3)^{\frac{1}{2}},
$$

$$
a_7=(c_2\zeta_{24}/6)(A_0/2\pi\nu_4)^{\frac{1}{2}},\quad a_8=(c_3\zeta_{23}/2)(A_0/2\pi\nu_3)^{\frac{1}{2}},\quad a_9=(-c_4\zeta_{24}/6)(A_0/2\pi\nu_4)^{\frac{1}{2}},
$$

$$a_{10} = -\tfrac{1}{2}(A_0/2\pi)^{\frac{1}{2}}[(c_2\zeta_{24}/\nu_4^{\frac{1}{2}})(\nu_3/\nu_4)^{\frac{1}{2}} - (c_1\zeta_{23}/\nu_3^{\frac{1}{2}})(\nu_4/\nu_3)^{\frac{1}{2}}],$$

$$a_{11} = -\tfrac{1}{2}(A_0/2\pi)^{\frac{1}{2}}[(c_4\zeta_{24}/\nu_4^{\frac{1}{2}}(\nu_3/\nu_4)^{\frac{1}{2}} - (c_1\zeta_{23}/\nu_3^{\frac{1}{2}})(\nu_4/\nu_3)^{\frac{1}{2}}].$$

τ_{yxyz}, τ_{zxzy}, G_y', G_z', H_{yz}', H_{zx}' are obtained from the above by cyclic rotation of q_1, q_2, q_3; p_1, p_2, p_3; q_4, q_5, q_6; p_4, p_5, p_6; v_x, v_y, v_z; $p_{v_x}, p_{v_y}, p_{v_z}$.

We are now in a position to calculate by perturbation theory the alterations of the energy caused by the second-order Hamiltonian. We shall treat each of 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 $\nu_2+\nu_4$ separately. In doing so we shall employ the degenerate perturbation methods for while certain degeneracies have been removed those in the quantum numbers K and M still exist. The matrix $H^{(2)\prime}$ will be a step matrix with a step for each value of J. Each step will have $2J+1$ rows and columns corresponding to the $2J+1$ values of the quantum number K for a given J value. Since $H^{(2)\prime}$ contains terms which are functions of P_α the degeneracy in K is removed in this approximation so that these steps will contain elements which are nondiagonal. The elements of the matrix $H^{(2)\prime}$ are obtained for any one of the above states by evaluating the integrals

$$(\nu_j : K|H^{(2)\prime}|\nu_j : K') = \int \bar{\Psi}_{JKM}(\nu_j, s)H^{(2)\prime}\Psi_{JKM}(\nu_j, s)dv, \tag{15}$$

where $\Psi_{JKM}(\nu_j : s)$ is the stabilized wave function for the state in question.

The state $V_1\nu_1$, of which the normal state may be regarded as a special case, is entirely nondegenerate in the vibrational coordinates and the functions $\Psi_{JKM}(\nu, s)$ is simply the function (10) where all the quantum numbers V, save V_1, are set equal to zero. For these states, the only nonvanishing matrix elements are the $(K|K)$ and $(K|K\pm 4)$ elements which are given below:

$$\begin{aligned}(K|H^{(2)\prime}|K)_{V_1\nu_1} = (\hbar^2/2A_0)\{&R_0(V_1\nu_1) + J(J+1)R_1(V_1\nu_1) + J^2(J+1)^2R_2(V_1\nu_1)\\ &+[6J(J+1)K^2 - 5K^2 - 7K^4]R_3(V_1\nu_1)\},\end{aligned} \tag{16}$$

