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Vibration–Rotation Energies of Planar ZXY_2 Molecules

Part I. The Vibrational Modes and Frequencies

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The normal modes and frequencies of planar ZXY_2 molecules are investigated using the most general potential function consistent with the symmetry. The equilibrium configuration has the symmetry of the group C_{2V} and consequently the frequencies are all non-degenerate. By developing a set of generalized coordinates having the same symmetry properties as the normal coordinates, the secular determinant is factored directly into one third-order determinant, one linear factor, and one second-order determinant.

1. INTRODUCTION

CERTAIN discrepancies exist between the interpretations of the infra-red spectra and the electronic spectra of formaldehyde.[1] Preparatory to a re-investigation of the infra-red data we felt it would be desirable to have a complete unified treatment of the vibration-rotation energies of planar ZXY_2 molecules. In the present paper we develop the normal coordinates and frequencies; in Part II we shall consider the quantum-mechanical Hamiltonian and its eigenvalues and special problems which are pertinent to the interpretation of the formaldehyde spectrum.

The vibrational frequencies have been studied previously by Lechner[2] for a valence force model and by Bernstein[3] who studied the symmetrical modes under the same type of force system. In the formulation presented here a general potential function is used so that, if desired, other force models can be investigated. Also we give the normal coordinate transformation which is needed for subsequent work.

2. THE SYMMETRY COORDINATES

We take as our system of axes the principal axes of the equilibrium configuration. The YZ plane is the plane of the molecule and the Z axis coincides with the twofold axis of symmetry. The coordinates of the equilibrium positions are designated as x_K^0, y_K^0, z_K^0 (the X atom being numbered 1, the Z atom 2, the Y atoms 3 and 4). The components of the displacement of the kth atom from its equilibrium position are x_K, y_K, z_K. The coordinate system and the symmetry elements of the molecule are shown in Fig. 1, and in Table I are listed the coordinates of the equilibrium positions.

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[1] A brief summary of these spectra is given by H. Sponer and E. Teller, Rev. Mod. Phys. **13**, 113 (1941).
[2] F. Lechner, Ber. Wien. Akad. Wiss. [IIa] **141**, 633 (1932).
[3] H. J. Bernstein, J. Chem. Phys. **6**, 718 (1938).

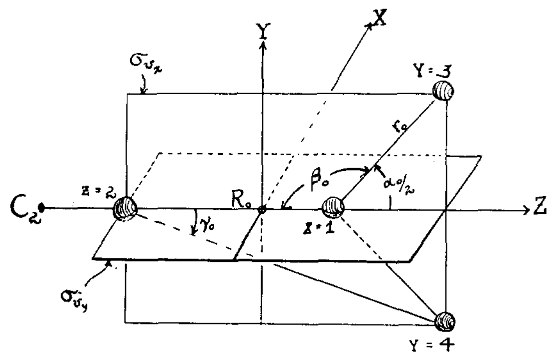

FIG. 1. The equilibrium configuration and its symmetry elements. R_0 is the Z–X distance; r_0, the X–Y distance; β_0, the ZXY angle.

The equilibrium configuration has the symmetry of the group C_{2v}. The irreducible representations of this group are given in Table II. Applying the group theory analysis of Wigner[4] and Wilson[5] we find that the normal coordinates are all non-degenerate and fall into the following symmetry classes: three, totally symmetric, transforming according to the irreducible representation A_1, one transforming according to B_1, and two transforming according to B_2. The secular equation can, therefore, be factored into one third-order factor, one linear factor, and one factor of second degree. Accordingly, we seek three symmetry coordinates belonging to class A_1, one coordinate belonging to class B_1, and two coordinates belonging to class B_2. The single coordinate of class B_1 is the normal coordinate of that symmetry type.

