Vibrations of Tetrahedral Pentatomic Molecules. Part I. Potential Energy. Part II. Kinetic Energy and Normal Frequencies of Vibration

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Part I. It is shown that the most general potential energy function consistent with tetrahedral symmetry involves five force constants, also that with a suitable choice of variables this expression may be written in a quite simple form convenient for the discussion of different types of vibration. Special cases of potential energy such as the "valence" force and the central force cases involving less than five force constants are considered and their connection with the general case discussed.

Part II. Expressions for the vibration frequencies of molecules of the type YX_3X^* and $YX_2X_2^*$ (X^* being an isotope of X) are derived in terms of constants in the potential energy function and the masses of the various atoms. These expressions are valid for any value of $\Delta m/m$ where m is the mass of X and $m+\Delta m$ the mass of X^*. Hence the results are applicable to the isotopes of hydrogen. While YX_4 has one single, one double and two triple frequencies, the slight asymmetry introduced by X^* in YX_3X^* partially removes the degeneracy giving three single and three double frequencies. For $YX_2X_2^*$ the degeneracy is completely removed and the molecule has nine single frequencies.

THE methods used[1] to derive vibration frequencies of molecules of the type YXX^* and YX_2X^* may be extended to symmetrical tetrahedral pentatomic molecules YX_3X^* and $YX_2X_2^*$. We begin by setting up expressions for the potential energy V and the kinetic energy T. The normal frequencies of vibration ω are then given by the roots of the determinantal equation $|\lambda T - V| = 0$ where $\lambda = 4\pi^2\omega^2$.

PART I

Consider a symmetrical molecule YX_4. At equilibrium the X atoms form the corners of a regular tetrahedron with the Y atom at the center. We study this system when it vibrates with a very small amplitude around its position of equilibrium. Following Dennison[2] we assume that the potential energy function V has the same symmetry as the geometrical configuration of the system; this will be the *only* assumption used in the derivation of an expression for V.

Let the positions of the four X atoms be given by the points A_1, A_2, A_3, A_4 and let A_5 be the position of the Y atom. We denote by the superscript 0 the equilibrium positions of the various atoms. Let:

$$A_iA_j = q_{ij} = q^0 + \delta q_{ij};\quad A_5A_i = r_i = r^0 + \delta r_i \quad \text{and} \quad \angle A_iA_5A_j = 2\Omega_{ij} = 2(\Omega + \delta\Omega_{ij})$$
$$(i, j = 1, \cdots 4,\ i \neq j,\ q_{ij} = q_{ji}). \quad (1)$$

$r^0 = \frac{1}{2}\sqrt{\frac{3}{2}}q^0$ (since the equilibrium configuration is that of a regular tetrahedron) and the various δq_{ij} and δr_i are taken to be small quantities of the first order.

Since the system has only nine degrees of internal freedom only nine of the ten quantities defined by Eq. (1) are linearly independent. It is, however, convenient to use ten variables in writing V with the same symmetry as the geometrical configuration; one of the variables is then eliminated by the relation which gives the linear dependence.

We have the potential energy then as a function of the mutual displacements of the particles:

$$V = V(\delta q_{12},\ \delta q_{13} \cdots \delta q_{34},\ \delta r_1,\ \cdots \delta r_4)$$

[1] E. O. Salant and J. E. Rosenthal, Phys. Rev. **42**, 812 (1932).

[2] D. M. Dennison, Rev. Mod. Phys. **3**, 303 (1931).

and, with force constants K_1, $K_2\cdots K_7$, it is written in the most general symmetrical form in the δq_{ij} and the δr_i

$$V=\tfrac{1}{2}\Big[K_1\sum_{i,j}\tfrac{1}{2}\delta q_{ij}^2+K_2\sum_{i,j,n}\tfrac{1}{2}\delta q_{ij}\delta q_{jn}+K_3\sum_{i\neq j\neq n\neq 1}\tfrac{1}{2}\delta q_{1j}\delta q_{in}+K_4\sum_i \delta r_i^2+K_5\sum_{i,j}\tfrac{1}{2}\delta r_i\delta r_j+K_6\sum_{i,j}\delta r_i\delta q_{ij}+K_7\sum_{i,j,n}\tfrac{1}{2}\delta r_i\delta q_{jn}\Big]. \quad (2)$$

We use $i\neq j\neq n$ and unless otherwise indicated all summations extend from 1 to 4. V may also be written

$$V=\tfrac{1}{2}\Big[(K_1-\tfrac{1}{2}K_2)\sum_{i,j}\tfrac{1}{2}\delta q_{ij}^2+\tfrac{1}{2}K_2(\sum_{i,j}\tfrac{1}{2}\delta q_{ij})^2+(K_3-K_2)\sum_{i\neq j\neq n\neq 1}\tfrac{1}{2}\delta q_{1i}\delta q_{jn}+(K_4-\tfrac{1}{2}K_5)\sum_i \delta r_i^2+\tfrac{1}{2}K_5(\sum_i \delta r_i)^2+K_6(\sum_i \delta r_i)(\sum_{j,n}\tfrac{1}{2}\delta q_{jn})+(K_7-K_6)\sum_{i,j,n}\tfrac{1}{2}\delta r_i\delta q_{jn}\Big]. \quad (3)$$

This expression for the potential energy is, however, not convenient for the study of vibrations of the system YX_4 and therefore new variables in which to express V are introduced. As will be seen below, these new variables are the components of vectors giving the displacements of one particle with respect to the center of gravity of others.

