Vibration-Rotation Energies of Planar ZXY$_2$ Molecules

Part II. The Quantum-Mechanical Hamiltonian and the Energy Values[1]

SAMUEL SILVER

Mendenhall Laboratory of Physics, The Ohio State University, Columbus, Ohio, * and*
Department of Physics, University of Oklahoma, Norman, Oklahoma

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Nielsen's treatment of the vibration-rotation energies of a general polyatomic molecule is applied to the planar ZXY_2 molecular model. Due to the low symmetry of the model, the vibrational modes are non-degenerate, and, if the frequencies are well separated in their values, Nielsen's general formulation can be applied directly. For this case the elements of the secular equation are evaluated to include all the first- and second-order terms in the Hamiltonian. With the view of applying the theory to the analysis of the fundamental bands of formaldehyde, the effect of an approximate degeneracy between a pair of perpendicular vibrations, of symmetry types B_1 and B_2, respectively, is considered. For this case, the vibration-rotation energies of the states giving rise to the fundamental bands are investigated to the first order of approximation. It is shown how, by a modification of Nielsen's general treatment, the secular equations can be set up with little difficulty to include all the first-order terms in the Hamiltonian. The secular equations for values of $J = 0, 1, 2, 3, 4$ are given explicitly.

THE quantum-mechanical calculation of the vibration-rotation energies and the associated spectra of planar ZXY_2 molecules has been carried out previously subject to a number of simplifying assumptions.[2] Recently Nielsen[3] expanded the Wilson-Howard Hamiltonian for the vibration-rotation energies of a general polyatomic molecule and delineated a procedure for evaluating the energies to the second order of approximation. In the present paper the general treatment is applied to the planar ZXY_2 model and the constants appearing in the elements of the secular equation are evaluated in terms of the coefficients of the normal coordinate transformation, developed in the preceding paper (Part I), and the coefficients of the cubic and quartic anharmonic terms in the potential energy.

1. THE QUANTUM-MECHANICAL HAMILTONIAN†

The quantum-mechanical Hamiltonian for the system, arranged in terms according to orders of magnitude, is

$$H_0 = \frac{1}{2}\left(\frac{P_x^2}{I_{xx}^0} + \frac{P_y^2}{I_{yy}^0} + \frac{P_z^2}{I_{zz}^0}\right) + \frac{1}{2}\sum_{k=1}^{6} \hbar\omega_k\left(\frac{p_{q_k}^2}{\hbar^2} + q_k^2\right); \quad \omega_k = 2\pi c \nu_k. \tag{1a}$$

$$H_1 = -\frac{i\hbar^{\frac{1}{2}}}{4}\sum_{k=1}^{3}\sigma_k p_{q_k} - \frac{\hbar^{\frac{1}{2}}}{2}\sum_{k=1}^{3}\left[a_k\frac{P_x^2}{I_{xx}^{0\,2}} + b_k\frac{P_y^2}{I_{yy}^{0\,2}} + c_k\frac{P_z^2}{I_{zz}^{0\,2}}\right]q_k/\omega_k^{\frac{1}{2}}$$

$$+ \frac{\hbar^{\frac{1}{2}}}{2I_{yy}^0 I_{zz}^0}(P_y P_z + P_z P_y)\sum_{k=4}^{5}e_k q_k/\omega_k^{\frac{1}{2}} - \left[\frac{p_x P_x}{I_{xx}^0} + \frac{p_y P_y}{I_{yy}^0} + \frac{p_z P_z}{I_{zz}^0}\right] + U_1. \tag{1b}$$

$$H_2 = -\frac{i\hbar}{2}\sum_{k=1}^{6}s_{kk}q_k p_{q_k} + \frac{1}{2}\sum_{k=1}^{6}\frac{\hbar}{\omega_k}q_k^2\left[\epsilon_{xk}\frac{P_x^2}{I_{xx}^{0\,2}} + \epsilon_{yk}\frac{P_y^2}{I_{yy}^{0\,2}} + \epsilon_{zk}\frac{P_z^2}{I_{zz}^{0\,2}}\right] + \frac{1}{2}\left(\frac{p_x^2}{I_{xx}^0} + \frac{p_y^2}{I_{yy}^0} + \frac{p_z^2}{I_{zz}^0}\right) + U_2, \tag{1c}$$

[1] This paper was presented at the meeting of Section B, The American Association for the Advancement of Science, held in Dallas, December, 1941. Abstract, Phys. Rev. **61**, 383 (1942).

* The work covered by this and the preceding paper was initiated at the Ohio State University while the author was in residence there during 1940–1941.

[2] H. H. Nielsen, Phys. Rev. **38**, 1432 (1931); J. Chem. Phys. **5**, 818 (1937); Phys. Rev. **55**, 289 (1939).

[3] H. H. Nielsen, Phys. Rev. **60**, 794 (1941).

† Only the essential results are given here. For the details of the development of the Hamiltonian, the reader is referred to reference 3 above.

plus terms which make no contribution to the second order of approximation. q_k is related to the normal coordinate Q_k by $q_k = (\omega_k/h)^{\frac{1}{2}}Q_k$; p_k is the momentum conjugate to q_k; U_1 and U_2 are the cubic and quartic anharmonic terms in the potential energy. From the symmetry properties of the normal coordinates (and hence, the q_k), it is seen that the most general forms for U_1 and U_2 are

$$U_1 = hc\{\beta_{111}q_1^3 + \beta_{222}q_2^3 + \beta_{333}q_3^3 + \beta_{112}q_1^2q_2 + \beta_{113}q_1^2q_3 + \beta_{221}q_2^2q_1 + \beta_{223}q_2^2q_3 + \beta_{331}q_3^2q_1 + \beta_{332}q_3^2q_2$$

$$+ \beta_{441}q_4^2q_1 + \beta_{442}q_4^2q_2 + \beta_{443}q_4^2q_3 + \beta_{551}q_5^2q_1 + \beta_{552}q_5^2q_2 + \beta_{553}q_5^2q_3 + \beta_{661}q_6^2q_1 + \beta_{662}q_6^2q_2$$

$$+ \beta_{663}q_6^2q_3 + \beta_{123}q_1q_2q_3 + \beta_{145}q_1q_4q_5 + \beta_{245}q_2q_4q_5 + \beta_{345}q_3q_4q_5\}, \quad (2)$$

$$U_2 = hc\{\sum_{k=1}^{6} \gamma_{kkkk}q_k^4 + \gamma_{1112}q_1^3q_2 + \gamma_{1113}q_1^3q_3 + \gamma_{2221}q_2^3q_1 + \gamma_{2223}q_2^3q_3 + \gamma_{3331}q_3^3q_1 + \gamma_{3332}q_3^3q_2$$

$$+ \gamma_{4445}q_4^3q_5 + \gamma_{5554}q_5^3q_4 + \gamma_{1122}q_1^2q_2^2 + \gamma_{1133}q_1^2q_3^2 + \gamma_{1144}q_1^2q_4^2 + \gamma_{1155}q_1^2q_5^2 + \gamma_{1166}q_1^2q_6^2$$