It is convenient to set up first the coordinates expressing infinitesimal rigid translations and rotations. These are

$$Q_\alpha{}^T=\frac{1}{M^{\frac{1}{2}}}\sum_{i=1}^{4} m_i^{\frac{1}{2}}\xi_{i\alpha}$$

$$(\alpha=x,\ y,\ z\,;\ \xi_{ix}=\xi_i,\ \xi_{iy}=\eta_i\,;\ \xi_{iz}=\zeta_i), \qquad (1)$$

and

$$Q_{\omega\alpha}=\frac{1}{(\overset{0}{I}_{\alpha\alpha})^{\frac{1}{2}}}\sum_{i=1}^{4} m_i^{\frac{1}{2}}(\overset{0}{x}_{i\beta}\xi_{i\gamma}-\overset{0}{x}_{i\gamma}\xi_{i\beta})$$

$$(\alpha,\beta,\gamma=x,y,\text{ or } z\,;\ \overset{0}{x}_{ix}=x_i{}^0\,;\ \overset{0}{x}_{iy}=y_i{}^0,\text{ etc.}), \qquad (2)$$

where we have introduced mass-reduced coordinates $\xi_{i\alpha}=m_i^{\frac{1}{2}}x_{i\alpha}$. $M=\sum m_i$ and $\overset{0}{I}_{\alpha\alpha}$ are the equilibrium moments of inertia. The choice of the principal axes as our coordinate system insures the orthogonality of the above coordinates. Setting $Q_\alpha{}^T=0$ and $Q_{\omega\alpha}=0$ is equivalent to using Eckart's conditions[6] when the vibrational motion is referred to rotating axes.

We require that all the symmetry coordinates be mutually orthogonal and also be orthogonal to the translational and rotational coordinates. The totally symmetric coordinates must be linear combinations of ζ_1, ζ_2, $(\zeta_3+\zeta_4)$, and $(\eta_3-\eta_4)$. The coordinates of class B_2 are linear combinations of η_1, η_2, $(\eta_3+\eta_4)$, and $(\zeta_3-\zeta_4)$. The single coordinate of class B_1 is a linear function of the ξ_i only. Except for the above restrictions, the A_1 and B_2 coordinates are completely arbitrary. We have chosen them so that, when the ZXY_2 model is reduced to the symmetrical XY_3 model, they reduce to the symmetry coordinates developed for the latter model by Silver and Shaffer.[7] We give below the inverse transformation expressing the $\xi_{i\alpha}$ in terms of the symmetry coordinates. To get the

TABLE I. Coordinates of the equilibrium positions.

k	$x_k{}^0$	$y_k{}^0$	$z_k{}^0$
1	0	0	$\dfrac{m_ZR_0+2m_Yr_0\cos\beta_0}{M}$
2	0	0	$\dfrac{2m_Yr_0\cos\beta_0-(m_X+2m_Y)R_0}{M}$
3	0	$r_0\sin\beta_0$	$\dfrac{m_ZR_0-(m_X+m_Z)r_0\cos\beta_0}{M}$
4	0	$-r_0\sin\beta_0$	(same as 3)

$M=m_X+m_Z+2m_Y$.

TABLE II. Irreducible representations of the group C_{2v}.

	E	C_2	σv_x	σv_y
A_1; z	1	1	1	1
B_1; x	1	-1	-1	1
A_2	1	1	-1	-1
B_2; y	1	-1	1	-1

[4] E. Wigner, Göttingen Nachrichten, p. 133 (1930).
[5] E. B. Wilson, Jr., Phys. Rev. 45, 706 (1934).
[6] C. Eckart, Phys. Rev. 47, 552 (1935).
[7] S. Silver and W. H. Shaffer, J. Chem. Phys. 9, 599 (1941).

latter explicitly, simply interchange rows and columns.