We start by defining a cartesian coordinate system x, y, z with its origin at the center of gravity of the tetrahedron; the xy plane is parallel to the $A_1A_2A_3$ plane and the x axis is parallel to A_2A_3, the positive direction being from $A_2\rightarrow A_3$. We let (x_j, y_j, z_j) represent the point $A_j(x_j=x_j^0+\delta x_j$, etc.). We then define new variables ξ, η, ζ, x, y, z, u, v, s by the relations:

$$\xi=x_5-\tfrac{1}{4}\sum_i x_i,\quad \eta=y_5-\tfrac{1}{4}\sum_i y_i,\quad \zeta=z_5-\tfrac{1}{4}\sum_i z_i,\quad x=x_4-\tfrac{1}{3}(x_3+x_2+x_1),\quad y=y_4-\tfrac{1}{3}(y_3+y_2+y_1),$$
$$q^0\surd\tfrac{2}{3}+z=z_4-\tfrac{1}{3}(z_3+z_2+z_1),\quad u=x_1-\tfrac{1}{2}(x_2+x_3),\quad v+\tfrac{1}{2}q^0\surd 3=y_1-\tfrac{1}{2}(y_2+y_3),$$
$$z_1-\tfrac{1}{2}(z_2+z_3)=0,\quad q^0+s=x_3-x_2,\quad y_3-y_2=0,\quad z_3-z_2=0. \quad (4)$$

Our problem then is to find $V(\xi, \eta, \zeta, x, y, z, u, v, s)=V(\delta q_{12}\cdots\delta q_{34}, \delta r_1\cdots\delta r_4)$. The old variables are, or course, expressed in terms of x_j, y_j, z_j by:

$$q_{ij}^2=(q^0+\delta q_{ij})^2=(x_i-x_j)^2+(y_i-y_j)^2+(z_i-z_j)^2 \qquad (i, j=1\cdots 4,\ i\neq j),$$
$$r_i^2=(r^0+\delta r_i)^2=(x_5-x_i)^2+(y_5-y_i)^2+(z_5-z_i)^2. \quad (5)$$

Eliminating the various x_j, y_j, z_j between Eqs. (4) and (5) we obtain the following relations:

$$r_1^2+r_2^2+r_3^2+r_4^2=4(\xi^2+\eta^2+\zeta^2)+\tfrac{3}{4}[x^2+y^2+(q^0\surd\tfrac{2}{3}+z)^2]+\tfrac{2}{3}[u^2+(\tfrac{1}{2}q^0\surd 3+v)^2]+\tfrac{1}{2}(q^0+s)^2,$$
$$\tfrac{1}{3}(r_1^2+r_2^2+r_3^2)-r_4^2=2[\xi x+\eta y+\zeta(z+q^0\surd\tfrac{2}{3})]-\tfrac{1}{2}[x^2+(z+q^0\surd\tfrac{2}{3})^2+y^2]+2[u^2+(v+\tfrac{1}{2}q^0\surd 3)^2]/9+\tfrac{1}{6}(q^0+s)^2,$$
$$\tfrac{1}{2}(r_2^2+r_3^2)-r_1^2=2[\xi u+(v+\tfrac{1}{2}q^0\surd 3)\eta]+\tfrac{1}{2}[ux+(v+\tfrac{1}{2}q^0\surd 3)y]-\tfrac{1}{3}[u^2+(v+\tfrac{1}{2}q^0\surd 3)^2]+\tfrac{1}{4}(q^0+s)^2,$$
$$r_2^2-r_3^2=2(q^0+s)(\xi+\tfrac{1}{4}x+\tfrac{1}{3}u). \quad (6)$$
$$q_{14}^2+q_{24}^2+q_{34}^2=3[x^2+y^2+(z+q^0\surd\tfrac{2}{3})^2]+\tfrac{2}{3}[u^2+(v+\tfrac{1}{2}q^0\surd 3)^2]+\tfrac{1}{2}(q^0+s)^2,$$
$$\tfrac{1}{2}(q_{24}^2+q_{34}^2)-q_{14}^2=2[ux+(v+\tfrac{1}{2}q^0\surd 3)y]-\tfrac{1}{3}[u^2+(v+\tfrac{1}{2}q^0\surd 3)^2]+\tfrac{1}{4}(q^0+s)^2,$$
$$q_{24}^2-q_{34}^2=2(q^0+s)(x+\tfrac{1}{3}u),$$
$$q_{12}^2+q_{13}^2+q_{23}^2=2[u^2+(v+\tfrac{1}{2}q^0\surd 3)^2]+3(q^0+s)^2/2,$$
$$\tfrac{1}{2}(q_{12}^2+q_{13}^2)-q_{23}^2=u^2+(v+\tfrac{1}{2}q^0\surd 3)^2-\tfrac{3}{4}(q^0+s)^2,$$
$$q_{12}^2-q_{13}^2=2(q^0+s)u.$$