$$+ \gamma_{2233}q_2^2q_3^2 + \gamma_{2244}q_2^2q_4^2 + \gamma_{2255}q_2^2q_5^2 + \gamma_{2266}q_2^2q_6^2 + \gamma_{3344}q_3^2q_4^2 + \gamma_{3355}q_3^2q_5^2 + \gamma_{3366}q_3^2q_6^2$$

$$+ \gamma_{4455}q_4^2q_5^2 + \gamma_{4466}q_4^2q_6^2 + \gamma_{5566}q_5^2q_6^2 + \gamma_{1233}q_1q_2q_3^2 + \gamma_{1244}q_1q_2q_4^2 + \gamma_{1255}q_1q_2q_5^2 + \gamma_{1266}q_1q_2q_6^2$$

$$+ \gamma_{1322}q_1q_3q_2^2 + \gamma_{1344}q_1q_3q_4^2 + \gamma_{1355}q_1q_3q_5^2 + \gamma_{1366}q_1q_3q_6^2 + \gamma_{2311}q_2q_3q_1^2 + \gamma_{2344}q_2q_3q_4^2$$

$$+ \gamma_{2355}q_2q_3q_5^2 + \gamma_{2366}q_2q_3q_6^2 + \gamma_{1145}q_1^2q_4q_5 + \gamma_{2245}q_2^2q_4q_5 + \gamma_{3345}q_3^2q_4q_5 + \gamma_{6645}q_6^2q_4q_5$$

$$+ \gamma_{1245}q_1q_2q_4q_5 + \gamma_{1345}q_1q_3q_4q_5 + \gamma_{2345}q_2q_3q_4q_5\}. \quad (3)$$

Although the coordinates q_4 and q_5 cannot appear singly in the first degree, the product term q_4q_5 is admissible since both coordinates transform in the same way under the operations of the symmetry group.

The operators p_x, p_y, p_z are the components of the vibrational angular momentum and are given by:

$$p_x = \sum_{k=1}^{3} \left\{ \zeta_{k4}\left[\left(\frac{\nu_k}{\nu_4}\right)^{\frac{1}{2}}q_4 p_{q_k} - \left(\frac{\nu_4}{\nu_k}\right)^{\frac{1}{2}}q_k p_{q_4}\right] + \zeta_{k5}\left[\left(\frac{\nu_k}{\nu_5}\right)^{\frac{1}{2}}q_5 p_{q_k} - \left(\frac{\nu_5}{\nu_k}\right)^{\frac{1}{2}}q_k p_{q_5}\right]\right\},$$

$$p_y = \sum_{k=1}^{3} \left\{ \zeta_{k6}\left[\left(\frac{\nu_6}{\nu_k}\right)^{\frac{1}{2}}q_k p_{q_6} - \left(\frac{\nu_k}{\nu_6}\right)^{\frac{1}{2}}q_6 p_{q_k}\right]\right\}, \quad (4)$$

$$p_z = \sum_{k=4}^{5} \left\{ \zeta_{k6}\left[\left(\frac{\nu_k}{\nu_6}\right)^{\frac{1}{2}}q_6 p_{q_k} - \left(\frac{\nu_6}{\nu_k}\right)^{\frac{1}{2}}q_k p_{q_6}\right]\right\}.$$

The constants appearing in H are defined by

$$\sigma_k = \omega_k^{\frac{1}{2}}\left(\frac{a_k}{I^0_{xx}} + \frac{b_k}{I^0_{yy}} + \frac{c_k}{I^0_{zz}}\right),$$

$$s_{kk} = \frac{A_{kk}}{I^0_{xx}} + \frac{B_{kk}}{I^0_{yy}} + \frac{C_{kk}}{I^0_{zz}} - \frac{1}{2}\left(\frac{a_k^2}{I^{0\,2}_{xx}} + \frac{b_k^2}{I^{0\,2}_{yy}} + \frac{c_k^2}{I^{0\,2}_{zz}}\right), \quad k = 1, 2, 3$$

$$s_{kk} = \frac{A_{kk}}{I^0_{xx}} + \frac{B_{kk}}{I^0_{yy}} + \frac{C_{kk}}{I^0_{zz}} - \frac{e_k^2}{I^0_{yy} I^0_{zz}}, \quad k = 4, 5$$

$$s_{66} = \frac{B_{66}}{I^0_{yy}} + \frac{C_{66}}{I^0_{zz}},$$

$$\epsilon_{xk} = \frac{a_k^2}{I^0_{xx}} - A_{kk}; \quad \epsilon_{yk} = \frac{b_k^2}{I^0_{yy}} - B_{kk} + \frac{e_k^2}{I^0_{zz}}; \quad \epsilon_{zk} = \frac{c_k^2}{I^0_{zz}} - C_{kk} + \frac{e_k^2}{I^0_{yy}}, \quad (5)$$

where

$$a_k = 2\left\{\left[\frac{2m_Y m_Z}{m_Z + 2m_Y \cos^2\beta_0}\right]^{\frac{1}{2}}(r_0 - R_0 \cos\beta_0)l_{1k} + \left[\frac{m_X M}{m_Z + 2m_Y}\right]^{\frac{1}{2}}z_1{}^0 l_{2k}\right.$$

$$\left. - \left[\frac{2m_Y}{(m_Z + 2m_Y)(m_Z + 2m_Y \cos^2\beta_0)}\right]^{\frac{1}{2}} M z_1{}^0 \sin\beta_0 l_{3k}\right\}, \quad k = 1, 2, 3$$

$$b_k = 2\left\{\left[\frac{2m_Y m_Z}{m_Z + 2m_Y \cos^2\beta_0}\right]^{\frac{1}{2}}(z_2{}^0 - z_3{}^0)\cos\beta_0 l_{1k} + \left[\frac{m_X M}{m_Z + 2m_Y}\right]^{\frac{1}{2}}z_1{}^0 l_{2k}\right. \tag{6a}$$

$$\left. + m_Z\left[\frac{2m_Y}{(m_Z + 2m_Y)(m_Z + 2m_Y \cos^2\beta_0)}\right]^{\frac{1}{2}}(z_2{}^0 - z_3{}^0)\sin\beta_0 l_{3k}\right\}, \quad k = 1, 2, 3$$

$$c_k = 2\left\{\left[\frac{2m_Y m_Z}{m_Z + 2m_Y \cos^2\beta_0}\right]^{\frac{1}{2}}y_3{}^0 \sin\beta_0 l_{1k} - \left[\frac{2m_Y(m_Z + 2m_Y)}{m_Z + 2m_Y \cos^2\beta_0}\right]^{\frac{1}{2}}y_3{}^0 \cos\beta_0 l_{3k}\right\}, \quad k = 1, 2, 3$$

$$a_k = b_k = c_k = 0, \quad (k > 3); \quad e_k = 0, \quad (k = 1, 2, 3, 6); \quad e_k = 2[I_{yy}^0 I_{zz}^0 / I_{xx}^0]^{\frac{1}{2}}l_{5k}, \quad (k = 4, 5).$$

$$A_{kk} = 1 - (\zeta_{k4}^2 + \zeta_{k5}^2), \quad (k = 1, 2, 3); \quad A_{kk} = 1 - \sum_{j=1}^{3}\zeta_{jk}^2, \quad (k = 4, 5); \quad A_{66} = 0,$$