$$\xi_1=\left(\frac{2m_Ym_Z}{MI^0_{yy}}\right)^{\frac{1}{2}}(z_3{}^0-z_2{}^0)Q_6;\quad \xi_2=\left(\frac{2m_Xm_Y}{MI^0_{yy}}\right)^{\frac{1}{2}}(z_1{}^0-z_3{}^0)Q_6;\quad \xi_3=\xi_4=\left(\frac{m_Xm_Z}{2MI^0_{yy}}\right)^{\frac{1}{2}}(z_2{}^0-z_1{}^0)Q_6. \tag{3a}$$

$$\eta_1=\left(\frac{2m_Ym_Z}{MI^0_{yy}}\right)^{\frac{1}{2}}(z_3{}^0-z_2{}^0)S_4+\left(\frac{m_XI^0_{zz}}{I^0_{yy}I^0_{xx}}\right)^{\frac{1}{2}}z_1{}^0S_5;$$

$$\eta_2=\left(\frac{2m_Xm_Y}{MI^0_{yy}}\right)^{\frac{1}{2}}(z_1{}^0-z_3{}^0)S_4+\left(\frac{m_ZI^0_{zz}}{I^0_{yy}I^0_{xx}}\right)^{\frac{1}{2}}z_2{}^0S_5;$$

$$\left.\begin{matrix}\eta_3\\ \eta_4\end{matrix}\right\}=\begin{matrix}+\\-\end{matrix}\left[\frac{m_Z{}^{\frac{1}{2}}\sin\beta_0}{[2(m_Z+2m_Y\cos^2\beta_0)]^{\frac{1}{2}}}S_1-\cos\beta_0\left[\frac{m_Z+2m_Y}{2(m_Z+2m_Y\cos^2\beta_0)}\right]^{\frac{1}{2}}S_3\right]$$
$$+\left(\frac{m_Xm_Z}{2mI^0_{yy}}\right)^{\frac{1}{2}}(z_2{}^0-z_1{}^0)S_4+\left(\frac{m_YI^0_{zz}}{I^0_{xx}I^0_{yy}}\right)^{\frac{1}{2}}z_3{}^0S_5. \tag{3b}$$

$$\zeta_1=\left[\frac{m_Z+2m_Y}{M}\right]^{\frac{1}{2}}S_2;$$

$$\zeta_2=\frac{2m_Y{}^{\frac{1}{2}}\cos\beta_0}{[2(m_Z+2m_Y\cos^2\beta_0)]^{\frac{1}{2}}}S_1-\left[\frac{m_Xm_Z}{M(m_Z+2m_Y)}\right]^{\frac{1}{2}}S_2+\frac{2(m_Ym_Z{}^{\frac{1}{2}})\sin\beta_0}{[2(m_Z+2m_Y)(m_Z+2m_Y\cos^2\beta_0)]^{\frac{1}{2}}}S_3;$$

$$\left.\begin{matrix}\zeta_3\\ \zeta_4\end{matrix}\right\}=-\frac{m_Z{}^{\frac{1}{2}}\cos\beta_0}{[2(m_Z+2m_Y\cos^2\beta_0)]^{\frac{1}{2}}}S_1-\left[\frac{m_Xm_Y}{M(m_Z+2m_Y)}\right]^{\frac{1}{2}}S_2$$
$$-\frac{m_Z\sin\beta_0}{[2(m_Z+2m_Y)(m_Z+2m_Y\cos^2\beta_0)]^{\frac{1}{2}}}S_3\pm\left(\frac{I^0_{yy}}{2I^0_{xx}}\right)^{\frac{1}{2}}S_5. \tag{3c}$$

S_1, S_2, S_3 are the totally symmetric coordinates; they reduce to Q_1, S_{2a}, and S_{4a} of the XY_3 case, respectively. S_4 and S_5 are of class B_2 and reduce to S_{2b} and S_{4b} of the XY_3 problem. Q_6 is unique; it corresponds to Q_3 of the XY_3 molecule, representing the bending of the plane of the molecule. The coordinates are all normalized to unity. It is readily verified that, because the symmetry coordinates are orthogonal to the translational and rotational coordinates, the $\xi_{i\alpha}$ satisfy Eckart's conditions.