where

$$\begin{aligned}R_0(V_1\nu_1) = (1/4)\{&27/2[(\omega_3/\omega_4)+(\omega_4/\omega_3)]\zeta_{23}^2\zeta_{24}^2 + 3[(\omega_2/\omega_3)+(\omega_3/\omega_2)]\zeta_{23}^2 + 3[(\omega_2/\omega_4)+(\omega_4/\omega_2)]\zeta_{24}^2\\
&-27\zeta_{23}^2\zeta_{24}^2 - 9\} + (3A_0/2)\{3d_1+d_3+3d_5+d_6+d_{10}+2d_{11}+d_{21}+d_{22}-\tfrac{1}{2}(d_{23}+d_{29})+d_{27}\\
&+d_{28}+3d_{33}+(2V_1+1)(d_{18}+d_{20}+d_{31})+(2V_1^2+2V_1+1)d_{30}\} - (A_0/4)\{c_1^2/3\omega_3\\
&+3c_2^2/(2\omega_3+\omega_4)+3c_3^2/(2\omega_4+\omega_3)+c_4^2/3\omega_3+3(12\omega_3^2-5\omega_1^2)c_5^2/\omega_1(4\omega_3^2-\omega_1^2)\\
&+18(c_5c_7+c_5c_{12}+c_7c_{12})/\omega_1+3c_6^2[\omega_1(\omega_1^2-\omega_3^2-\omega_4^2)+2\omega_1\omega_3\omega_4]/(\omega_1^4+\omega_3^4+\omega_4^4-2\omega_1^2\omega_3^2\\
&-2\omega_1^2\omega_4^2-2\omega_3^2\omega_4^2)+3(12\nu_4^2-5\nu_1^2)c_7/\omega_1(4\omega_4^2-\omega_1^2)+6c_8^2/(2\omega_3+\omega_2)+6c_{10}^2/(2\omega_4+\omega_2)\\
&+36(2\omega_2^2-\omega_1^2)c_{12}^2/\omega_1(4\omega_2^2-\omega_1^2)+5c_{13}^2/16\omega_2+3c_9^2[\omega_3(\omega_3^2-\omega_4^2-\omega_2^2)+\omega_4(\omega_4^2-\omega_1^2-\omega_2^2)\\
&+\omega_2(\omega_2^2-\omega_3^2-\omega_4^2)+2\omega_2\omega_3\omega_4]/(\omega_2^4+\omega_3^4+\omega_4^4-2\omega_2^2\omega_3^2-2\omega_3^2\omega_4^2-2\omega_2^2\omega_4^2)\}\\
&-(2V_1+1)(A_0/2)\{9(c_5+c_7+c_{12})(c_{11}/\nu_1)+6\omega_3c_5^2/(4\omega_3^2-\omega_1^2)+6\omega_4c_7^2/(4\omega_4^2-\omega_1^2)\\
&+18\omega_2c_{12}^2/(4\omega_2^2-\omega_1^2)+(3c_6^2/2)[\omega_3(\omega_3^2-\omega_4^2-\omega_1^2)+\omega_4(\omega_4^2-\omega_3^2-\omega_1^2)]/(\omega_1^4+\omega_3^4+\omega_4^4\\
&-2\omega_1^2\omega_3^2-2\omega_1^2\omega_4^2-2\omega_3^2\omega_4^2)\} - (A_0c_{11}^2/4\omega_1)(30V_1^2+30V_1+11),\end{aligned}$$

$$\begin{aligned}R_1(V_1\nu_1) = (\hbar/A_0)\{&(5\omega_2^2-\omega_2\omega_3+2\omega_3^2)\zeta_{23}^2/4\omega_2\omega_3(\omega_2+\omega_3)+(2V_1+1)/\omega_1+(1/2\omega_2)\\
&+(5\omega_2^2-\omega_2\omega_4+2\omega_4^2)\zeta_{24}^2/4\omega_2\omega_4(\omega_2+\omega_4)+\zeta_{34}^2(\omega_3-\omega_4)^2/\omega_3\omega_4(\omega_3+\omega_4)\\
&+(3A_0/2\omega_1^3)^{\frac{1}{2}}[c_5+c_7+c_{12}+(2V_1+1)c_{11}]+(\hbar/2A_0\omega_2^2)\},\end{aligned}$$

$$R_2(V_1\nu_1)=(-\hbar^2/6A_0{}^2)\{(8/\omega_1{}^2)+(5/2\omega_2{}^2)+(3/4)(\zeta_{23}{}^2/\omega_3{}^2+\zeta_{24}{}^2/\omega_4{}^2)\},$$

$$R_3(V_1\nu_1)=(\hbar^2/4A_0{}^2)\{(1/\omega_2{}^2)-\tfrac{1}{2}(\zeta_{23}{}^2/\omega_3{}^2+\zeta_{24}{}^2/\omega_4{}^2)\}$$

and

$$(K|H^{(2)\prime}|K\pm 4)=\{[f-K(K\pm 1)][f-(K\pm 1)(K\pm 2)][f-(K\pm 2)(K\pm 3)]$$
$$\times[f-(K\pm 3)(K\pm 4)]\}^{\frac{1}{2}}(\hbar^2/4A_0)R_3(V_1\nu_1). \quad (17)$$

We have for the sake of brevity introduced the notation $f=J(J+1)$ and $\hbar=(h/2\pi)$.

The state ν_2 becomes excited when V_2 is set equal to unity. This may take place in two ways, i.e., by setting $n_7=1$, $n_8=0$ or $n_7=0$, $n_8=1$, so that this frequency is twofold degenerate. It, also, is uneffected by the presence of $H^{(1)\prime}$ and the stabilized form for that part of the wave function characteristic of ν_2 is readily formed to be:

$$\left.\begin{matrix} U(\nu_2) \\ V(\nu_2) \end{matrix}\right\}=2^{-\frac{1}{2}}\{\Phi(n_7=1,\ n_8=0)\mp\Phi(n_7=0,\ n_8=1)\}. \quad (18)$$