Expanding and neglecting all small quantities of the second order we obtain

$$
\begin{aligned}
\delta r_1+\delta r_2+\delta r_3+\delta r_4 &= z+\tfrac{2}{3}v\sqrt{2}+s\sqrt{\tfrac{2}{3}},\\
\tfrac{1}{3}(\delta r_1+\delta r_2+\delta r_3)-\delta r_4 &= 4\zeta/3-\tfrac{2}{3}z+2v\sqrt{2/9}+\tfrac{1}{3}s\sqrt{\tfrac{2}{3}},\\
\tfrac{1}{2}(\delta r_3+\delta r_2)-\delta r_1 &= \eta\sqrt{2}+y/\sqrt{2}-\tfrac{1}{3}v\sqrt{2}+\tfrac{1}{2}s\sqrt{\tfrac{2}{3}},\\
\delta r_2-\delta r_3 &= 2\sqrt{\tfrac{2}{3}}(\xi+\tfrac{1}{4}x+\tfrac{1}{3}u),\\
\delta q_{14}+\delta q_{24}+\delta q_{34} &= z\sqrt{6}+v/\sqrt{3}+\tfrac{1}{2}s,\\
\tfrac{1}{2}(\delta q_{34}+\delta q_{24})-\delta q_{14} &= \tfrac{1}{2}y\sqrt{3}+\tfrac{1}{2}(-v+\tfrac{1}{2}s\sqrt{3})/\sqrt{3},\\
\delta q_{24}-\delta q_{34} &= x+u/3,\\
\delta q_{12}+\delta q_{13}+\delta q_{23} &= (v+\tfrac{1}{2}s\sqrt{3})\sqrt{3},\\
\tfrac{1}{2}(\delta q_{12}+\delta q_{13})-\delta q_{23} &= -\tfrac{1}{2}(-v+\tfrac{1}{2}s\sqrt{3})\sqrt{3},\\
\delta q_{12}-\delta q_{13} &= u.
\end{aligned}
\tag{7}
$$

It follows from Eq. (7) that

$$(\delta r_1+\delta r_2+\delta r_3+\delta r_4)\sqrt{6}=(\delta q_{12}+\delta q_{13}+\delta q_{14}+\delta q_{23}+\delta q_{24}+\delta q_{34}),\tag{8}$$

which is the equation of linear dependence,[3] and by using it we may rewrite Eq. (3) as:

$$V=\tfrac{1}{2}\Big[k_1\sum_{i,\,j}\tfrac{1}{2}\delta q_{ij}{}^2+k_2\sum_{i,\,j,\,n\neq 1}\tfrac{1}{2}\delta q_{1i}\delta q_{jn}+k_3\sum_i\delta r_i{}^2+k_4\big(\sum_i\delta r_i\big)^2+k_5\sum_{i,\,j,\,n}\tfrac{1}{2}\delta r_i\,\delta q_{jn}\Big],\tag{9}$$

making use of *only five* independent force constants. The k's are related to the K's by

$$
\begin{aligned}
&k_1=K_1-\tfrac{1}{2}K_2, \qquad k_2=K_3-K_2, \qquad k_3=K_4-\tfrac{1}{2}K_5,\\
&k_4=\tfrac{1}{2}K_5+3K_2+K_6\sqrt{6}, \qquad k_5=K_7-K_6.
\end{aligned}
\tag{10}
$$

The form of Eqs. (7) suggests that a further simplification may be obtained by introducing new coordinates defined by:

$$
\begin{aligned}
&\alpha=x+4u/3, \qquad \beta=y-4v/3+2s/\sqrt{3}, \qquad \gamma=-2z+(\tfrac{2}{3}v+s/\sqrt{3})\sqrt{2},\\
&\rho=x-2u/3, \qquad \sigma=y+2v/3-s/\sqrt{3}, \qquad \tau=2z+(4v/3+2s/\sqrt{3})\sqrt{2}.
\end{aligned}
\tag{11}
$$

We then substitute[4] in Eq. (9) the expressions for the various δq_{ij} and δr_i in terms of the new variables and we obtain:

$$
\begin{aligned}
V&=\tfrac{1}{2}[A(\xi^2+\eta^2+\zeta^2)+B(\alpha^2+\beta^2+\gamma^2)+C(\rho^2+\sigma^2)+2D(\xi\alpha+\eta\beta+\zeta\gamma)+E\tau^2]\\
&=\tfrac{1}{2}[(A\xi^2+B\alpha^2+2D\xi\alpha)+(A\eta^2+B\beta^2+2D\eta\beta)+(A\zeta^2+B\gamma^2+2D\zeta\gamma)+C\rho^2+C\sigma^2+E\tau^2]\\
&=V_1(\xi,\alpha)+V_1(\eta,\beta)+V_1(\zeta,\gamma)+V_2(\rho)+V_2(\sigma)+V_3(\tau).
\end{aligned}
\tag{13}
$$

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[3] The exact expression which will be used later is:

$$\sum_{i,\,j}\tfrac{1}{2}\delta q_{ij}-\sqrt{6}\sum_i\delta r_i=2\Big[\sum_i\delta r_i{}^2-4(\xi^2+\eta^2+\zeta^2)-\tfrac{1}{4}\sum_{i,\,j}\tfrac{1}{2}\delta q_{ij}{}^2\Big]/q^0.\tag{8'}$$