$$B_{kk} = \left\{\frac{(m_Z + 2m_Y)\cos^2\beta_0}{m_Z + 2m_Y \cos^2\beta_0}l_{1k}^2 + \frac{m_X}{M}l_{2k}^2 + \frac{m_Z \sin^2\beta_0}{m_Z + 2m_Y \cos^2\beta_0}l_{3k}^2\right.$$

$$\left. + \frac{2[m_Z(m_Z + 2m_Y)]^{\frac{1}{2}}}{m_Z + 2m_Y \cos^2\beta_0}\sin\beta_0 \cos\beta_0 l_{1k}l_{3k}\right\} - \zeta_{k6}^2, \quad (k = 1, 2, 3) \tag{6b}$$

$$B_{kk} = (I_{yy}^0 / I_{xx}^0)l_{5k}^2, \quad (k = 4, 5); \quad B_{66} = 1 - \sum_{j=1}^{3}\zeta_{j6}^2;$$

$$C_{kk} = 1 - B_{kk} - \zeta_{k6}^2, \quad (k = 1 \cdots 5); \quad C_{66} = 1 - (\zeta_{46}^2 + \zeta_{56}^2),$$

with

$$\zeta_{kj} = \left[\frac{M m_X}{I_{yy}^0(m_Z + 2m_Y \cos^2\beta_0)}\right]^{\frac{1}{2}}z_1{}^0 \cos\beta_0 l_{1k}l_{4j} + M\left[\frac{m_Z}{I_{xx}^0 I_{yy}^0(m_Z + 2m_Y \cos^2\beta_0)}\right]^{\frac{1}{2}}z_1{}^0 z_2{}^0 \sin\beta_0 l_{1k}l_{5j}$$

$$+ \left[\frac{2m_Y m_Z}{I_{yy}^0(m_Z + 2m_Y)}\right]^{\frac{1}{2}}(z_3{}^0 - z_2{}^0)l_{2k}l_{4j} + \left[\frac{M m_X I_{zz}^0}{I_{xx}^0 I_{yy}^0(m_Z + 2m_Y)}\right]^{\frac{1}{2}}z_1{}^0 l_{2k}l_{5j}$$

$$+ \left[\frac{m_X m_Z M}{I_{yy}^0(m_Z + 2m_Y)(m_Z + 2m_Y \cos^2\beta_0)}\right]^{\frac{1}{2}}z_1{}^0 \sin\beta_0 l_{3k}l_{4j}$$

$$+ \frac{M I_{yy}^0 z_1{}^0 + m_z I_{xx}^0(z_2{}^0 - z_3{}^0)}{r_0[I_{xx}^0 I_{yy}^0(m_Z + 2m_Y)(m_Z + 2m_Y \cos^2\beta_0)]^{\frac{1}{2}}}l_{3k}l_{5j}, \quad (k = 1, 2, 3; j = 4, 5)$$

$$\tag{7}$$

$$\zeta_{k6} = \left[\frac{m_X M}{I_{yy}^0(m_Z + 2m_Y \cos^2\beta_0)}\right]^{\frac{1}{2}}z_1{}^0 \cos\beta_0 l_{1k} + \left[\frac{2m_Y m_Z}{I_{yy}^0(m_Z + 2m_Y)}\right]^{\frac{1}{2}}(z_3{}^0 - z_2{}^0)l_{2k}$$

$$+ \left[\frac{m_X m_Z M}{I_{yy}^0(m_Z + 2m_Y)(m_Z + 2m_Y \cos^2\beta_0)}\right]^{\frac{1}{2}}z_1{}^0 \sin\beta_0 l_{3k}, \quad (k = 1, 2, 3)$$

$$\zeta_{k6} = l_{4k}, \quad (k = 4, 5).$$

The coefficients l_{kj} and the equilibrium coordinates $z_k{}^0$ are given in Part I.

2. TRANSFORMATION OF THE HAMILTONIAN AND THE ENERGY VALUES

Shaffer, Nielsen, and Thomas[4] have shown that the perturbation calculation can be simplified to a considerable extent by applying a contact transformation to the operator H, $H' = THT^{-1}$, which carries terms of first order in H into second-order terms in H'. Details of the method are to be found in the paper by SNT; a table of the operators comprising the transformation function T, appropriate for the coordinates used here, has been published by Silver and Shaffer.[5]

Due to the low symmetry of the system, the vibrational modes of the planar ZXY_2 molecule are all non-degenerate. In this case, it is possible to remove all the terms from H_1 into H_2'. The transformed Hamiltonian is

$$H_0' = H_0; \quad H_1' = 0; \tag{8a}$$

$$H_2' = -hc\{\tau_{xxxx}P_x^4 + \tau_{yyyy}P_y^4 + \tau_{zzzz}P_z^4 + \tau_{xxyy}(P_x^2 P_y^2 + P_y^2 P_x^2) + \tau_{yyzz}(P_y^2 P_z^2 + P_z^2 P_y^2)$$

$$+ \tau_{zzxx}(P_z^2 P_x^2 + P_x^2 P_z^2) + \tau_{yzyz}(P_y P_z + P_z P_y)^2\}$$

$$+ \left\{\left(\sum_{k=1}^{6} a_{kk}q_k^2\right)\frac{P_x^2}{I_{xx}^{0\,2}} + \left(\sum_{k=1}^{6} b_{kk}q_k^2\right)\frac{P_y^2}{I_{yy}^{0\,2}} + \left(\sum_{k=1}^{6} c_{kk}q_k^2\right)\frac{P_z^2}{I_{zz}^{0\,2}}\right\} + hcg_0 + \frac{1}{2}\left(\frac{p_x^2}{I_{xx}^0} + \frac{p_y^2}{I_{yy}^0} + \frac{p_z^2}{I_{zz}^0}\right)$$

$$- hc\sum_{k=1}^{3}\frac{\beta_{kkk}^2}{\nu_k}\left[\frac{3p_{q_k}^2 q_k^2}{\hbar^2} + 1 + \frac{3}{2}q_k^4\right] + hc\left\{\sum_{k=1}^{6}\gamma_{kkkk}q_k^4 + \sum_{j=1}^{5}\sum_{k>j}^{6}(\gamma_{jjkk} - N_{jjkk})q_j^2 q_k^2\right\}$$

$$- hc\left\{\sum_{j=1}^{3}\sum_{k=1}^{3}\frac{\beta_{jjk}^2(1-\delta_{jk})}{2\nu_k(4\nu_j^2 - \nu_k^2)}[(2\nu_j^2 - \nu_k^2)q_j^4 + 4\nu_j\nu_k q_j^2 q_k^2 + 2\nu_j^2 q_j^2 p_{q_j}^2/\hbar^2]\right\}$$

$$- hc\left\{\sum_{j=4}^{6}\sum_{k=1}^{3}\frac{\beta_{jjk}^2}{2\nu_k(4\nu_j^2 - \nu_k^2)}[(2\nu_j^2 - \nu_k^2)q_j^4 + 4\nu_j\nu_k q_j^2 q_k^2 + 2\nu_j^2 q_j^2 p_{q_j}^2/\hbar^2]\right\}, \tag{8b}$$

