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Theory of Vibrational Isotope Effects in Polyatomic Molecules

By E. O. SALANT AND JENNY E. ROSENTHAL
New York University

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Following Dennison's general, noncentral force treatment of the normal modes of vibration of symmetrical triatomic and tetratomic molecules, we derive expressions for the effects of isotopy on the normal frequencies. The isotope effect of any particular normal frequency depends on and may serve to evaluate the force constants of the molecule, but sums of certain isotope effects are independent of the constants. For triatomic molecules, the isotope effect of the vibration perpendicular to the symmetry axis depends on the value of the apex angle of the molecule. The sum of the isotope effects of the parallel vibrations is calculable from the masses alone. Definite criteria of collinearity of the molecule from isotope effects are given. For tetratomic molecules, the sum of isotope effects of vibrations parallel to the altitude of the molecular pyramid is calculable from the masses alone, the sum of isotope effects perpendicular to the altitude from the masses and from the ratio of the altitude to the length of side of the triangular base. Whereas the molecule YX_3 has four distant normal frequencies of vibration, it is shown that replacement of one of the X atoms of mass m by an atom of mass $m+\Delta m$ removes the degeneracy of the motion, the resulting molecule having six normal frequencies of vibration. Special relations between the various isotope effects serve as criteria for co-planar molecules.

INTRODUCTION

THERE have been few investigations, experimental or theoretical, of isotope effects in band spectra of polyatomic molecules, the most outstanding being the studies of the vibrational effects in the electronic bands of chlorine dioxide, made by Goodeve and Stein[1] and by Urey and Johnston.[2] Besides the interest of the isotope effects themselves, Urey and Johnston showed them to be of value as an aid in the assignment of certain spectral frequencies to particular modes of vibration of the ClO_2 molecule.

This they accomplished by comparing the measured isotope effects with those calculated from their expressions for the effects of isotopy of the Y atoms on the normal vibrations of symmetrical triatomic molecules YX_2; the expressions were derived from equations of Bjerrum[3] for the normal vibrations of symmetrical triatomic molecules, Bjerrum's equations having been based upon the special assumption of valence forces.

It is our purpose here to begin with the more general noncentral force equations of Dennison[4] for the vibrations of polyatomic molecules and to derive therefrom expressions for the isotope effects of the normal frequencies. We shall obtain equations for the effects of isotopy of the Y atoms, and also of the X atoms, in symmetrical triatomic molecules YX_2 and symmetrical

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[1] C. F. Goodeve and C. P. Stein, Trans. Faraday Soc. **25**, 736 (1929).

[2] H. C. Urey and H. Johnston, Phys. Rev. **38**, 2131 (1931).

[3] N. Bjerrum, Verh. d. deutsch. phys. Ges. **16**, 737 (1914).

[4] D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).

tetratomic molecules YX_3; we have already referred briefly to some of the results of this study.[5] In Dennison's treatment, it may be recalled, knowledge of the quantitative values of the force constants is quite unnecessary to determine the directions of the displacements with respect to the molecular axis of symmetry, the character of the vibrations following from the basic postulate that the potential energy follows the geometrical symmetry of the molecule.

Besides the assumptions of Dennison's theory, we assume also that, as for diatomic molecules, the forces involved are invariant for an isotopic change of mass. We shall denote the mass of the Y atom by M and the mass of an X atom by m and shall call effects due to isotopes of Y atoms "central isotope effects" and effects due to isotopes of X atoms "end isotope effects." We treat the ratios $\Delta m/m$ and $\Delta M/M$ as small, consequently our results do not apply to isotopes of H atoms.

The general method outlined by Dennison for describing the potential energies T and V will be followed, the normal frequencies ω_i being given by the roots λ_i of the determinental equation

$$\left.\begin{aligned} |\lambda T - V| &= 0 \\ \text{and} \qquad 4\pi^2\omega_i^2 &= \lambda_i \end{aligned}\right\}. \tag{I}$$

The roots and frequencies of molecules $Y^{(M)}X_2^{(m)}$ and $Y^{(M)}X_3^{(m)}$ will be denoted by λ_i and ω_i, the roots and frequencies of molecules having one or more atoms $Y^{(M+\Delta M)}$ or $X^{(m+\Delta m)}$ will be denoted by λ_i^* and ω_i^*. The isotope shift $\Delta\omega_i$ of the normal frequency of vibration ω_i will then be given by

$$\Delta\omega_i/\omega_i = \tfrac{1}{2}(\lambda_i^*/\lambda_i - 1). \tag{II}$$

Since, as has been shown by Dennison,[6] the expressions for the transition probabilities of the normal vibrations involve the masses, an isotopic change of mass will affect the Einstein coefficients as well as the frequencies. We regard such effects as small, however, and certainly inextricable from the tangle of polyatomic band lines.