[4] This substitution is greatly simplified by making use of the identities

$$
\begin{aligned}
a_1^2+a_2^2+a_3^2&\equiv\tfrac{1}{3}(a_1+a_2+a_3)^2+\tfrac{2}{3}[\tfrac{1}{2}(a_2+a_3)-a_1]^2+\tfrac{1}{2}(a_3-a_2)^2,\\
a_1b_1+a_2b_2+a_3b_3&\equiv\tfrac{1}{3}(a_1+a_2+a_3)(b_1+b_2+b_3)+\tfrac{2}{3}[\tfrac{1}{2}(a_2+a_3)-a_1][\tfrac{1}{2}(b_2+b_3)-b_1]+\tfrac{1}{2}(a_3-a_2)(b_3-b_2),\\
a_1^2+a_2^2+a_3^2+a_4^2&\equiv\tfrac{1}{4}(a_1+a_2+a_3+a_4)^2+\tfrac{3}{4}[\tfrac{1}{3}(a_1+a_2+a_3)-a_4]^2+\tfrac{2}{3}[\tfrac{1}{2}(a_2+a_3)-a_1]^2+\tfrac{1}{2}(a_2-a_3)^2.
\end{aligned}
\tag{12}
$$

This form of the potential energy function is very convenient[5] for the study of the vibrations of the molecule YX_4. The constants in Eq. (13) are related to the k's by:

$$A=4k_3/3;\qquad B=\tfrac{1}{4}k_1-\tfrac{1}{8}k_2+k_3/12-\tfrac{1}{2}k_5/\surd 6;\qquad C=\tfrac{1}{4}(k_1+\tfrac{1}{2}k_2);$$
$$D=\tfrac{1}{3}k_3-k_5/\surd 6;\qquad E=\tfrac{1}{4}[k_1+\tfrac{1}{2}k_2+\tfrac{1}{4}k_3+k_4+k_5(3/2)^{\frac{1}{2}}]. \tag{14}$$

This general expression for the potential energy has the disadvantage of involving five independent force constants while (in the absence of isotopic shifts) the spectrum of the symmetrical tetrahedral molecule consists of only four fundamental frequencies. It is possible, however, to reduce the number of these constants by means of suitable physical assumptions. These assumptions and the special potential energy functions they give rise to having been discussed by Urey and Bradley,[6] we shall consider here only the connection between the general expression and some special cases. The potential energy expression which includes central forces and the forces perpendicular to the lines of bonds is:[6a]

$$V'=(\partial V'/\partial q)^0(\sum_{i,j}\tfrac{1}{2}\delta q_{ij}-6^{\frac{1}{2}}\sum_i\delta r_i)+\tfrac{1}{2}(\partial^2 V'/\partial r^2)^0\sum_i\delta r_i^2+\tfrac{1}{2}(\partial^2 V'/\partial q^2)^0\sum_{i,j}\tfrac{1}{2}\delta q_{ij}^2$$
$$+\tfrac{1}{2}f_2'\sum_{i,j}\tfrac{1}{2}(r^0\delta\Omega_{ij})^2. \tag{15}$$

The prime is used to distinguish this function from the general V. Henceforth all quantities referring to V' (the potential energy with four force constants) will be marked by a prime. Similarly we shall indicate by a double prime the central force case and by a triple prime the valence force case.

To compare Eqs. (2) and (15) we have to express the last term in Eq. (15) in terms of the δr_i and the δq_{ij}.[7]

$$r^0\delta\Omega_{ij}=\tfrac{1}{2}[\delta q_{ij}-\sin\Omega(\delta r_i+\delta r_j)]/\cos\Omega=\tfrac{1}{2}\delta q_{ij}\surd 3-(\delta r_i+\delta r_j)/\surd 2. \tag{16}$$

Let

$$(\partial^2 V'/\partial r^2)^0=f_1',\qquad (\partial^2 V'/\partial q^2)^0=f_3',\qquad (\partial V'/\partial q)^0/q^0=f_4'. \tag{17}$$

With the use of Eqs. (17), (16) and (8′) we may write:

$$V'=\tfrac{1}{2}[(\tfrac{3}{4}f_2'+f_3'-f_4')\sum_{i,j}\tfrac{1}{2}\delta q_{ij}^2+(f_1'+(3/2)f_2'+4f_4')\sum_i\delta r_i^2+f_2'\sum_{i,j}\tfrac{1}{2}\delta r_i\delta r_j$$
$$-(3/2)^{\frac{1}{2}}f_2'\sum_{i,j}\delta r_i\delta q_{ij}-16f_4'(\xi^2+\eta^2+\zeta^2)], \tag{18}$$

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[5] In some cases, however, it is better to define

$$\eta'=(\eta\surd 2+\zeta)/\surd 3,\qquad \beta'=(\beta\surd 2+\gamma)/\surd 3,\qquad \zeta'=(\eta-\zeta\surd 2)/\surd 3,\qquad \gamma'=(\beta-\gamma\surd 2)/\surd 3, \tag{11'}$$

and write

$$V=V_1(\xi,\alpha)+V_1(\eta',\beta')+V_1(\zeta',\gamma')+V_2(\rho)+V_2(\sigma)+V_3(\tau). \tag{13'}$$

This change of variables is equivalent to a rotation of the y and z axes such that the y axis becomes parallel to the direction $A_1^0A_4^0$. Hence η', ζ', β', γ' are suitable variables in any case in which there is a preferred direction $A_1^0A_4^0$ in the molecule.