3. THE POTENTIAL ENERGY

Let δr_{ij} be the changes in the $Z-X$ and $X-Y_i$ distances, δq_{ij} be the variations in the $Z-Y_i$ and Y_i-Y_j distances. The most general quadratic potential consistent with the symmetry is

$$\begin{aligned}2V=&K_1\delta r_{12}^2+K_2(\delta r_{13}^2+\delta r_{14}^2)+K_3(\delta q_{23}^2+\delta q_{24}^2)+K_4\delta q_{34}^2+2K_5\delta r_{12}(\delta r_{13}+\delta r_{14})\\&+2K_6\delta r_{12}(\delta q_{23}+\delta q_{24})+2K_7\delta r_{12}\delta q_{34}+2K_8\delta r_{13}\delta r_{14}+2K_9(\delta r_{13}\delta q_{23}+\delta r_{14}\delta q_{24})\\&+2K_{10}(\delta r_{13}\delta q_{24}+\delta r_{14}\delta q_{23})+2K_{11}(\delta r_{13}+\delta r_{14})\delta q_{34}+2K_{12}\delta q_{23}\delta q_{24}+2K_{13}(\delta q_{23}+\delta q_{24})\delta q_{34}.\end{aligned} \tag{4}$$

This does not include the energy associated with the bending of the plane of the molecule. The same difficulty arises in all planar molecules, since for the latter type of deformation the δr_{ij} and δq_{ij} are zero to the first order of infinitesimals. It is necessary to add a special term for this motion. Since Q_6 is the normal coordinate for this vibrational mode, we can write for the potential energy associated with the bending of the plane of the molecule

$$V_{B_1}=(k_{66}/2)Q_6{}^2. \tag{5}$$

Returning to (4), we express V in terms of the symmetry coordinates by calculating the δr_{ij} and δq_{ij} in terms of them and substituting into (4). The labor is considerably reduced by considering the A_1 and B_2 modes separately. In the totally symmetric modes we have

$$\delta r_{13}=\delta r_{14},\quad \delta q_{23}=\delta q_{24}=\delta r_{12}\cos\gamma_0-\frac{\cos\gamma_0}{\cos\beta_0}\delta r_{13}+\frac{1}{2}\frac{\sin(\beta_0+\gamma_0)}{\cos\beta_0}\delta q_{34}.$$

For these modes the potential energy reduces to

$$2V_{A1}=\Lambda_{11}\delta r_{12}^2+\Lambda_{22}\delta r_{13}^2+\Lambda_{33}\delta q_{34}^2+2\Lambda_{12}\delta r_{12}\delta r_{13}+2\Lambda_{13}\delta r_{12}\delta q_{34}+2\Lambda_{23}\delta r_{13}\delta q_{34},\tag{6}$$

where

$$\begin{aligned}
\Lambda_{11}&=K_1+2(K_3+K_{12})\cos^2\gamma_0+4K_6\cos\gamma_0,\\
\Lambda_{22}&=2(K_2+K_8)+2(K_3+K_{12})\cos^2\gamma_0/\cos^2\beta_0-4(K_9+K_{10})\cos\gamma_0/\cos\beta_0,\\
\Lambda_{33}&=K_4+(K_3+K_{12})\sin^2(\beta_0+\gamma_0)/2\cos^2\beta_0+2K_{13}\sin(\beta_0+\gamma_0)/\cos\beta_0,\\
\Lambda_{12}&=2K_5-2(K_3+K_{12})\frac{\cos^2\gamma_0}{\cos\beta_0}-2K_6\frac{\cos\gamma_0}{\cos\beta_0}+2(K_9+K_{10})\cos\gamma_0,\\
\Lambda_{13}&=K_7+(K_3+K_{12})\frac{\sin(\beta_0+\gamma_0)\cos\gamma_0}{\cos\beta_0}+K_6\frac{\sin(\beta_0+\gamma_0)}{\cos\beta_0}+2K_{13}\cos\gamma_0,\\
\Lambda_{23}&=2K_{11}-(K_3+K_{12})\frac{\sin(\beta_0+\gamma_0)\cos\gamma_0}{\cos^2\beta_0}+(K_9+K_{10})\frac{\sin(\beta_0+\gamma_0)}{\cos\beta_0}-2K_{13}\cos\gamma_0/\cos\beta_0.
\end{aligned}\tag{7}$$