where

$$\tau_{xxxx} = \frac{1}{8hcI_{xx}^{04}}\left(\frac{a_1^2}{\omega_1^2} + \frac{a_2^2}{\omega_2^2} + \frac{a_3^2}{\omega_3^2}\right),$$

$$\tau_{yyyy} = \frac{1}{8hcI_{yy}^{04}}\left(\frac{b_1^2}{\omega_1^2} + \frac{b_2^2}{\omega_2^2} + \frac{b_3^2}{\omega_3^2}\right),$$

$$\tau_{zzzz} = \frac{1}{8hcI_{zz}^{04}}\left(\frac{c_1^2}{\omega_1^2} + \frac{c_2^2}{\omega_2^2} + \frac{c_3^2}{\omega_3^2}\right),$$

$$\tau_{xxyy} = \frac{1}{8hc(I_{xx}^0 I_{yy}^0)^2}\left(\frac{a_1 b_1}{\omega_1^2} + \frac{a_2 b_2}{\omega_2^2} + \frac{a_3 b_3}{\omega_3^2}\right),$$

$$\tau_{yyzz} = \frac{1}{8hc(I_{yy}^0 I_{zz}^0)^2}\left(\frac{b_1 c_1}{\omega_1^2} + \frac{b_2 c_2}{\omega_2^2} + \frac{b_3 c_3}{\omega_3^2}\right),$$

$$\tau_{zzxx} = \frac{1}{8hc(I_{zz}^0 I_{xx}^0)^2}\left(\frac{c_1 a_1}{\omega_1^2} + \frac{c_2 a_2}{\omega_2^2} + \frac{c_3 a_3}{\omega_3^2}\right),$$

$$\tau_{yzyz} = \frac{1}{8hc(I_{yy}^0 I_{zz}^0)^2}\left(\frac{e_4^2}{\omega_4^2} + \frac{e_5^2}{\omega_5^2}\right), \tag{9a}$$

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

[5] S. Silver and W. H. Shaffer, J. Chem. Phys. 9, 599 (1941). In addition to the elements given in this table we need a term in S,

$$S = -a_{klm}\left\{\omega_k(\omega_k^2 - \omega_l^2 - \omega_m^2)\frac{p_k q_l q_m}{\hbar^2} + \omega_l(\omega_l^2 - \omega_m^2 - \omega_k^2)\frac{q_k p_l q_m}{\hbar^2} + \omega_m(\omega_m^2 - \omega_k^2 - \omega_l^2)\frac{q_k q_l p_m}{\hbar^2} - 2\omega_k\omega_l\omega_m p_k p_l p_m/\hbar^2\right\} \Big/$$

$$\hbar(\omega_k^2 + \omega_l^4 + \omega_m^4 - 2\omega_k^2\omega_l^2 - 2\omega_l^2\omega_m^2 - 2\omega_m^2\omega_k^2)$$

to remove the $a_{klm}q_k q_l q_m$ term from H_1.

$$\frac{a_{kk}}{hc}=\frac{\epsilon_{xk}}{8\pi^2c^2\nu_k}+\sum_{j=1}^{3}\frac{(1+2\delta_{jk})}{2h^{\frac{1}{2}}\omega_j^{\frac{3}{2}}}a_j\beta_{kkj}+\frac{1}{8\pi^2c^2\nu_k}\sum_{j=4}^{5}\frac{\zeta_{kj}^2(3\nu_k^2+\nu_j^2)}{\nu_k^2-\nu_j^2}, \quad (k=1,2,3)$$

$$\frac{a_{kk}}{hc}=\frac{\epsilon_{xk}}{8\pi^2c^2\nu_k}+\sum_{j=1}^{3}\frac{a_j\beta_{kkj}}{2h^{\frac{1}{2}}\omega_j^{\frac{3}{2}}}+\frac{1}{8\pi^2c^2\nu_k}\sum_{j=1}^{3}\frac{\zeta_{jk}^2(3\nu_k^2+\nu_j^2)}{\nu_k^2-\nu_j^2}, \quad (k=4,5)$$

$$\frac{a_{66}}{hc}=\frac{\epsilon_{x6}}{8\pi^2c^2\nu_6}+\sum_{j=1}^{3}\frac{a_j\beta_{66j}}{2h^{\frac{1}{2}}\omega_j^{\frac{3}{2}}},$$

$$\frac{b_{kk}}{hc}=\frac{\epsilon_{yk}}{8\pi^2c^2\nu_k}+\sum_{j=1}^{3}\frac{(1+2\delta_{jk})b_j\beta_{kkj}}{2h^{\frac{1}{2}}\omega_j^{\frac{3}{2}}}+\frac{\zeta_{k6}^2(3\nu_k^2+\nu_6^2)}{8\pi^2c^2\nu_k(\nu_k^2-\nu_6^2)}, \quad (k=1,2,3)$$

$$\frac{b_{kk}}{hc}=\frac{\epsilon_{yk}}{8\pi^2c^2\nu_k}+\sum_{j=1}^{3}b_j\beta_{kkj}/2h^{\frac{1}{2}}\omega_j^{\frac{3}{2}}, \quad (k=4,5)$$

$$\frac{b_{66}}{hc}=\frac{\epsilon_{y6}}{8\pi^2c^2\nu_6}+\sum_{j=1}^{3}\frac{b_j\beta_{66j}}{2h^{\frac{1}{2}}\omega_j^{\frac{3}{2}}}+\frac{1}{8\pi^2c^2\nu_6}\sum_{j=1}^{3}\frac{\zeta_{j6}^2(3\nu_6^2+\nu_j^2)}{\nu_6^2-\nu_j^2},$$

$$\frac{c_{kk}}{hc}=\frac{\epsilon_{zk}}{8\pi^2c^2\nu_k}+\sum_{j=1}^{3}\frac{(1+2\delta_{jk})}{2h^{\frac{1}{2}}\omega_j^{\frac{3}{2}}}c_j\beta_{kkj}, \quad (k=1,2,3)$$

$$\frac{c_{kk}}{hc}=\frac{\epsilon_{zk}}{8\pi^2c^2\nu_k}+\sum_{j=1}^{3}\frac{c_j\beta_{kkj}}{2h^{\frac{1}{2}}\omega_j^{\frac{3}{2}}}+\frac{\zeta_{k6}^2(3\nu_k^2+\nu_6^2)}{8\pi^2c^2\nu_k(\nu_k^2-\nu_6^2)}, \quad (k=4,5)$$

$$\frac{c_{66}}{hc}=\frac{\epsilon_{z6}}{8\pi^2c^2\nu_6}+\sum_{j=1}^{3}\frac{c_j\beta_{66j}}{2h^{\frac{1}{2}}\omega_j^{\frac{3}{2}}}+\sum_{j=4}^{5}\frac{\zeta_{j6}^2(3\nu_6^2+\nu_j^2)}{8\pi^2c^2\nu_6(\nu_6^2-\nu_j^2)}, \tag{9b}$$