[6] H. C. Urey and C. A. Bradley, Phys. Rev. **38**, 1969 (1931).

[6a] The last term in this expression—a sum of six terms depending on the square of the change in angle between two bond lines—is not equivalent to the sum of four terms depending on the square of the displacement of the bond line from its equilibrium position (the term in k_2 in Eq. (1) of reference 6). Hence our potential energy function differs to that extent from the expression (1) in reference 6. The only result of this difference, however, is that our frequency $\omega_{(\rho)(\sigma)}$ given by Eqs. (19) and (31) depends in a different way on the "valence" force constant than the corresponding frequency ν_2 in the above reference.

[7] Eq. (16) is obtained by differentiating $2r_ir_j\cos 2\Omega_{ij}=r_i^2+r_j^2-q_{ij}^2$ and retaining only the linear terms in the δr_i and δq_{ij}.

comparing the coefficients in Eq. (18) with those in Eq. (2)[8] we obtain as the connection between the f' and the constants in Eq. (13)

$$A'=4(f_1'+f_2'-8f_4')/3;\qquad B'=(f_1'+\tfrac{1}{4}f_2'+3f_3'+f_4')/12;\qquad C'=\tfrac{1}{4}(\tfrac{3}{4}f_2'+f_3'-f_4');$$
$$D'=\tfrac{1}{3}(f_1'-\tfrac{1}{2}f_2'+4f_4');\qquad E'=(f_1'+4f_3')/16. \tag{19}$$

Of these five quantities only four are linearly independent. The equation of linear dependence may easily be found to be

$$D'=10B'-2C'-8E'. \tag{20}$$

Eq. (19) may then be solved uniquely for the various f's giving

$$f_1'=\tfrac{1}{4}A'+20B'-4C'-16E';\qquad f_2'=12B'+4C'-16E';$$
$$f_3'=-\tfrac{1}{16}A'-5B'+C'+8E';\qquad f_4'=-\tfrac{1}{16}A'+4B'-4E'. \tag{21}$$

Additional equations of linear dependence are obtained for the central force case where $f_2''=0$ and the valence force case where $f_3'''=f_4'''=0$.

PART II

To obtain the kinetic energy expression we begin by referring the positions of the particles to a fixed coordinate system XYZ, which may be made to coincide with the moving system xyz by means of a small rotation in space. The kinetic energy T is expressed in terms of the displacements δX, δY, δZ of the various particles from their positions of equilibrium. For the jth particle:

$$\delta X_j=\delta x_j+\psi y_j^0+\theta z_j^0;\qquad \delta Y_j=-\psi x_j^0+\delta y_j+\varphi z_j^0;\qquad \delta Z_j=-\theta x_j^0-\varphi y_j^0+\delta z_j, \tag{22}$$

combining Eq. (4) with Eq. (22) we obtain the direct connection between the various δX, δY, δZ and our nine variables ξ, η, ζ, x, y, z, u, v, s. We have also three relations of the type:

$$\sum_1^5 m_j\delta\dot{X}_j=0;\qquad \sum_1^5 m_j\delta\dot{Y}_j=0;\qquad \sum_1^5 m_j\delta\dot{Z}_j=0, \tag{23}$$

expressing the conservation of linear momentum. (m_j denotes the mass of the jth particle and may have different values for the two molecules YX_3X^* and $YX_2X_2^*$.) The kinetic energy is, of course:

$$T=\tfrac{1}{2}\sum_{j=1}^{5}\sum_{XYZ} m_j\delta\dot{X}_j^2. \tag{24}$$

Consider first molecule YX_3X^*. Let $m_5=M$, $m_4=m+\Delta m$, $m_3=m_2=m_1=m$. We may now substitute in Eq. (24) for the various $\delta\dot{X}$, $\delta\dot{Y}$, $\delta\dot{Z}$ their values in terms of $\dot\xi$, $\dot\eta$, $\dot\zeta$, $\dot x$, $\dot y$, $\dot z$, $\dot u$, $\dot v$, $\dot s$. (Calculations are greatly simplified by the symmetrical way in which the variables are defined.)

We obtain then:

$$T=\tfrac{1}{2}m\{(1-\epsilon\mu)^{-1}[4\mu(\dot\xi^2+\dot\eta^2+\dot\zeta^2)+\tfrac{3}{4}(1+3\epsilon-\epsilon\mu)((\dot x+q^0\dot\theta\sqrt{\tfrac{2}{3}})^2+(\dot y+q^0\dot\varphi\sqrt{\tfrac{2}{3}})^2+\dot z^2)$$
$$-6\mu\epsilon(\dot\xi(\dot x+q^0\dot\theta\sqrt{\tfrac{2}{3}})+\dot\eta(\dot y+q^0\dot\varphi\sqrt{\tfrac{2}{3}})+\dot\zeta\dot z)]+\tfrac{2}{3}[(\dot u+\tfrac{1}{2}q^0\dot\psi\sqrt{3})^2+\dot v^2+\tfrac{3}{4}\dot s^2+\tfrac{3}{4}(\dot\theta^2+\dot\varphi^2+\dot\psi^2)q^{02}]\}, \tag{25}$$