The degeneracy in ν_2 is removed by $H^{(2)\prime}$ and its matrix breaks up into two nearly identical steps in the vibration coordinates with the elements $U_{JKM} \vdots U_{JK'M}$ and $V_{JKM} \vdots V_{JK'M}$. The elements $U_{JKM} \vdots V_{JK'M}$ vanish identically. These steps will again be diagonal in all the rotation quantum numbers save K and the nonvanishing elements are the elements $(K|K)$ and $(K|K\pm 4)$, the values of which are given below:

$$(K|H^{(2)\prime}|K)_{\nu_2}=(\hbar^2/2A_0)\{R_0(\nu_2:1,2)+J(J+1)R_1(\nu_2:1,2)+J^2(J+1)^2R_2(\nu_2:1,2)$$
$$+[6J(J+1)K^2-5K^2-7K^4]R_3(\nu_2:1,2)+K^2R_4(\nu_2:1,2)\}, \quad (19)$$

where

$$R_0(\nu_2:1,2)=R_0(0)+(3/4)\{[(\omega_2/\omega_3)+(\omega_3/\omega_2)]\zeta_{23}{}^2+[(\omega_2/\omega_4)+(\omega_4/\omega_2)]\zeta_{24}{}^2\}$$
$$+(3A_0/2)\{d_{21}+2d_{22}+(\tfrac{1}{2}-2^{\frac{1}{2}}/6)(d_{23}+d_{29}+d_{27}+3d_{28}+d_{31}+6d_{33})\}$$
$$-(A_0/4)\{18c_7c_{12}/\omega_1+12\omega_3c_8{}^2/(4\omega_3{}^2-\omega_2{}^2)+12\omega_4c_{10}{}^2/(4\omega_4{}^2-\omega_2{}^2)+18c_{11}c_{12}/\omega_1$$
$$+36(3\omega_2+2\omega_1)c_{12}{}^2/\omega_1(2\omega_2+\omega_1)+(42\mp 12)c_{13}{}^2/16\omega_2+c_9{}^2[\omega_3(\omega_3{}^2-\omega_4{}^2-\omega_2{}^2)$$
$$+\omega_4(\omega_4{}^2-\omega_3{}^2-\omega_2{}^2)]/(\omega_2{}^4+\omega_3{}^4+\omega_4{}^4-2\omega_2{}^2\omega_3{}^2-2\omega_2{}^2\omega_4{}^2-2\omega_3{}^2\omega_4{}^2)\},$$

$$R_1(\nu_2:1,2)=R_1(0)+(\hbar/A_0\omega_2)\{(1\mp 1/8)-(\tfrac{1}{2}\pm 1/8)[(3\omega_2{}^2+\omega_3{}^2)\zeta_{23}{}^2/(\omega_2{}^2-\omega_3{}^2)$$
$$+(3\omega_2{}^2+\omega_4{}^2)\zeta_{24}{}^2/(\omega_2{}^2-\omega_4{}^2)]\},$$

$$R_2(\nu_2:1,2)=R_2(V_1\nu_1);\quad R_3(\nu_2:1,2)=R_3(V_1\nu_1),$$

$$R_4(\nu_2:1,2)=\pm(3\hbar/8A_0\omega_2)\{(3\omega_2{}^2+\omega_3{}^2)\zeta_{23}{}^2/(\omega_2{}^2-\omega_3{}^2)+(3\omega_2{}^2+\omega_4{}^2)\zeta_{24}{}^2/(\omega_2{}^2-\omega_4{}^2)+1\}$$

and

$$(K|H^{(2)\prime}|K\pm 4)_{\nu_2}=(K|H^{(2)\prime}|K\pm 4)_{V_1\nu_1}. \quad (20)$$

The state ν_3 is excited when V_3 takes the value unity. This may take place in three different ways, namely; when one of the three quantum numbers n_1, n_2, n_3 is set equal to one, so that the state ν_3 is threefold degenerate. This degeneracy is removed by $H^{(1)\prime}$ and the wave functions which we shall require for our second-order calculations are just the linear combinations of the basic functions (10) which will diagonalize $H^{(1)\prime}$. It is not difficult to show that the appropriate linear combinations of these[8] are of the form:

$$\Psi_{JKM}(\nu_3:s)=\{a_sF(\nu_3)R(K+1)+b_sG(\nu_3)+c_sH(\nu_3)R(K-1)\}\Psi(V_1V_2V_4),\quad s=I,II,III \tag{21}$$

where $F(\nu_3)$, $G(\nu_3)$ and $H(\nu_3)$ are the three linear combinations of the functions $(n_1n_2n_3)$:

$$\left.\begin{array}{l}F(\nu_3)\\ H(\nu_3)\end{array}\right\}=2^{-\frac{1}{2}}\{\Phi(n_1=1,\ n_2=n_3=0)\pm i\Phi(n_1=n_3=0,\ n_2=1)\},$$
$$G(\nu_3)=\Phi(n_1=n_2=0,\ n_3=1), \tag{22}$$