$$g_0=\frac{\beta_{123}^2\nu_1\nu_2\nu_3}{4D_{123}}+\sum_{k=1}^{3}\frac{\beta_{k45}^2\nu_k\nu_4\nu_5}{4D_{k45}}+\frac{h}{128\pi^2c}\sum_{k=1}^{3}\frac{\sigma_k^2}{\omega_k^2}+\frac{h}{16\pi^2c}\sum_{k=1}^{6}s_{kk};$$

$$D_{klm}=(\nu_k^4+\nu_l^4+\nu_m^4-2\nu_k^2\nu_l^2-2\nu_l^2\nu_m^2-2\nu_m^2\nu_k^2), \tag{9c}$$

$$N_{kkjj}=\frac{3\beta_{kkk}\beta_{jjk}}{\nu_k}+\frac{3\beta_{jjj}\beta_{kkj}}{\nu_j}+\frac{\beta_{kkl}\beta_{jjl}}{\nu_l}+\frac{\beta_{123}^2\nu_l(\nu_l^2-\nu_k^2-\nu_j^2)}{2D_{123}}, \quad (k-1,2,3; j=1,2,3; l=1,2,3)$$

$$N_{kk44}=\sum_{l=1}^{3}\frac{(1+2\delta_{kl})\beta_{kkl}\beta_{44l}}{\nu_l}+\frac{\beta_{k45}^2\nu_5(\nu_5^2-\nu_k^2-\nu_4^2)}{2D_{k45}}, \quad (k=1,2,3)$$

$$N_{kk55}=\sum_{l=1}^{3}\frac{(1+2\delta_{kl})\beta_{kkl}\beta_{55l}}{\nu_l}+\frac{\beta_{k45}^2\nu_4(\nu_4^2-\nu_k^2-\nu_5^2)}{2D_{k45}}, \quad (k=1,2,3)$$

$$N_{kk66}=\sum_{l=1}^{3}\frac{(1+2\delta_{kl})\beta_{kkl}\beta_{66l}}{\nu_l}, \quad (k=1,2,3)$$

$$N_{4455}=\sum_{l=1}^{3}\left[\frac{\beta_{44l}\beta_{55l}}{\nu_l}+\frac{\beta_{l45}^2\nu_l(\nu_l^2-\nu_4^2-\nu_5^2)}{2D_{l45}}\right],$$

$$N_{kk66}=\sum_{l=1}^{3}\frac{\beta_{kkl}\beta_{66l}}{\nu_l}. \quad (k=4,5) \tag{9d}$$

The general procedure is to set up the matrix of H' using as basic wave functions the harmonic oscillator functions $\psi V_i(q_i)$ corresponding to vibrational quantum numbers V_i, and the symmetrical top functions $\psi_R^0(J,K,M)$. H' is diagonal in the vibrational quantum numbers (to the second order of approximation) and in the quantum numbers, J and M, and has only $(K|K)$, $(K|K\pm 2)$,

$(K|K\pm4)$ elements in the quantum numbers $K=-J,\ -J+1,\ \cdots,\ J$. As is well known, the consequence of the latter fact is that the sub-matrix for a given vibrational state and J value can be reduced to a pair of sub-matrices corresponding to even and odd values of K, respectively. It was shown by Wilson[6] and in more detail by Shaffer and Nielsen[7] that by taking suitable linear combinations of the $\psi_R{}^0(J, K, M)$ each of the latter sub-matrices can be further reduced. The reduction indicated by Wilson can be effected also in the present case where $(K|K\pm4)$ elements are involved. Accordingly, we take as our set of basis functions

$$\Psi_{gK}=\prod_{i=1}^{6}\psi_{V_i}(q_i)\Lambda_K=\psi_V\frac{1}{\sqrt{2}}\{\psi_R{}^0(J,\ -K,\ M)+\psi_R{}^0(J,\ K,\ M)\}K>0,$$

$$\Psi_{g0}=\sum_{i=1}^{6}\psi_{V_i}(q_i)\Lambda_0=\psi_V\psi_R{}^0(J,\ O,\ M),\tag{10}$$

$$\Psi_{uK}=\prod_{i=1}^{6}\psi_{V_i}(q_i)\Phi_K=\psi_V\frac{1}{\sqrt{2}}\{\psi_R{}^0(J,\ -K,\ M)-\psi_R{}^0(J,\ K,\ M)\}K>0.$$

In terms of these we have

$$(\Psi_g{}^*|H'|\Psi_u)=(\Psi_u{}^*|H'|\Psi_g)=0\tag{11}$$

and the following non-vanishing elements:

$$\left.\begin{array}{l}(V,\ \Lambda_K|\ V,\ \Lambda_K)\\(V,\ \Phi_K|\ V,\ \Phi_K)\end{array}\right\}=(R_0+R_2K^2+R_3K^4)\pm\delta_{K1}(R_4+2R_5)f\pm\delta_{K2}R_6f(f-2),\quad(K=0,\ 1,\ \cdots,\ J)$$

$$(V,\ \Lambda_0|\ V,\ \Lambda_2)=(V,\ \Lambda_2|\ V,\ \Lambda_0)=(R_4+4R_5)[2f(f-2)]^{\frac{1}{2}},$$

$$\left.\begin{array}{l}(V,\ \Lambda_K|\ V,\ \Lambda_{K+2})\\(V,\ \Phi_K|\ V,\ \Phi_{K+2})\end{array}\right\}=(R_4+R_5[K^2+(K+2)^2])[\{f-K(K+1)\}\{f-(K+1)(K+2)\}]^{\frac{1}{2}}$$
$$\pm\delta_{K1}R_6f[(f-2)(f-6)]^{\frac{1}{2}},\quad(K>0)$$

$$\left.\begin{array}{l}(V,\ \Lambda_K|\ V,\ \Lambda_{K-2})\\(V,\ \Phi_K|\ V,\ \Phi_{K-2})\end{array}\right\}=(R_4+R_5[K^2+(K-2)^2])[\{f-K(K-1)\}\{f-(K-1)(K-2)\}]^{\frac{1}{2}}$$
$$\pm\delta_{K3}R_6f[(f-2)(f-6)]^{\frac{1}{2}},\quad(K>2)$$

$$(V,\ \Lambda_0|\ V,\ \Lambda_4)=(V,\ \Lambda_4|\ V,\ \Lambda_0)=R_6[2f(f-2)(f-6)(f-12)]^{\frac{1}{2}},$$

$$\left.\begin{array}{l}(V,\ \Lambda_K|\ V,\ \Lambda_{K\pm4})\\(V,\ \Phi_K|\ V,\ \Phi_{K\pm4})\end{array}\right\}=R_6[\{f-K(K\pm1)\}\{f-(K\pm1)(K\pm2)\}\{f-(K\pm2)(K\pm3)\}$$
$$\times\{f-(K\pm3)(K\pm4)\}]^{\frac{1}{2}},\quad(K+4\geq5,\ K-4\geq1)$$