The relative intensities of bands due to the same vibration in molecules differing only in their isotopes will, of course, be determined principally by the relative abundance of the isotopes. Relative abundance of molecules $Y^{(M)}X_n$ and $Y^{(M+\Delta M)}X_n$ will be the same as the relative abundance of the isotopes of the Y atoms. Relative abundances in the cases of isotopes of X atoms are, if the relative abundance of $X^{(m)}$ to $X^{(m+\Delta m)}$ is b/a

$$YX_2^{(m)}:YX^{(m)}X^{(m+\Delta m)}:YX_2^{(m+\Delta m)} = 1:b/a:b^2/a^2$$

$$YX_3^{(m)}:YX_2^{(m)}X^{(m+\Delta m)}:YX^{(m)}X_2^{(m+\Delta m)}:YX_3^{(m+\Delta m)} = 1:b/a:b^2/a^2:b^3/a^3.$$

I. TRIATOMIC MOLECULES

We consider a molecule composed of three particles denoted 1, 2, 3, forming at equilibrium the corners of an isosceles triangle of apex angle 2α and

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[5] E. O. Salant and J. E. Rosenthal, Phys. Rev. **39**, 161 (1932).

[6] D. M. Dennison, Phil. Mag. **1**, 195 (1926).

base $2a$, with particle 1 at the apex. Let q_1 be the change in relative displacement of the base particles 2 and 3, q_2 and q_3 the changes in relative displacements of the particles 1 and 2 and of the particles 2 and 3, respectively. The potential energy is then written:

$$V = \tfrac{1}{2}[K_1(q_2^2 + q_3^2) + K_2 q_1^2 + K_3 q_1(q_2 + q_3) + K_4 q_2 q_3] \tag{1}$$

where K_1, K_2, K_3, K_4 are constants (which may involve the angle).

We choose moving coordinates x, y with origin at the center of gravity of the molecule, and x-axis parallel to the direction $2 \rightarrow 3$, and define new variables q_1, u, v in this system (q_1 unchanged):

$$\left.\begin{aligned} q_1 &= \delta x_3 - \delta x_2 \\ u &= \delta x_1 - \tfrac{1}{2}(\delta x_2 + \delta x_3) = (q_3 - q_2)/2 \sin\alpha \\ v &= \delta y_1 - \tfrac{1}{2}(\delta y_2 + \delta y_3) = (q_2 + q_3 - q_1 \sin\alpha)/2 \cos\alpha \end{aligned}\right\} \tag{2}$$

δx_j and δy_j obviously referring to the displacements of the j-th particle. In these variables, the potential energy becomes

$$\left.\begin{aligned} V &= \tfrac{1}{2}(Aq_1^2 + Bu^2 + Cv^2 + 2Dvq_1), \\ \text{where}\quad A &= (K_1/2) \sin^2\alpha + K_2 + K_3 \sin^2\alpha + (K_4/4) \sin^2\alpha \\ B &= (2K_1 - K_4) \sin^2\alpha \\ C &= (2K_1 + K_4) \cos^2\alpha \quad {}^{7} \\ D &= (K_1 + K_3/\sin\alpha + K_4/2) \sin\alpha \cos\alpha \end{aligned}\right\}. \tag{3}$$

To obtain the expression for the kinetic energy of the vibrating molecule, we first transform to a fixed coordinate system X, Y in the same plane and with the same origin as the moving system,

$$X = x + \theta y; \quad Y = -\theta x + y$$

where θ denotes a small angle in the X, Y plane.

For the molecule $YX^{(m)}X^{(m+\Delta m)}$, let the Y atom be particle 1, $X^{(m+\Delta m)}$ particle 2, $X^{(m)}$ particle 3. Let

$$\mu = \frac{M}{2m + M}, \quad \mu^* = \frac{M}{2(m + \Delta m) + M}, \quad \rho = \frac{M}{2m + \Delta m + M}.$$

Then the transformation from Eq. (2) to the fixed coordinates and the expressions for the conservation of linear momentum lead to the following relations for the displacements δX_j, δY_j in the fixed system:

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[7] It is assumed that when $\cos\alpha = 0$; $C \neq 0$; hence $(2K_1 + K_4)$ involves α.