Calculating δr_{12}, δr_{13}, and δq_{34} in terms of S_1, S_2, and S_3, and substituting into (6), we obtain

$$2V_{A1}=k_{11}S_1^2+k_{22}S_2^2+k_{33}S_3^2+2k_{12}S_1S_2+2k_{13}S_1S_3+2k_{23}S_2S_3,\tag{8}$$

where

$$\begin{aligned}
k_{11}&=\frac{1}{m_Z+2m_Y\cos^2\beta_0}\bigg\{\frac{2m_Y\cos^2\beta_0}{m_Z}\Lambda_{11}+\frac{m_Z}{2m_Y}\Lambda_{22}+\frac{2m_Z\sin^2\beta_0}{m_Y}\Lambda_{33}\\
&\qquad-2\cos\beta_0\Lambda_{12}-4\sin\beta_0\cos\beta_0\Lambda_{13}+\frac{2m_Z\sin\beta_0}{m_Y}\Lambda_{23}\bigg\};\\
k_{22}&=\frac{M}{m_X(m_Z+2m_Y)}\{\Lambda_{11}+\Lambda_{22}\cos^2\beta_0+2\Lambda_{12}\cos\beta_0\};\\
k_{33}&=\frac{1}{m_Z+2m_Y\cos^2\beta_0}\bigg\{\frac{2m_Y\sin^2\beta_0}{m_Z+2m_Y}\Lambda_{11}+\frac{2m_Y\sin^2\beta_0\cos^2\beta_0}{m_Z+2m_Y}\Lambda_{22}+\frac{2(m_Z+2m_Y)\cos^2\beta_0}{m_Y}\Lambda_{33}\\
&\qquad+\frac{4m_Y\sin^2\beta_0\cos\beta_0}{m_Z+2m_Y}\Lambda_{12}+4\sin\beta_0\cos\beta_0\Lambda_{13}+4\sin\beta_0\cos^2\beta_0\Lambda_{23}\bigg\};\\
k_{12}&=\frac{M^{\frac{1}{2}}}{[2m_Xm_Ym_Z(m_Z+2m_Y)(m_Z+2m_Y\cos^2\beta_0)]^{\frac{1}{2}}}\{-2m_Y\cos\beta_0\Lambda_{11}+m_Z\cos\beta_0\Lambda_{22}\\
&\qquad+(m_Z-2m_Y\cos^2\beta_0)\Lambda_{12}+2m_Z\sin\beta_0\Lambda_{13}+2m_Z\sin\beta_0\cos\beta_0\Lambda_{23}\};\\
k_{13}&=\frac{1}{(m_Z+2m_Y\cos^2\beta_0)[m_Z(m_Z+2m_Y)]^{\frac{1}{2}}}\bigg\{2m_Y\sin\beta_0\cos\beta_0\Lambda_{11}-m_Z\sin\beta_0\cos\beta_0\Lambda_{22}\\
&\qquad-\frac{2m_Z(m_Z+2m_Y)}{m_Y}\sin\beta_0\cos\beta_0\Lambda_{33}-(m_Z-2m_Y\cos^2\beta_0)\sin\beta_0\Lambda_{12}\\
&\qquad+2[(m_Z+2m_Y)\cos^2\beta_0-m_Z\sin^2\beta_0]\Lambda_{13}-\frac{m_Z\cos\beta_0[m_Z+2m_Y(1+\sin^2\beta_0)]}{m_Y}\Lambda_{23}\bigg\};\\
k_{23}&=\frac{-M^{\frac{1}{2}}}{(m_Z+2m_Y)[2m_Xm_Y(m_Z+2m_Y\cos^2\beta_0)]^{\frac{1}{2}}}\{2m_Y\sin\beta_0\Lambda_{11}+2m_Y\sin\beta_0\cos^2\beta_0\Lambda_{22}\\
&\qquad+4m_Y\sin\beta_0\cos\beta_0\Lambda_{12}+2(m_Z+2m_Y)\cos\beta_0\Lambda_{13}+2(m_Z+2m_Y)\cos^2\beta_0\Lambda_{23}\}.
\end{aligned}\tag{9}$$