(12)

where $f=J(J+1)$, and

$$R_0=\frac{E_v}{hc}+J(J+1)\left\{\frac{X_e}{2}\left[1+2\sum_{k=1}^{6}\frac{a_{kk}}{I^0_{xx}}(V_k+\tfrac{1}{2})\right]+\frac{Y_e}{2}\left[1+2\sum_{k=1}^{6}\frac{b_{kk}}{I^0_{yy}}(V_k+\tfrac{1}{2})\right]\right.$$
$$\left.+\frac{h^4}{64\pi^4}(\tau_{xxxx}+\tau_{yyyy}-2\tau_{xxyy}-2\tau_{yzyz})\right\}-D_JJ^2(J+1)^2$$

with

$$X_e=\frac{h}{8\pi^2cI^0_{xx}};\quad Y_e=\frac{h}{8\pi^2cI^0_{yy}};\quad D_J=\frac{h^4}{128\pi^4}\{3(\tau_{xxxx}+\tau_{yyyy})+2\tau_{xxyy}\};$$

$$R_2=Z_e\left[1+2\sum_{k=1}^{6}\frac{c_{kk}}{I^0_{zz}}(V_k+\tfrac{1}{2})\right]-\frac{X_e}{2}\left[1+2\sum_{k=1}^{6}\frac{a_{kk}}{I^0_{xx}}(V_k+\tfrac{1}{2})\right]-\frac{Y_e}{2}\left[1+2\sum_{k=1}^{6}\frac{b_{kk}}{I^0_{yy}}(V_k+\tfrac{1}{2})\right]$$
$$-\frac{5h^4}{128\pi^4}(\tau_{xxxx}+\tau_{yyyy}-2\tau_{xxyy}-4\tau_{yzyz})-D_{JK}J(J+1)$$

[6] E. B. Wilson, Jr., J. Chem. Phys. 4, 313 (1936).
[7] W. H. Shaffer and H. H. Nielsen, Phys. Rev. 56, 188 (1939).

with

$$Z_e = \frac{h}{8\pi^2 c I^0_{zz}}; \quad D_{JK} = \frac{h^4}{8\pi^4}\{\tau_{yzyz}+\tfrac{1}{2}(\tau_{yyzz}+\tau_{zzxx})-\tfrac{1}{4}\tau_{xxyy}-\tfrac{3}{8}(\tau_{xxxx}+\tau_{yyyy})\};$$

$$R_3 = \frac{h^4}{8\pi^4}\{\tau_{yzyz}+\tfrac{1}{2}(\tau_{yyzz}+\tau_{zzxx})-\tfrac{1}{8}\tau_{xxyy}-\tfrac{1}{2}\tau_{zzzz}-\tfrac{3}{16}(\tau_{xxxx}+\tau_{yyyy})\};$$

$$R_4 = \frac{X_e}{4}\left[1+2\sum_{k=1}^{6}\frac{a_{kk}}{I^0_{xx}}(V_k+\tfrac{1}{2})\right]-\frac{Y_e}{4}\left[1+2\sum_{k=1}^{6}\frac{b_{kk}}{I^0_{yy}}(V_k+\tfrac{1}{2})\right]-\frac{5h^4}{64\pi^4}\tau_{yzyz}-\frac{h^4}{64\pi^4}(\tau_{xxxx}-\tau_{yyyy})J(J+1);$$

$$R_5 = \frac{h^4}{128\pi^4}\{(\tau_{xxxx}-\tau_{yyyy})-2\tau_{zzxx}+2\tau_{yyzz}+4\tau_{yzyz}\};$$

$$R_6 = \frac{h^4}{128\pi^4}\{\tau_{xxyy}-\tfrac{1}{2}(\tau_{xxxx}+\tau_{yyyy})\}. \tag{13}$$

The vibrational term in R_0 is defined by

$$\frac{E_v}{hc} = G_0 + \sum_{k=1}^{6}(V_k+\tfrac{1}{2})\nu_k + \sum_{k=1}^{6}G_{kk}(V_k+\tfrac{1}{2})^2 + \sum_{k=1}^{5}\sum_{j>k}^{6}G_{kj}(V_k+\tfrac{1}{2})(V_j+\tfrac{1}{2}), \tag{14}$$

where

$$G_0 = g_0 - \frac{7}{16}\sum_{k=1}^{3}\frac{\beta^2_{kkk}}{\nu_k} + \frac{3}{8}\sum_{k=1}^{6}\gamma_{kkkk} + \frac{3}{16}\left[\frac{\beta^2_{112}\nu_2}{4\nu_1^2-\nu_2^2} + \frac{\beta^2_{113}\nu_3^2}{4\nu_1^2-\nu_3^2} + \frac{\beta^2_{221}\nu_1}{4\nu_2^2-\nu_1^2} + \frac{\beta^2_{223}\nu_3}{4\nu_2^2-\nu_3^2} + \frac{\beta^2_{331}\nu_1}{4\nu_3^2-\nu_1^2}\right.$$

$$\left. + \frac{\beta^2_{332}\nu_2}{4\nu_3^2-\nu_2^2} + \sum_{k=1}^{3}\sum_{j=4}^{6}\frac{\beta^2_{jjk}\nu_k}{4\nu_j^2-\nu_k^2}\right] - \frac{X_e}{2}\sum_{k=1}^{3}(\zeta^2_{k4}+\zeta^2_{k5}) - \frac{Y_e}{2}\sum_{k=1}^{3}\zeta^2_{k6} - \frac{Z_e}{2}(\zeta^2_{46}+\zeta^2_{56});$$

$$G_{kk} = \frac{3}{2}\gamma_{kkkk} - \frac{15}{4}\frac{\beta^2_{kkk}}{\nu_k} - \sum_{l=1}^{3}(1-\delta_{kl})\frac{(8\nu_k^2-3\nu_l^2)}{4\nu_l(4\nu_k^2-\nu_l^2)}\beta^2_{kkl}; \quad (k=1,2,3)$$

$$G_{kk} = \frac{3}{2}\gamma_{kkkk} - \sum_{j=1}^{3}\frac{(8\nu_k^2-3\nu_j^2)}{4\nu_j(4\nu_k^2-\nu_j^2)}\beta^2_{kkj}; \quad (k=4,5,6)$$

$$G_{jk} = \gamma_{jjkk} - N_{jjkk} - 2\left[\frac{\beta^2_{jjk}\nu_j}{4\nu_j^2-\nu_k^2} + \frac{\beta^2_{kkj}\nu_k}{4\nu_k^2-\nu_j^2}\right]; \quad (k,j=1,2,3)$$

$$G_{jk} = \gamma_{jjkk} - N_{jjkk} - \frac{2\beta^2_{kkj}\nu_k}{4\nu_k^2-\nu_j^2} + g_k\zeta^2_{jk}\left(\frac{\nu_j}{\nu_k}+\frac{\nu_k}{\nu_j}\right); \quad (j=1,2,3; k=4,5)$$

$$g_4 = X_e; \quad g_5 = Y_e; \quad g_6 = Z_c.$$

$$G_{45} = \gamma_{4455} - N_{4455};$$

$$G_{k6} = \gamma_{kk66} - N_{kk66} + Z_e\zeta^2_{k6}\left(\frac{\nu_k}{\nu_6}+\frac{\nu_6}{\nu_k}\right); \quad (k=4,5). \tag{15}$$