$$\left.\begin{aligned}
\delta X_1 &= \left(\frac{2m+\Delta m}{M}\right)\rho(u + a\theta\cot\alpha) + \frac{\Delta m\rho}{2M}\,q_1;\\
\delta Y_1 &= \left(\frac{2m+\Delta m}{M}\right)\rho v - \frac{\Delta m\rho}{M}\,a\theta\\
\delta X_2 &= -\,\rho(u + a\theta\cot\alpha) - \frac{q_1}{2}\,\frac{\rho}{\mu};\qquad \delta Y_2 = -\,\rho v + a\theta\frac{\rho}{\mu}\\
\delta X_3 &= -\,\rho(u + a\theta\cot\alpha) + \frac{q_1}{2}\,\frac{\rho}{\mu^*};\qquad \delta Y_3 = -\,\rho v + \frac{a\theta\rho}{\mu^*}
\end{aligned}\right\}. \tag{4}$$

Writing down the expression for the kinetic energy and substituting for $\dot{\theta}$ its value obtained from the condition $\partial T/\partial\dot{\theta} = 0$ (conservation of angular momentum), we may then write the kinetic energy letting $\epsilon = \Delta m/(2m+\Delta m)$

$$T = \left(\frac{2m+\Delta m}{4}\right)\left[2\rho(\dot{u}^2 + \dot{v}^2) + \dot{q}_1^2 + 2\rho\epsilon\dot{u}\dot{q}_1 - \frac{2\rho^2}{1+\rho\cot^2\alpha}\left(\dot{u}\cot\alpha + \frac{\epsilon\dot{q}_1}{2}\cot\alpha - \epsilon\dot{v}\right)^2\right]. \tag{5}$$

Neglecting all terms in ϵ^2, none of whose coefficients are large, we then have

$$T = \left(\frac{2m+\Delta m}{4}\right)\left[2\rho\left(\frac{\dot{u}^2}{1+\rho\cot^2\alpha} + \dot{v}^2\right) + \frac{\dot{q}_1^2}{2} + \frac{2\rho\dot{u}\epsilon}{1+\rho\cot^2\alpha}(\dot{q}_1 - 2\rho\dot{v}\cot\alpha)\right]. \tag{6}$$

From Eq. (I), (3) and (6), the vibrations λ_1^*, λ_2^*, parallel to the symmetry axis of the molecule, and the vibration λ_3^* perpendicular to the symmetry axis, are given by

$$\left.\begin{aligned}
&\left(\frac{2m+\Delta m}{2}\right)^2\lambda^{*2} - \left(2A + \frac{C}{2\rho}\right)\left(\frac{2m+\Delta m}{2}\right)\lambda^* + \frac{1}{\rho}\left(AC - \frac{D^2}{4}\right) = 0 &&\text{(a)}\\
&\lambda_3^* = \frac{B(1/\rho + \cot^2\alpha)}{2m+\Delta m} &&\text{(b)}
\end{aligned}\right\}. \tag{7}$$

By setting $\Delta m = 0$, Eqs. (7) reduce to the known expressions for the normal frequencies of the molecule $YX_2^{(m)}$

$$\left.\begin{aligned}
&m^2\lambda^2 - (2A + C/2\mu)m\lambda + (1/\mu)(AC - D^2/4) = 0 &&\text{(a)}\\
&\lambda_3 = B(1/\mu + \cot^2\alpha)/2m &&\text{(b)}
\end{aligned}\right\}. \tag{8}$$

For a collinear molecule, $D=0$ and $\cot\alpha=0$, Eqs. (7) reducing to

$$\left.\begin{aligned} \lambda_1^* &= \frac{4A}{(2m+\Delta m)}\,;\ \lambda_2^* = \frac{C}{\rho(2m+\Delta m)} && \text{(a)} \\ \lambda_3^* &= B/(2m+\Delta m)\rho && \text{(b)} \end{aligned}\right\} . \tag{7'}$$

(a) Central isotope effects, molecules $Y^{(M)}X_2^{(m)}$ and $Y^{(M+\Delta M)}X_2^{(m)}$

The vibrations of molecules $Y^{(M+\Delta M)}X_2^{(m)}$ will be described by relations obtained by substituting $M+\Delta M$ for M in Eqs. (8). With these equations and with Eqs. (I), (II), and (8), we have the following relations for central isotope effects:

$$\frac{\Delta\omega_1}{\omega_1} = \frac{(8\pi^2 m\mu\omega_2^2 - C)\Delta M}{8\pi^2(\omega_1^2-\omega_2^2)M^2} \tag{9}$$

$$\omega_1\Delta\omega_1 + \omega_2\Delta\omega_2 = -\,C\Delta M/8\pi^2 M(M+\Delta M) \tag{10}$$

$$\frac{\Delta\omega_1}{\omega_1} + \frac{\Delta\omega_2}{\omega_2} = \frac{-\,m\Delta M}{(M+\Delta M)(2m+M)} \tag{11}$$

$$\frac{\Delta\omega_3}{\omega_3} = \frac{-\,m\Delta M}{M(M+\Delta M)(1/\mu+\cot^2\alpha)}\,. \tag{12}$$

Thus, whereas the isotope effect $\Delta\omega_1/\omega_1$ or $\Delta\omega_2/\omega_2$ of either parallel vibration depends on the force constants of the molecule and may have different values in the different electronic states, their sum has a constant value, calculable from the masses alone, for all electronic states. Obviously this relation, Eq. (11), provides a means of assigning bands to particular modes of vibration.