In the B_2 modes we have

$$\delta r_{12}=0\,;\quad \delta r_{13}=-\delta r_{14}\,;\quad \delta q_{23}=-\delta q_{24}\,;\quad \delta q_{34}=0,$$

whence,

$$2V_{B_2}=2(K_2-K_8)\delta r_{13}^2+2(K_3-K_{12})\delta q_{23}^2+4(K_9-K_{10})\delta r_{13}\delta q_{23}. \tag{10}$$

Calculating δr_{13} and δq_{23} in terms of S_4 and S_5 and substituting into (10), we obtain

$$2V_{B_2}=k_{44}S_4^2+k_{55}S_5^2+2k_{45}S_4S_5, \tag{11}$$

where

$$k_{44}=\frac{M}{m_YI^0_{yy}}\left\{\frac{m_Z(z_2^0)^2\sin^2\beta_0}{m_X}(K_2-K_8)+\frac{m_X}{m_Z}(z_1^0\sin\gamma_0)^2(K_3-K_{12})-2z_1^0z_2^0\sin\gamma_0\sin\beta_0(K_9-K_{10})\right\};$$

$$k_{55}=\frac{I^0_{xx}}{m_YI^0_{yy}}\{\cos^2\beta_0(K_2-K_8)+\cos^2\gamma_0(K_3-K_{12})-2\cos\beta_0\cos\gamma_0(K_9-K_{10})\}\,;$$

$$k_{45}=-\frac{1}{m_YI^0_{yy}}\left(\frac{MI^0_{xx}}{m_Xm_Z}\right)^{\frac{1}{2}}\{m_Zz_2^0\sin\beta_0\cos\beta_0(K_2-K_8)+m_Xz_1^0\sin\gamma_0\cos\gamma_0(K_3-K_{12})$$
$$-[m_Zz_2^0\sin\beta_0\cos\gamma_0+m_Xz_1^0\sin\gamma_0\cos\beta_0](K_9-K_{10})\}. \tag{12}$$

The Simple Valence Potential

The simple valence potential has found wide applicability as a starting point in the analysis of the vibrational frequencies of organic molecules. Accordingly, we give below the relations between the valence force constants and the generalized constants in the potential energy of the planar ZXY_2 molecule. For the latter molecule, the valence potential has the form

$$2V=k_{XZ}\delta r_{12}^2+k_{XY}(\delta r_{13}^2+\delta r_{14}^2)+k_{ZXY}(\delta\beta_1^2+\delta\beta_2^2)+k_{YXY}\delta\alpha^2, \tag{13}$$

where the deformation constants k_{ZXY} and k_{YXY} have dimensions of ergs/(radians)^2. Considering the A_1 and B_2 modes separately, as was done above, (13) is readily transformed into the general forms (6) and (10), respectively. In this way, we obtain

$$\Lambda_{11}=k_{XZ},$$
$$\Lambda_{22}=2k_{XY}+\frac{4\tan^2\beta_0}{r_0^2}\left(k_{YXY}+\frac{k_{ZXY}}{2}\right),$$
$$\Lambda_{33}=\frac{1}{r_0^2\cos^2\beta_0}\left(k_{YXY}+\frac{k_{ZXY}}{2}\right),$$
$$\Lambda_{12}=\Lambda_{13}=0,$$
$$\Lambda_{23}=-\frac{2\tan\beta_0}{r_0^2\cos\beta_0}\left(k_{YXY}+\frac{k_{ZXY}}{2}\right); \tag{14}$$

and

$$K_2-K_8=k_{XY}+k_{ZXY}\left\{\frac{R_0\cos\beta_0-r_0}{R_0r_0\sin\beta_0}\right\}^2,$$
$$K_3-K_{12}=\frac{k_{ZXY}}{R_0^2\sin^2\gamma_0},$$
$$K_9-K_{10}=\frac{k_{ZXY}(R_0\cos\beta_0-r_0)}{R_0^2r_0\sin\beta_0}. \tag{15}$$