The energies (in term value form) are the roots of the secular equations

$$|(\Psi^*_{g,K}|H'|\Psi_{g,K'})-\epsilon\delta_{KK'}| = 0 \tag{16a}$$

and

$$|(\Psi^*_{u,K}|H'|\Psi_{u,K'})-\epsilon\delta_{KK'}| = 0. \tag{16b}$$

It is evident from Eqs. (12) that (16a) and (16b) can each be factored into sub-determinants corresponding to even and odd values of K, respectively. Illustrations of this reduction are given by Shaffer and Nielsen.[7]

3. TREATMENT OF AN APPROXIMATE DEGENERACY

The planar ZXY_2 model is of particular interest in connection with the formaldehyde molecule. Ebers and Nielsen[8] have attributed the complex structure of its infra-red absorption spectrum in the 7.5–10μ region to a Coriolis type interaction between a pair of perpendicular vibrations,†† one of class B_1 and one of class B_2. Their point of view is that such interactions may become prominent when two fundamental frequencies happen to be nearly equal. Nielsen[3] has considered the effect for a restricted model,
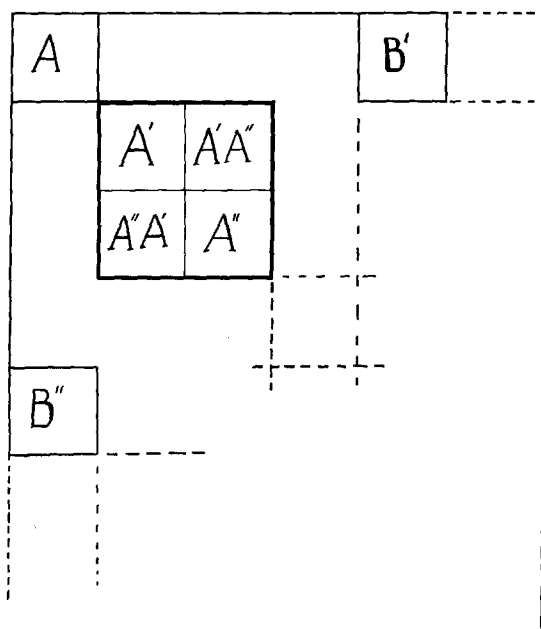

FIG. 1. Matrix of the transformed Hamiltonian when an approximate degeneracy exists between a pair of vibrational frequencies.

assuming formaldehyde to be a symmetrical top and neglecting the anharmonic terms in the potential energy. Wilson[6] has given a more general discussion for the asymmetrical top, but likewise neglected the anharmonic terms and other perturbing influences. He derived certain symmetry conditions which must be satisfied by the wave functions for the Coriolis perturbation to be significant. The states associated with the

[8] E. S. Ebers and H. H. Nielsen, J. Chem. Phys. 5, 822 (1937).
†† The abstract in reference 1 contains an error of statement concerning the pair of modes considered in this section.
[9] H. H. Nielsen, J. Chem. Phys. 5, 818 (1937).

frequencies noted above satisfy these conditions. In the present section we present a more complete treatment for the lower energy states associated with these frequencies, taking into account all the first-order terms in the Hamiltonian. We denote the frequencies as ν_5 (class B_2) and ν_6 (class B_1), respectively.

The effect of the accidental degeneracy makes itself felt in applying the contact transformation to remove from H_1 the ζ_{56} term in the p_z component of the vibrational angular momentum (Eq. (4)). The element in the transformation function T required to remove this term is[5]

$$\zeta_{56}\frac{P_z}{T^0_{zz}}\left\{\frac{(\omega_5^2+\omega_6^2)q_5q_6+2\omega_5\omega_6 p_{q_5}p_{q_6}/\hbar^2}{(\omega_5\omega_6)^{\frac{1}{2}}(\omega_6^2-\omega_5^2)}\right\}.$$

When the denominator becomes small, requirements as to orders of magnitude make such a term inadmissible. However, the contact transformation can be applied to remove all other terms in H_1, and we obtain in this case,

$$H_0'=H_0;$$

$$H_1'=-\frac{\zeta_{56}P_z}{T^0_{zz}}\left[\left(\frac{\nu_5}{\nu_6}\right)^{\frac{1}{2}}q_6 p_{q_5}-\left(\frac{\nu_6}{\nu_5}\right)^{\frac{1}{2}}q_5 p_{q_6}\right]. \quad (17)$$

H_2' retains the same form as in 8(b) except that we delete the ζ_{56} terms from the definitions of c_{55} and c_{66}. $\quad$ (18)

Using the set of wave functions defined in Eq. (10) as basis functions, we proceed as in Section 2 to set up the matrix of H'. As before, H' is diagonal in J and $V_1, \cdots, V_4$. The infinite sub-matrix for a given J value and set of vibrational quantum numbers $V_1, \cdots, V_4$ has the form shown in Fig. 1, corresponding to the totality of values of V_5 and V_6. The diagonal elements $A, A', A'', \cdots$ arise entirely from H_0' and H_2' and have precisely the same form as the sub-matrices of H' for given vibrational states developed in the preceding section. The definitions of $R_0, \cdots, R_6$ carry over completely except for the modification noted in (18). The non-diagonal elements are contributed entirely by H_1'. Elements $A'A''$ connect the pairs of states between which the approximate degeneracy exists, i.e., V_5, V_6 and $V_5\pm1$, $V_6\mp1$. Elements $B', B'', \cdots$ connect the states V_5, V_6 and $V_5\pm1$, $V_6\pm1$. The ratio of the orders of magnitude of the B' elements to the $A'A''$ elements is

$(\nu_5 - \nu_6)/(\nu_5 + \nu_6)$, while the contribution of the elements B' to the energies of the lower states is of order of magnitude $(\nu_5 - \nu_6)^2/\nu^3$. We are interested here in the ground state and the first excited states which give rise to the fundamental bands ν_5 and ν_6. To the first order of approximation, we may, therefore, neglect the elements B', B'', $\cdots$. Accordingly, the energies of the ground state are given by the developments in Section 2, setting $V_i = 0$. For the first excited states we set up the matrix using the set of functions

$$\Psi_{ga}(K) = \Psi_g(V_5 = 1, V_6 = 0, K);$$
$$\Psi_{gb}(K) = \Psi_g(V_5 = 0, V_6 = 1, K),$$
$$\Psi_{ua}(K) = \Psi_u(V_5 = 1, V_6 = 0, K); \quad (19)$$
$$\Psi_{ub}(K) = \Psi_u(V_5 = 0, V_6 = 1, K).$$

The elements of A' and A'', as noted above, are given by Eq. (12). Since

$$P_z\Lambda_k = -Kh\Phi_k; \quad P_z\Lambda_0 = 0;$$
$$P_z\Phi_k = -Kh\Lambda_k, \quad (20)$$

the only non-vanishing elements of $A'A''$ and $A''A'$ are:

$$(\Psi_{ga}^*|H_1'|\Psi_{ub}) = (\Psi_{ua}^*|H_1'|\Psi_{gb}) = -(\Psi_{ub}^*|H_1'|\Psi_{ga})$$
$$= -(\Psi_{gb}|H_1'|\Psi_{ua}^*) = iR_1 Khc; \quad (21)$$

where

$$R_1 = \frac{\zeta_{56}h}{8\pi^2 cI_{zz}^0}\left[\frac{\nu_5 + \nu_6}{(\nu_5\nu_6)^{\frac{1}{2}}}\right]. \quad (21a)$$