where $\epsilon=\Delta m/(4m+\Delta m)$ and $\mu=M/(4m+M)$. We eliminate $q^0\dot\theta$, $q^0\dot\psi$ and $q^0\dot\varphi$ by means of the equations of conservation of angular momentum ($\partial T/\partial\dot\theta=0$; $\partial T/\partial\dot\varphi=0$; $\partial T/\partial\dot\psi=0$) and transform to the new set of variables α, β, γ, ρ, σ, τ. We then have T in the form:

$$T=T^{(1)}(\dot\xi,\dot\alpha,\dot\rho)+T^{(1)}(\dot\eta,\dot\beta,\dot\sigma)+T^{(2)}(\dot\zeta,\dot\gamma,\dot\tau), \tag{26}$$

where

[8] Attention must be paid to the presence of a term in $(\xi^2+\eta^2+\zeta^2)$.

$$T^{(1)}(\dot{\xi},\dot{\alpha},\dot{\rho})=\tfrac{1}{2}m(1+3\epsilon/2-\epsilon\mu)^{-1}[4\mu(1+3\epsilon/2)\dot{\xi}^2+\tfrac{1}{8}(1+2\epsilon-\epsilon\mu)\dot{\alpha}^2+\tfrac{1}{4}(1+5\epsilon/2-\epsilon\mu)\dot{\rho}^2$$
$$+\tfrac{1}{4}\epsilon\dot{\alpha}\dot{\rho}-\mu\epsilon\dot{\xi}(\dot{\alpha}+2\dot{\rho})].\qquad(27)$$
$$T^{(2)}(\dot{\zeta},\dot{\gamma},\dot{\tau})=\tfrac{1}{2}m(1-\epsilon\mu)^{-1}[4\mu\dot{\zeta}^2+\tfrac{1}{8}(1+2\epsilon-\epsilon\mu)\dot{\gamma}^2+\tfrac{1}{16}(1+\epsilon-\epsilon\mu)\dot{\tau}^2-\tfrac{1}{4}\epsilon\dot{\gamma}\dot{\tau}+\epsilon\mu\dot{\zeta}(2\dot{\gamma}-\dot{\tau})].$$

On account of Eq. (26) we may break up the nine rowed determinant into two three rowed ones, one of which is squared:

$$\{|\lambda T^{(1)}-V^{(1)}|\}^2=0,\qquad |\lambda T^{(2)}-V^{(2)}|=0.\text{[9]}\qquad(28)$$

Expanding Eq. (28) we get the equations for the frequencies. Instead of numbering the frequencies we shall merely indicate by a series of subscripts as to what variables, hence to what types of motion, they correspond. Double frequencies will be indicated by two sets of subscripts each in a separate parenthesis.

Letting $\tfrac{1}{4}\Delta m/(m+\Delta m)=\kappa$

$$[m^3\lambda^3{}_{(\xi\alpha\rho),\,(\eta\beta\sigma)}-P_1m^2\lambda^2+P_2m\lambda-P_3]^2=0,\qquad m^3\lambda^3{}_{(\zeta\gamma\tau)}-R_1m^2\lambda^2+R_2m\lambda-R_3=0,$$
$$P_1=\tfrac{1}{4}A(1-\mu\kappa)/\mu+8B(1-\tfrac{1}{2}\kappa)+2\kappa D+4C(1-\kappa),$$
$$P_2=AC(1-\kappa-\mu\kappa)/\mu+32BC(1-3\kappa/2)+8\kappa DC+2(AB-D^2)(1-\tfrac{1}{2}\kappa-\mu\kappa)/\mu,$$
$$P_3=8C(AB-D^2)(1-3\kappa/2-\mu\kappa)/\mu,\qquad(29)$$
$$R_1=\tfrac{1}{4}A(1-\mu\kappa)/\mu+8B(1-2\kappa)-4\kappa D+16E(1-\kappa),$$
$$R_2=4AE(1-\kappa-\mu\kappa)/\mu+128BE(1-3\kappa)-64\kappa DE+2(AB-D^2)(1-2\kappa-\kappa\mu)/\mu,$$
$$R_3=32E(AB-D^2)(1-3\kappa-\kappa\mu)/\mu.$$

It may be pointed out that whereas the results in Part I were approximate these expressions are *exact* and hence valid for any value of κ. In particular Eq. (29) may be used to compute isotope shifts due to the presence of the heavy isotope of hydrogen.

If $\kappa^2\ll 1$ Eqs. (29) take the somewhat simpler form

$$[m\lambda_{(\rho),\,(\sigma)}-4C(1-\kappa)]^2\{m^2\lambda^2{}_{(\xi\alpha),\,(\eta\beta)}-m\lambda[\tfrac{1}{4}A(1-\mu\kappa)/\mu+8B(1-\tfrac{1}{2}\kappa)+2\kappa D]$$
$$+2(AB-D^2)(1-\tfrac{1}{2}\kappa-\mu\kappa)/\mu\}^2=0,\qquad(30)$$
$$[m\lambda_{(\tau)}-16E(1-\kappa)]\{m^2\lambda^2{}_{(\zeta\gamma)}-m\lambda[\tfrac{1}{4}A(1-\mu\kappa)/\mu+8B(1-2\kappa)-4\kappa D]$$
$$+2(AB-D^2)(1-2\kappa-\kappa\mu)/\mu\}=0.$$