which will be recognized as the three wave functions for the three-dimensionally isotropic oscillator treated in spherical polar coordinates. The coefficients a_s, b_s and c_s are the following quantities:

$$a_I=\left\{\frac{(J-K)(J-K+1)}{2(J+1)(2J+1)}\right\}^{\frac{1}{2}},\quad b_I=\left\{\frac{(J-K+1)(J+K+1)}{(J+1)(2J+1)}\right\}^{\frac{1}{2}},\quad c_I=-\left\{\frac{(J+K)(J+K+1)}{2(J+1)(2J+1)}\right\}^{\frac{1}{2}},$$

$$a_{II}=\left\{\frac{(J-K)(J+K+1)}{2J(J+1)}\right\}^{\frac{1}{2}},\quad b_{II}=\left\{\frac{K^2}{J(J+1)}\right\}^{\frac{1}{2}},\quad c_{II}=\left\{\frac{(J+K)(J-K+1)}{2J(J+1)}\right\}^{\frac{1}{2}},$$

$$a_{III}=\left\{\frac{(J+K)(J+K+1)}{2J(2J+1)}\right\}^{\frac{1}{2}},\quad b_{III}=-\left\{\frac{(J+K)(J-K)}{J(2J+1)}\right\}^{\frac{1}{2}},\quad c_{III}=-\left\{\frac{(J-K)(J-K+1)}{2J(2J+1)}\right\}^{\frac{1}{2}}$$

and $R(K')$ are the wave functions of the spherical top. These functions lead to the well-known values for the first-order energy corrections

$$E_I^{(1)}=J\zeta_3\hbar^2/A_0,\quad E_{II}^{(1)}=-\zeta_3\hbar^2/A_0\quad\text{and}\quad E_{III}^{(1)}=-(J+1)\zeta_3\hbar^2/A_0.$$

With the aid of the function (21) where $\Psi(V_1V_2V_4)$ is set equal to $\Phi(V_1)\Phi(n_7=n_8=0)\Phi(V_4=0)$ we now evaluate the elements of the second-order matrix $H^{(2)\prime}$ for the states $V_1\nu_1+\nu_3$ of which the fundamental state is a special case where $V_1=0$. For these states the matrix $H^{(2)\prime}$ breaks up into three-step matrices with the elements $\Psi_{JKM}(V_1\nu_1+\nu_3:s)\vdots\Psi_{JKM}(V_1\nu_1+\nu_3:s)$. This will be true because the functions $\Psi_{JKM}(V_1\nu_1+\nu_3:I,II,III)$ are the eigenfunctions of $H^{(0)}+H^{(1)\prime}$ in which ν_3 is nondegenerate so that to this approximation the elements $\Psi_{JKM}(V_1\nu_1+\nu_3:s)\vdots\Psi_{JKM}(V_1\nu_1+\nu_3:r)$, $r\neq s$, may be neglected. Each step will again be diagonal in the quantum numbers J and M and will have the following nonvanishing elements in K:

$$\begin{aligned}(K|H^{(2)\prime}|K)_{V_1\nu_1+\nu_3}=(\hbar^2/2A_0)\{&R_0(V_1\nu_1+\nu_3)+fR_1(V_1\nu_1+\nu_3)+[(a_i^2+c_i^2)(f-K^2-1)-2K(a_i^2-c_i^2)\\&+2b_i^2K^2]R_3(V_1\nu_1+\nu_3)+a_ic_i[f-K(K-1)]^{\frac{1}{2}}[f-K(K+1)^{\frac{1}{2}}](R_3+R_4)\\&+2^{\frac{1}{2}}b_i[(2K+1)a_i(f-K(K+1))^{\frac{1}{2}}+(2K-1)c_i[f-K(K-1)]^{\frac{1}{2}}]R_4\\&+[6fK^2-5K^2-7K^4+2(a_i^2+c_i^2)(3f-6-21K^2)\\&+2(a_i^2-c_i^2)K(6f-19-14K^2)]R_5-[(a_i^2+c_i^2)(24K^2+9-4f)\\&+(a_i^2-c_i^2)K(8K^2+25-4f)]R_6+2^{-\frac{1}{2}}b_i[(2f-6K^2-6K-3)a_i\\&\times(f-K(K+1))^{\frac{1}{2}}-(2f-6K^2+6K-3)c_i(f-K(K-1))^{\frac{1}{2}}]R_6\},\end{aligned} \tag{23}$$

---

[8] The transformation matrix which transforms functions (10) into (21) may be obtained from Condon and Shortley, *The Theory of Atomic Spectra* (Cambridge Univ. Press, 1935), p. 76, when their discussion is made applicable to our problem. This is not surprising since the case here under consideration is just a trivial case of the vector addition of angular momenta in quantum mechanics. This method is particularly useful in obtaining the wave functions for combination states between ν_3 and ν_4 as well as for the overtones of ν_3 and ν_4.