From these results and the discussion in Section 2 of the elements entering into A' and A'' it is evident that the matrix can be reduced to two sub-matrices involving elements of Ψ_{ga} with Ψ_{ub} and Ψ_{gb} with Ψ_{ua}, respectively, and that each sub-matrix can be further reduced into a set of two according to odd and even values of K, respectively. The secular equations for $J = 0, \cdots, 4$ are given below:

$J = 0$
$$\epsilon = R_{0a}; \quad \epsilon = R_{0b}. \quad (22)$$
$J = 1$
$$\epsilon = R_{0a}; \quad \epsilon = R_{0b}. \quad (23)$$

$$\epsilon^2 - [R_{0a} + R_{2a} + R_{3a} + R_{0b} + R_{2b} + R_{3b} + \{R_{4a} - R_{4b} + 2(R_{5a} - R_{5b})\}f]\epsilon$$
$$+ [R_{0a} + R_{2a} + R_{3a} + (R_{4a} + 2R_{5a})f][R_{0b} + R_{2b} + R_{3b} - (R_{4b} + 2R_{5b})f] - R_1^2 = 0, \quad (24)$$

$$\epsilon^2 - [R_{0a} + R_{2a} + R_{3a} + R_{0a} + R_{2b} + R_{3b} - \{R_{4a} - R_{4b} + 2(R_{5a} - R_{5b})\}f]\epsilon$$
$$+ [R_{0a} + R_{2a} + R_{3a} - (R_{4a} + 2R_{5a})f][R_{0b} + R_{2b} + R_{3b} + (R_{4b} + 2R_{5b})f] - R_1^2 = 0. \quad (25)$$

$J = 2$
Equations (24) and (25), and

$$\begin{vmatrix} R_{0a} - \epsilon & (R_{4a} + 4R_{5a})[2f(f-2)]^{\frac{1}{2}} & 0 \\ (R_{4a} + 4R_{5a})[2f(f-2)]^{\frac{1}{2}} & R_{0a} + 4R_{2a} + 16R_{3a} & 2iR_1 \\ & +R_{6a}f(f-2) - \epsilon & \\ 0 & -2iR_1 & R_{0b} + 4R_{2b} + 16R_{3b} \\ & & -R_{6b}f(f-2) - \epsilon \end{vmatrix} = 0. \quad (26)$$

Equations (26) with a and b interchanged. $\quad (27)$

$J = 3$
Equations (26) and (27), and

$$\begin{vmatrix} R_{0a} + R_{2a} + R_{3a} & [R_{4a} + 10R_{5a} + R_{6a}f] & iR_1 & 0 \\ +(R_{4a} + 2R_{5a})f - \epsilon & \times\{(f-2)(f-6)\}^{\frac{1}{2}} & & \\ [R_{4a} + 10R_{5a} + R_{6a}f] & R_{0a} + 9R_{2a} & 0 & 3iR_1 \\ \times\{(f-2)(f-6)\}^{\frac{1}{2}} & +81R_{3a} - \epsilon & & \\ -iR_1 & 0 & R_{0b} + R_{2b} + R_{3b} & [R_{4b} + 10R_{5b} - R_{6b}f] \\ & & -(R_{4b} + 2R_{5b})f - \epsilon & \times\{(f-2)(f-6)\}^{\frac{1}{2}} \\ 0 & -3iR_1 & [R_{4b} + 10R_{5b} - R_{6b}f] & R_{0b} + 9R_{2b} \\ & & \times\{(f-2)(f-6)\}^{\frac{1}{2}} & +81R_{3b} - \epsilon \end{vmatrix} = 0. \quad (28)$$

Equation (28) with a and b interchanged. (29)

$J = 4$

Equations (28) and (29), and

$$
\begin{vmatrix}
R_{0a}-\epsilon & \begin{matrix}(R_{4a}+2R_{5a})\\ \times\{2f(f-2)\}^{\frac{1}{2}}\end{matrix} & \begin{matrix}R_{6a}\{2f(f-2)\\ \times(f-6)(f-12)\}^{\frac{1}{2}}\end{matrix} & 0 & 0 \\
\begin{matrix}(R_{4a}+2R_{5a})\\ \times\{2f(f-2)\}^{\frac{1}{2}}\end{matrix} & \begin{matrix}R_{0a}+4R_{2a}+16R_{3a}\\ +R_{6a}f(f-2)-\epsilon\end{matrix} & \begin{matrix}(R_{4a}+20R_{5a})\\ \times\{(f-6)(f-12)\}^{\frac{1}{2}}\end{matrix} & 2iR_1 & 0 \\
\begin{matrix}R_{6a}\{2f(f-2)\\ \times(f-6)(f-12)\}^{\frac{1}{2}}\end{matrix} & \begin{matrix}(R_{4a}+20R_{5a})\\ \times\{(f-6)(f-12)\}^{\frac{1}{2}}\end{matrix} & \begin{matrix}R_{0a}+16R_{2a}\\ +256R_{3a}-\epsilon\end{matrix} & 0 & 4iR_1 \\
0 & -2iR_1 & 0 & \begin{matrix}R_{0b}+4R_{2b}+16R_{3b}\\ -R_{6b}f(f-2)-\epsilon\end{matrix} & \begin{matrix}(R_{4b}+20R_{5b})\\ \times\{(f-6)(f-12)\}^{\frac{1}{2}}\end{matrix} \\
0 & 0 & -4iR_1 & \begin{matrix}(R_{4b}+20R_{5b})\\ \times\{(f-6)(f-12)\}^{\frac{1}{2}}\end{matrix} & \begin{matrix}R_{0b}+16R_{2b}\\ +256R_{3b}-\epsilon\end{matrix}
\end{vmatrix}=0. \quad (30)
$$

Equation (30) with a and b interchanged and R_1 replaced by $-R_1$. (31)

R_{ka} is the value of the constant R_k for the state $V_5=1$, $V_6=0$, and the given J-value; R_{kb} is the corresponding constant for the state $V_5=0$, $V_6=1$. The secular equations for the state $V_5=V_6=0$ can be obtained from the above by setting $R_1=0$ in each case and deleting the subscripts a and b. In the latter case only one of a pair of equations (e.g., (26) and (27)) need be used. The reduction of the secular equation, discussed in Section 2, effected by the use of the basis functions (10) is directly evident in the above equations.

The treatment above has given more than is required for a first-order approximation since the definitions of constants R_k contain terms contributed by H_2. These can be dropped from the final results with little difficulty. It should be noted that when the degeneracy is complete, i.e., $\nu_5-\nu_6=0$, the non-diagonal elements B', B'', $\cdots$ vanish and the secular Eqs. (22)–(31) give the energies to the second order of approximation.

The application of the results obtained in this paper to the analysis of the formaldehyde spectrum is in progress and will be reported in a later publication.

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