For molecule $YX_2X_2{}^*$, $m_5=M$; $m_4=m_1=m$; $m_3=m_2=m+\Delta m$. We obtain then instead of Eqs. (25) to (30), Eqs. (25′) to (30′) given below.

$$T=\tfrac{1}{2}m(1-2\epsilon'\mu)^{-1}\{4\mu(\dot{\xi}^2+\dot{\eta}^2+\dot{\zeta}^2)+\tfrac{1}{4}(1+2\epsilon'-2\mu\epsilon')[(\dot{x}+q^0\dot{\theta}\sqrt{\tfrac{2}{3}}+4\dot{u}/3+2q^0\dot{\psi}/\sqrt{3})^2$$
$$+(\dot{y}+q^0\dot{\varphi}\sqrt{\tfrac{2}{3}}+4\dot{v}/3)^2+(\dot{z}-2q^0\dot{\varphi}/\sqrt{3})^2]+4\epsilon'\mu[\dot{\xi}(\dot{x}+q^0\dot{\theta}\sqrt{\tfrac{2}{3}}+4\dot{u}/3+2q^0\dot{\psi}/\sqrt{3})$$
$$+\eta(\dot{y}+q^0\dot{\varphi}\sqrt{\tfrac{2}{3}}+4\dot{v}/3)+\dot{\zeta}(\dot{z}-2q^0\dot{\varphi}/\sqrt{3})]\}+\tfrac{1}{2}m\{\tfrac{1}{2}[(\dot{x}+q^0\dot{\theta}\sqrt{\tfrac{2}{3}}-\tfrac{2}{3}\dot{u}-q^0\dot{\psi}/\sqrt{3})^2$$
$$+(\dot{y}+q^0\dot{\varphi}\sqrt{\tfrac{2}{3}}-\tfrac{2}{3}\dot{v})^2+(\dot{z}+q^0\dot{\varphi}/\sqrt{3})^2]+\tfrac{1}{2}(1+2\epsilon')(1-2\epsilon')^{-1}(\dot{s}^2+q^{02}\dot{\psi}^2+q^{02}\dot{\theta}^2)\},\qquad(25')$$

where $\epsilon'=\epsilon/(1+\epsilon)$, ξ, η', ζ', α, β', γ', ρ, σ, τ are suitable variables for this case in which there obviously is a preferred direction $A_1{}^0A_4{}^0$ in the molecule. It is also convenient to define $\theta'=\theta\sqrt{\tfrac{2}{3}}+2\psi/\sqrt{3}$, $\psi'=\theta\sqrt{\tfrac{2}{3}}-\psi/\sqrt{3}$ and use $\partial T/\partial\dot{\theta}'=\partial T/\partial\dot{\psi}'=\partial T/\partial\dot{\varphi}=0$. Then we obtain T as:

$$T=T_1'(\dot{\xi},\dot{\alpha})+T_1''(\dot{\zeta}',\dot{\gamma}')+T_2(\dot{\rho})+T^*(\dot{\eta}',\dot{\beta}',\dot{\sigma},\dot{\tau}),\qquad(26')$$

[9] $V^{(1)}(\xi,\alpha,\rho)=V_1(\xi,\alpha)+V_2(\rho)$, $V^{(2)}(\zeta,\gamma,\tau)=V_1(\zeta,\gamma)+V_3(\tau)$.

where

$$T_1'(\dot\xi,\,\dot\alpha)=\tfrac{1}{2}m(1+2\epsilon')(1-2\mu\epsilon'+\epsilon'-2\epsilon'^2)^{-1}[4\mu(1-\epsilon')\dot\xi^2+\tfrac{1}{8}(1+2\epsilon'-2\mu\epsilon')\dot\alpha^2+2\epsilon'\mu\dot\xi\dot\alpha],$$
$$T_1''(\dot\zeta',\,\dot\gamma')=\tfrac{1}{2}m(1-2\mu\epsilon'+\epsilon')^{-1}[4\mu(1+\epsilon')\dot\zeta'^2+\tfrac{1}{8}(1+2\epsilon-2\mu\epsilon')\dot\gamma'^2-2\epsilon'\mu\dot\zeta'\dot\gamma'],$$
$$T_2(\dot\rho)=\tfrac{1}{2}m[\tfrac{1}{4}(1+2\epsilon')\dot\rho^2],$$
$$\begin{aligned}T^*(\dot\eta',\,\dot\beta',\,\dot\sigma,\,\dot\tau)=\tfrac{1}{2}m(1-2\mu\epsilon')^{-1}(1-2\epsilon')^{-1}[4\mu(1-2\epsilon')\dot\eta'^2+\tfrac{1}{8}(1-2\mu\epsilon')\dot\beta'^2\\+\tfrac{1}{4}(1-2\mu\epsilon'-8\epsilon'^2/3+8\mu\epsilon'^2/3)\dot\sigma^2+\tfrac{1}{16}(1-2\mu\epsilon'-4\epsilon'^2/3+4\mu\epsilon'^2/3)\dot\tau^2-\tfrac{1}{3}\epsilon'^2(1-\mu)\dot\sigma\dot\tau\sqrt{2}\\-\epsilon'(1-2\mu\epsilon')\dot\sigma\dot\beta'/\sqrt{6}+\tfrac{1}{2}\epsilon'(1-2\mu\epsilon')\dot\tau\dot\beta'/\sqrt{3}+4\mu\epsilon'(1-2\epsilon')\dot\eta'\dot\sigma\sqrt{\tfrac{2}{3}}+2\mu\epsilon'(1-2\epsilon')\dot\eta'\dot\tau/\sqrt{3}].\end{aligned}\qquad(27')$$