$$
\begin{aligned}
(K|H^{(2)\prime}|K+2)=(\hbar^2/2A_0)\{&-a_ia_i(+2)[f-(K+1)(K+2)]^{\frac{1}{2}}[f-(K+2)(K+3)]^{\frac{1}{2}}\\
&+2b_ib_i(+2)[f-K(K+1)]^{\frac{1}{2}}[f-(K+1)(K+2)]^{\frac{1}{2}}c_ic_i(+2)[f-K(K-1)]^{\frac{1}{2}}\\
&\times[f-K(K+1)]^{\frac{1}{2}}+a_ic_i(+2)[2f-6(K+1)^2]\}(A_0\omega_3R_6/4\hbar), \qquad (24)
\end{aligned}
$$

$$(K+2|H^{(2)\prime}|K)=(K|H^{(2)\prime}|K+2),$$

$$
\begin{aligned}
(K|H^{(2)\prime}|K+4)=(\hbar^2/2A_0)\{&[f-(K+1)(K+2)]^{\frac{1}{2}}[f-(K+2)(K+3)]^{\frac{1}{2}}\}\{a_ic_i(+4)\\
&\times[(R_3/2)-(R_6/4)]+2^{-\frac{1}{2}}[f-(K+3)(K+4)]^{\frac{1}{2}}a_ib_i(+4)(R_6/4)\\
&-2^{-\frac{1}{2}}[f-K(K+1)]^{\frac{1}{2}}b_ic_i(+4)(R_6/4)-[f-(K+3)(K+4)]^{\frac{1}{2}}\\
&\times[f-(K+4)(K+5)]^{\frac{1}{2}}a_ia_i(+4)(R_5/2)-[f-K(K+1)]^{\frac{1}{2}}[f-(K+3)\\
&\times(K+4)]^{\frac{1}{2}}b_ib_i(+4)(R_5/2)-[f-K(K-1)]^{\frac{1}{2}}[f-K(K+1)]^{\frac{1}{2}}c_ic_i(+4)(R_5/2)\};
\end{aligned}
$$

$$(K+4|H^{(2)\prime}|K)=(K|H^{(2)\prime}|K+4), \qquad (25)$$

where

$$
\begin{aligned}
R_0(V_1\nu_1+\nu_3)=(1/4)[&18\zeta_{23}^4-24\zeta_{23}^2-1+5((\omega_2/\omega_3)+(\omega_3/\omega_2))\zeta_{23}^2+3((\omega_2/\omega_4)+(\omega_4/\omega_2))\zeta_{24}^2\\
&-27\zeta_{23}^2\zeta_{24}^2+(45/2)((\omega_4/\omega_3)+(\omega_3/\omega_4))\zeta_{23}^2\zeta_{24}^2]+(A_0/2)\{21d_1+5d_3+9d_5+7d_6\\
&+3d_{10}+10d_{11}+3(2V_1+1)[d_{20}+d_{31}+(5d_{18}/3)]+5d_{21}+10d_{22}-(5d_{23}/2)+3d_{27}+6d_{28}\\
&-3d_{29}+3(2V_1^2+2V_1+1)d_{30}+9d_{33}\}-(A_0/4)\{(5c_1^2/3\omega_3)+(7\omega_4+4\omega_3)c_2^2/\omega_4(\omega_4+2\omega_3)\\
&+(3\omega_3-10\omega_4)c_3^2/(\omega_3^2-4\omega_4^2)+(c_4^2/3\omega_4)+[(2V_1+1)(3\omega_3(\omega_3^2-\omega_4^2-\omega_1^2)\\
&+5\omega_4(\omega_4^2-\omega_3^2-\omega_1^2))+5\omega_1(\omega_1^2-\omega_3^2-\omega_4^2)+6\omega_1\omega_3\omega_4]c_6^2(\omega_1^4+\omega_3^4+\omega_4^4-2\omega_1^2\omega_3^2\\
&-2\omega_1^2\omega_4^2-2\omega_3^2\omega_4^2)^{-1}+[100\omega_3^2-35\omega_1^2+20(2V_1+1)\omega_1\omega_3]c_5^2/\omega_1(4\omega_3^2-\omega_1^2)\\
&+[3\omega_3(\omega_3^2-\omega_4^2-\omega_2^2)+5\omega_4(\omega_4^2-\omega_3^2-\omega_1^2)+5\omega_2(\omega_2^2-\omega_3^2-\omega_4^2)+6\omega_2\omega_3\omega_4]\\
&\times(\omega_2^4+\omega_3^4+\omega_4^4-2\omega_2^2\omega_3^2-2\omega_2^2\omega_4^2-2\omega_3^2\omega_4^2)^{-1}+(3c_7^2/\omega_1)[4(2V+1)\omega_1\omega_4-5\omega_1^2\\
&+12\omega_4^2]/(4\omega_4^2-\omega_1^2)+2(4\omega_3+7\omega_2)c_8^2/\omega_2(\omega_2+2\omega_3)+6c_{10}^2/(\omega_2+2\omega_4)\\
&+(30V_1^2+30V_1+11)c_{11}^2/\omega_1+(5/16)c_{13}^2/\omega_2+18[4\omega_2^2-2\omega_1^2+2(2V_1+1)\omega_1\omega_2]c_{12}^2\\
&/\omega_1(4\omega_2^2-\omega_1^2)+(2V_1+1)(30c_5+18c_7+18c_{12})(c_{11}^2/\omega_1)+30(c_7+c_{12})c_5/\omega_1+18c_7c_{12}/\omega_1\},
\end{aligned}
$$