4. THE SECULAR EQUATIONS

Since the symmetry coordinates are orthogonal and are normalized to unity, the kinetic energy expressed in terms of them is a sum of squares:

$$T=\tfrac{1}{2}(\dot{S}_1^2+\dot{S}_2^2+\dot{S}_3^2)+\tfrac{1}{2}\dot{Q}_6^2+\tfrac{1}{2}(\dot{S}_4^2+\dot{S}_5^2). \tag{16}$$

The frequencies are the roots of the secular determinants

$$|k_{ij}-\lambda\delta_{ij}|=0; \quad \lambda=4\pi^2\nu^2c^2. \tag{17}$$

It is directly evident that Q_6 is the normal coordinate of class B_1, corresponding to the frequency (in wave numbers)

$$\nu_6=\frac{1}{2\pi c}\sqrt{k_{66}}. \tag{18}$$

The totally symmetric coordinates give rise to a third-order determinantal equation; the frequencies are the roots of the cubic,

$$\lambda^3-(k_{11}+k_{22}+k_{33})\lambda^2+(k_{11}k_{22}+k_{11}k_{33}+k_{22}k_{33}-k_{13}^2-k_{12}^2-k_{23}^2)\lambda \\ +k_{11}k_{23}^2+k_{22}k_{13}^2+k_{33}k_{12}^2-2k_{12}k_{13}k_{23}-k_{11}k_{22}k_{33}=0. \tag{19}$$

Let λ_1, λ_2, λ_3 be the roots and Q_1, Q_2, Q_3 be the respective normal coordinates. The transformation from the symmetry coordinates to the normal coordinates is then,

$$\begin{pmatrix} S_1 \\ S_2 \\ S_3 \end{pmatrix}=\begin{pmatrix} l_{11} & l_{12} & l_{13} \\ l_{21} & l_{22} & l_{23} \\ l_{31} & l_{32} & l_{33} \end{pmatrix}\begin{pmatrix} Q_1 \\ Q_2 \\ Q_3 \end{pmatrix}, \tag{20}$$

where

$$l_{1k}=\frac{k_{13}(k_{22}-\lambda_k)-k_{12}k_{23}}{D_k}; \quad l_{2k}=\frac{k_{23}(k_{11}-\lambda_k)-k_{12}k_{13}}{D_k}; \quad l_{3k}=\frac{k_{12}^2-(k_{11}-\lambda_k)(k_{22}-\lambda_k)}{D_k}, \tag{21}$$

with

$$D_k=\{[k_{13}(k_{22}-\lambda_k)-k_{12}k_{23}]^2+[k_{23}(k_{11}-\lambda_k)-k_{12}k_{13}]^2+[(k_{11}-\lambda_k)(k_{22}-\lambda_k)-k_{12}^2]^2\}^{\frac{1}{2}}.$$

The B_2 frequencies are obtained from the roots of the quadratic equation

$$\lambda^2-(k_{44}+k_{55})\lambda+k_{44}k_{55}-k_{45}^2=0. \tag{22}$$

Denoting these frequencies as ν_4 and ν_5, we have

$$\nu_{4,5}=\frac{1}{2\pi c}\left\{\frac{k_{44}+k_{55}}{2}\pm\left[\left(\frac{k_{44}-k_{55}}{2}\right)^2+k_{45}^2\right]^{\frac{1}{2}}\right\}^{\frac{1}{2}}. \tag{23}$$

The transformation from S_4 and S_5 to the corresponding normal coordinates Q_4 and Q_5 is

$$S_4=l_{44}Q_4+l_{45}Q_5, \quad S_5=l_{54}Q_4+l_{55}Q_5, \tag{24}$$

where

$$l_{44}=l_{55}=\frac{k_{45}}{[(k_{44}-\lambda_4)^2+k_{45}^2]^{\frac{1}{2}}}; \quad l_{45}=-l_{54}=\frac{k_{44}-\lambda_4}{[(k_{44}-\lambda_4)^2+k_{45}^2]^{\frac{1}{2}}}. \tag{25}$$