The determinantal equations are:[10]

$$|\lambda T_1'-V_1|=0,\qquad |\lambda T_1''-V_1|=0,\qquad |\lambda T_2-V_2|=0,\qquad |\lambda T^*-V^*|=0,\qquad(28')$$

which on expansion give:

$$\begin{aligned}&m^2\lambda^2{}_{(\xi\alpha)}-[\tfrac{1}{4}A(1-2\mu\kappa)/\mu+8B(1-3\kappa)-4\kappa D]m\lambda+2(AB-D^2)(1-3\kappa-2\mu\kappa+4\mu\kappa^2)/\mu=0,\\&m^2\lambda^2{}_{(\zeta'\gamma')}-[\tfrac{1}{4}A(1-2\mu\kappa)/\mu+8B(1-\kappa)+4\kappa D]m\lambda+2(AB-D^2)(1-\kappa-2\mu\kappa)/\mu=0,\\&m\lambda_{(\rho)}-4C(1-2\kappa)=0,\\&m^4\lambda^4{}_{(\eta'\beta'\sigma\tau)}-Q_1m^3\lambda^3+Q_2m^2\lambda^2-Q_3m\lambda+Q_4=0,\\&Q_1=\tfrac{1}{4}A(1-2\mu\kappa)/\mu+(8B+4C+16E)(1-2\kappa),\\&Q_2=64CE(1-2\kappa)^2+2(AB-D^2)(1-2\kappa)(1-2\kappa\mu)/\mu\\&\qquad+4C[\tfrac{1}{4}A(1-2\kappa-2\mu\kappa+\tfrac{1}{3}4\mu\kappa^2)/\mu+8B(1-4\kappa+\tfrac{1}{3}8\kappa^2)+\tfrac{1}{3}16\kappa^2D]\\&\qquad+16E[\tfrac{1}{4}A(1-2\kappa-2\mu\kappa+\tfrac{1}{3}8\mu\kappa^2)/\mu+8B(1-4\kappa+\tfrac{1}{3}4\kappa^2)-\tfrac{1}{3}16\kappa^2D],\\&Q_3=64CE(1-2\kappa)[\tfrac{1}{4}A(1-2\kappa-2\mu\kappa)/\mu+8B(1-4\kappa)]+2\mu^{-1}(AB-D^2)[4C(1-4\kappa-2\mu\kappa+\tfrac{1}{3}8\kappa^2\\&\qquad+\tfrac{1}{3}16\mu\kappa^2)+16E(1-4\kappa-2\mu\kappa+\tfrac{1}{3}4\kappa^2+\tfrac{1}{3}20\mu\kappa^2)],\\&Q_4=128CE(AB-D^2)(1-4\kappa)(1-2\kappa-2\mu\kappa)/\mu.\end{aligned}\qquad(29')$$

If we had assumed for the masses $m_4=m_1=m+\Delta m$ and $m_3=m_2=m$, the expressions for $\lambda_{(\xi\alpha)}$ and $\lambda_{(\zeta'\gamma')}$ would have been interchanged. The assumption actually used has the advantage of simplifying calculations.

For $\kappa^2\ll 1$ the fourth power equation becomes

$$\begin{aligned}m^2\lambda^2{}_{(\eta'\beta')}-[\tfrac{1}{4}A(1-2\mu\kappa)/\mu+8B(1-2\kappa)]m\lambda+2(AB-D^2)(1-2\kappa-2\mu\kappa)/\mu=0,\\ [m\lambda_{(\sigma)}-4C(1-2\kappa)][m\lambda_{(\tau)}-16E(1-2\kappa)]=0.\end{aligned}\qquad(30')$$

Since for YX_4 (i.e., for $\kappa=0$), the frequencies are given by

$$\begin{aligned}[m^2\lambda^2{}_{(\xi\alpha),\,(\eta\beta),\,(\zeta\gamma)}-(\tfrac{1}{4}A/\mu+8B)m\lambda+2(AB-D^2)/\mu]^3=0,\\ [m\lambda_{(\rho),\,(\sigma)}-4C]^2=0,\qquad m\lambda_{(\tau)}-16E=0,\end{aligned}\qquad(31)$$

we see that the substitution of X^* for X in YX_4 partially removes the degeneracy of the motion and gives rise to six frequencies. For $YX_2X_2^*$ the degeneracy is completely removed even though two of the frequencies differ only by terms of the order of magnitude of κ^2.

The application of the above results to experimental data together with a discussion of the intensities is postponed until a later paper.

In conclusion I wish to thank Professor E. O. Salant for his interest and advice in this work.

[10] $V^*(\eta',\,\beta',\,\sigma,\,\tau)=V_1(\eta',\,\beta')+V_2(\sigma)+V_3(\tau)$.