$$
\begin{aligned}
R_1(V_1\nu_1+\nu_3)=(\hbar/2A_0)\{&(\omega_3^2+3\omega_2^2)\zeta_{23}^2/\omega_2\omega_3(\omega_2+\omega_3)+3\zeta_{24}^2/2\omega_4+(c_8/\omega_2)(A_0/3\omega_2)^{\frac{1}{2}}+2(2V_1+1)/\omega_1\\
&+(1/\omega_2)+2\zeta_{34}^2(\omega_3^3-6\omega_3^2\omega_4+3\omega_3\omega_4^2-2\omega_4^3)/\omega_3\omega_4(\omega_3^2-\omega_4^2)+(\hbar/A_0\omega_2^2)\\
&+2(2A_0/3\omega_1^3)^{\frac{1}{2}}(5c_5+3c_7+3c_{11}+3c_{12})\},
\end{aligned}
$$

$$R_2(V_1\nu_1+\nu_3)=R(V_1\nu_1),$$

$$
\begin{aligned}
R_3(V_1\nu_1+\nu_3)=(\hbar/2A_0)\{&[(3/4)(7\omega_2^2+5\omega_3^2)\zeta_{23}^2/\omega_3(\omega_2^2-\omega_3^2)]-(3A_0/\omega_2)^{\frac{1}{2}}(c_8/2\omega_2)\\
&+[(\omega_4^2+3\omega_3^2)\zeta_{34}^2/\omega_3(\omega_3^2-\omega_4^2)]\},
\end{aligned}
$$

$$R_4(V_1\nu_1+\nu_3)=(\hbar/A_0)\{(3\zeta_{23}^2/4\omega_3)+\zeta_{23}c_1(A_0/\omega_3^3)^{\frac{1}{2}}-\zeta_{24}c_2(A_0/\omega_4^3)^{\frac{1}{2}}+[(\omega_4^2+3\omega_3^2)\zeta_{34}^2/\omega_3(\omega_3^2-\omega_4^2)]\},$$

$$R_5(V_1\nu_1+\nu_3)=R_3(V_1\nu_1),$$

$R_6(V_1\nu_1+\nu_3)=(\zeta_{23}^2\hbar^2/4A_0^2\omega_3^2)$; the subscript i assumes the three values of s in (21).

The coefficients a_s, b_s, c_s which have already been defined are always to be associated with the quantum number $K=K$. In (24) and (25) a notation $a(+2)$, $b(+2)$, etc. is introduced to denote the values of the coefficients a_s, b_s and c_s where the quantum number K is replaced by $K+2$.

In the same manner by setting $\Psi(V_1V_2V_3)$ equal to $\Phi(V_1=0)U(\nu_2)$ and $\Phi(V_1=0)V(\nu_2)$ we may determine also the matrix $H^{(2)\prime}$ for the state $\nu_2+\nu_3$. From the foregoing it will become apparent that for this state the matrix will split up into three sets of two nearly identical steps which are diagonal in J and M, but have elements nondiagonal in K. The $(K|K)$ elements are identical in form with (23) where the parameters $R_0(V_1\nu_1+\nu_3)$, etc., are replaced by $R_0(\nu_2+\nu_3)$, etc. These are given below:

$$\begin{aligned}
R_0(\nu_2+\nu_3:i:1,2) &= R_0(\nu_3)+(1/8)(10\pm1\mp3b_i^2)\zeta_{23}^2[(\omega_2/\omega_3)+(\omega_3/\omega_2)]+(A_0/4)\{(10\mp1\pm3b_i^2)d_{21}\\
&\quad+(20\pm1\mp3b_i^2)d_{22}-(5\pm1\mp3b_i^2)d_{23}+6d_{27}+12d_{28}+6d_{31}+36d_{33}\}\\
&\quad-(A_0/8)\{(30c_5+18c_7)(c_{12}/\omega_1)+(10\pm1\pm3b_i^2)[2\omega_3c_8^2/(4\omega_3^2-\omega_2^2)]\\
&\quad+[12\omega_4c_{10}^2/(4\omega_4^2-\omega_2^2)]+36(3\omega_2+2\omega_1)[c_{12}^2/\omega_1(2\omega_2+\omega_1)]+(7\pm2)(3c_{13}^2/8\omega_2)\\
&\quad+[15\omega_3(\omega_3^2-\omega_4^2-\omega_2^2)+\tfrac{1}{2}(10\mp1\pm3b_i^2)\omega_4(\omega_4^2-\omega_3^2-\omega_2^2)]c_9^2\\
&\quad/[\omega_2^4+\omega_3^4+\omega_4^4-2\omega_2^2\omega_3^2-2\omega_2^2\omega_4^2-2\omega_3^2\omega_4^2]\},\\
R_1(\nu_2+\nu_3:1,2) &= R_1(\nu_3)+(\hbar/2A_0)\{(6A_0/\omega_1^3)^{\frac{1}{2}}c_{12}+(1\mp1/4)/\omega_2\\
&\quad-(1\pm1/4)\zeta_{24}^2[(3\omega_2^2+\omega_4^2)/\omega_2(\omega_2^2-\omega_4^2)]\},
\end{aligned}\tag{26}$$

$$R_2(\nu_2+\nu_3)=R_2(\nu_3),$$

$$R_3(\nu_2+\nu_3:1,2)-R_3(\nu_3)=R_4(\nu_2+\nu_3:1,2)-R_4(\nu_3)=-(1\pm1/4)(\zeta_{23}^2\hbar/2A_0)[(3\omega_2^2+\omega_3^2)/\omega_2(\omega_2^2-\omega_3^2)],$$

$$\begin{aligned}
R_5(\nu_2+\nu_3:1,2)-R_5(\nu_3) &= R_8(\nu_2+\nu_3:1,2)-R_8(\nu_3)\\
&= \pm(3\omega_2\hbar/2A_0)\{[\zeta_{23}^2/(\omega_2^2-\omega_3^2)]+[\zeta_{24}^2(\omega_2^2-\omega_4^2)]\},
\end{aligned}$$

$$R_6(\nu_2+\nu_3)=R_6(\nu_3);\quad R_7(\nu_2+\nu_3)=R_7(\nu_3);\quad R_9(\nu_2+\nu_3)=R_9(\nu_3);\quad R_{10}(\nu_2+\nu_3)=R_{10}(\nu_3)$$

and

$$\begin{aligned}
(K|H^{(2)\prime}|K+2) &= (K+2|H^{(2)\prime}|K)=(\hbar^2/2A_0)\{[2f-6(K+1)^2]a_ic_i(+2)R_{11}+[f-K(K+1)]^{\frac{1}{2}}\\
&\quad\times[f-(K+1)(K+2)]^{\frac{1}{2}}b_ib_i(+2)(2R_{11}-R_{15})\}+(\hbar^2/2A_0)(R_{11}+R_{15})\\
&\quad\times\{[f-K(K-1)]^{\frac{1}{2}}[f-K(K+1)]^{\frac{1}{2}}c_ic_i(+2)-[f-(K+1)(K+2)]^{\frac{1}{2}}\\
&\quad\times[f-(K+2)(K+3)]^{\frac{1}{2}}a_ia_i(+2)\},
\end{aligned}\tag{27}$$

where

$$R_{11}(\nu_2+\nu_3)=R_{11}(\nu_3);\quad 2R_{15}(\nu_2+\nu_3:1,2)=R_5(\nu_2+\nu_3:1,2)-R_5(\nu_3)$$

and $(K|H^{(2)\prime}|K\pm4)$ which are entirely identical with those for the state ν_3 given in (25).

Since the nature of the frequency ν_4 is entirely analogous to ν_3 the elements of the matrix $H^{(2)\prime}$ for the states $V_1\nu_1+\nu_4$ and $\nu_2+\nu_3$ may be obtained from the relations (23) to (27) simply by replacing $R_s(V_1\nu_1+\nu_3)$ by $R_s(V_1\nu_1+\nu_4)$ and $R_s(\nu_2+\nu_3)$ by $R_s(\nu_2+\nu_4)$ where these may be obtained by replacing in $R_s(\nu_j+\nu_3)$ the following quantities which are included in parentheses: (ζ_{23}, ζ_{24}), (ω_3, ω_4), (d_1, d_5), (d_6, d_{10}), (d_{18}, d_{20}), (d_{21}, d_{27}), (d_{22}, d_{28}), (d_{23}, d_{29}), (c_1, c_4), (c_2, c_3), (c_5, c_7), (c_8, c_{10}). Thus for example $R_{11}(V_1\nu_1+\nu_4)$ becomes $(\hbar\zeta_{24}^2/8A_0\omega_4)$.

The actual values of the rotation-vibration energies for the above states may be had by diagonalizing the corresponding matrices H. This is most readily accomplished by solving for the roots of the secular determinant $|(K|H|K')-E\delta_{K'}{}^{K}|$, $\delta_{K'}{}^{K}$ being the Kronecker symbol. The actual unperturbed wave functions $\chi_{JM}(\nu_j:s)$ for a rotation-vibration state τ, τ being simply an index number running from $-J$ to $+J$, which are the limiting values of the actual perturbed wave functions may now be written as an expansion in terms of the wave functions $\Psi_{JKM}(\nu_j:s)$:

$$\chi_{JM}(\nu_j:s)=\sum_{K=-J}^{+J} A_{JM}{}^{(K)}\Psi_{JKM}(\nu_j:s), \quad (28)$$

where the coefficients $A_{JM}{}^{(K)}$ are the normalized first minors of the secular determinant.

IV. The Selection Rules and Intensities

To determine the selection rules we have to determine what are the nonvanishing matrix elements of the electric moment. To second approximation the classical expression for the body fixed components of this are the quantities:

$$\Pi_x=A_1q_1+A_2q_4+B_1q_2q_3+B_2(q_2q_6+q_3q_5)$$
$$+B_3q_5q_6+B_5q_1q_9+B_6q_4q_9+B_7q_1u_x+B_8q_4u_x,$$

Π_y and Π_z being obtained by cyclic rotation of q_1, q_2, q_3; q_4, q_5, q_6; u_x, u_y and u_z. The matrix elements of the electric moment are given by the integrals

$$\int \bar{\chi}_{JKM}(\nu_j:s)\Pi_\beta\bar{\chi}_{J'K'M'}(\nu_j{}':s')dv$$

where Π_β are the components of Π along the spaced fixed axes; $\chi_{J,K,M}(\nu_j:s)$ and $\chi_{J'K'M'}\times(\nu_j{}', s')$ the wave functions of the initial and final states. The function $\chi_{JKM}(\nu_j:s)$ may to a good approximation be replaced by $\Psi_{JKM}(\nu_j:s)$ in computing the intensities because the actual splitting of the rotation levels is small so that all the $A_{J\tau M}{}^{(K)}$, except the one where $\tau=K$, will be small.

Inspection of the quantity Π shows it to have no linear terms in q_7, q_8 or q_9. For the frequencies ν_1 and ν_2 the above integral will therefore vanish and they will consequently be optically inactive, giving no bands in the infra-red. For transitions from the normal state to the states $V_1\nu_1+\nu_3$ and $\nu_2+\nu_3$ the above integral will not vanish so that these frequencies may be expected to occur in the spectrum.

In evaluating the integral for the electric moment it is found that the selection rules for the rotational quantum numbers are the same for ν_3, $\nu_1+\nu_3$ and $\nu_2+\nu_3$, from which the inference may be drawn that also for higher combination frequencies of this type the selection rules will be the same. For J the selection rule is $\Delta J=+1$, 0 or -1 as the transition is from the normal state to the states $\nu_{3,\,I}$, $\nu_{3,\,II}$ or $\nu_{3,\,III}$, respectively, which verifies the conclusions drawn by other investigators. In addition we have the selection rules for M and K, $\Delta M=\pm 1$, 0 and $\Delta K=0$. An interesting result which prevails is that the quantum mechanical amplitudes are independent of the quantum numbers J and K. One obtains for the square of the electric moment Π^2, which is $\Pi_{x'}{}^2+\Pi_{y'}{}^2+\Pi_{z'}{}^2$, simply

$$(J|\Pi^2|J)=(J|\Pi^2|J\pm 1)=1. \quad (29)$$

The actual intensity of a spectral line, ignoring all symmetry properties, will very nearly be proportional to

$$I(J,K;J',K')=N(J)(J'|\Pi^2|J)(g_{J'}/g_J), \quad (30)$$

where $N(J)$ is the number of molecules in the state J and g_J and $g_{J'}$ are the statistical weights of the state J and J', respectively. For the three cases $\Delta J=-1$, 0 and $+1$ the relation (30) will become

$$\begin{aligned} I(J,K;J-1,K)&=(2J-1)\\ &\quad\times\exp(-E(JK)/kT),\\ I(J,K;J,K)&=(2J+1)\\ &\quad\times\exp(-E(JK)/kT), \quad (31)\\ I(J,K;J+1,K)&=(2J+3)\\ &\quad\times\exp(-E(JK)/kT). \end{aligned}$$

These results appear to be in agreement with those of Jahn derived from other considerations.

To arrive at the actual intensities the relations (31) must be multipled by the appropriate spin factor. This problem has been considered by Wilson[9] for the cases where the four Y particles are protons and deuterons and need not here be discussed. For these cases the actual nuclear spin factors for the various rotation states have been evaluated and may be obtained by reference to this work.

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[9] E. Bright Wilson, Jr., J. Chem. Phys. 3, 276 (1935).