The isotope effect of the perpendicular vibration, $\Delta\omega_3/\omega_3$, may be used to evaluate the molecular angle 2α; before this can be done, however, it must be known that the frequency being so used is actually the perpendicular frequency, information which will have to come from other data, such as intensities.

For a collinear molecule ($2\alpha=180°$, $D=0$), we have

$$\left.\begin{aligned} \Delta\omega_1 &= 0 \\ \frac{\Delta\omega_2}{\omega_2} &= \frac{\Delta\omega_3}{\omega_3} = \frac{-\,m\Delta M}{(M+\Delta M)(2m+M)} \end{aligned}\right\} \tag{13}$$

a relation that may be used to determine whether or not a given molecule is collinear.

Since change in electronic state may be accompanied by change in the molecular angle, it is of interest to consider how this will affect the isotope effects. Consider $\Delta M>0$. When the molecule is collinear, the inactive frequency ω_1 shows no isotope effect, the isotope effect $\Delta\omega/\omega$ of each active frequency is the same and negative. As the molecule bends away from a straight line, the perpendicular isotope effect takes on smaller absolute values, approaching zero as the equilibrium positions of the two X atoms approach each other. The absolute value $|\Delta\omega_1/\omega_1|$ increases, but without knowledge of the force constants, it cannot be predicted whether $\Delta\omega_1/\omega_1$ will be positive or negative; the change in $\Delta\omega_1/\omega_1$ will be in the opposite direction to the change in $\Delta\omega_2/\omega_2$, of course, in virtue of (11) and (13).

TABLE I. *Triatomic molecules.* Calculated values of some central isotope effects.

2α	ClO_2	MgI_2	SO_2	H_2S
	$m=16$	127	16	1
	$M=35$	24	32	32
	$\Delta M=2$	1	1	1
	$10^2(\Delta\omega_1/\omega_1+\Delta\omega_2/\omega_2)$ −1.293	−1.82	−0.76	−0.089
180°	$10^2(\Delta\omega_3/\omega_3)$ −1.293	−1.82	−0.76	−0.089
150°	" −1.245	−1.81	−0.73	−0.083
120°	" −1.01	−1.77	−0.65	−0.068
90°	" −0.849	−1.68	−0.51	−0.046
60°	" −0.502	−1.43	−0.30	−0.023

In Table I are some values of $\Delta\omega_3/\omega_3$ as a function of the molecular angle, calculated for several different molecules, and also values of $\Delta\omega_1/\omega_1+\Delta\omega_2/\omega_2$ for the same molecules. For $2\alpha=180°$, Eq. (13) holds.

A relatively heavy end (X) atom renders the perpendicular isotope effect comparatively insensitive to changes in the molecular angle, as may be seen by comparing the values of this effect for MgI_2 and any of the other molecules in the table. Consequently, the isotope effect will not be so reliable in following changes in the angle of molecules with a large m/M.

(b) End isotope effects

The isotope effects for molecules $Y^{(M)}X_2^{(m)}$ and $Y^{(M)}X^{(m)}X^{(m+\Delta m)}$ are easily obtained from Eqs. (I), (II), (7) and (8). Each parallel effect $\Delta\omega_1/\omega_1$ and $\Delta\omega_2/\omega_2$ depends on the force constants, but the sum of the parallel effects is independent of the interatomic forces:

$$\frac{\Delta\omega_1}{\omega_1}+\frac{\Delta\omega_2}{\omega_2}=\frac{-(\mu+1)\Delta m}{2(2m+\Delta m)}\cdot \tag{14}$$

The perpendicular isotope effect depends upon the molecular angle:

$$\frac{\Delta\omega_3}{\omega_3}=\frac{-(1+\cot^2\alpha)\Delta m}{2(1/\mu+\cot^2\alpha)(2m+\Delta m)}\cdot \tag{15}$$

For a collinear molecule

$$\mu\frac{\Delta\omega_1}{\omega_1}=\frac{\Delta\omega_2}{\omega_2}=\frac{\Delta\omega_3}{\omega_3}=\frac{-\mu\Delta m}{2(2m+\Delta m)}\cdot \tag{16}$$

In Table II are calculated values of the perpendicular isotope effect for a few molecules and several angles.

It is seen that, contrary to the behavior of the central isotope effect, the end isotope effect of the perpendicular vibration increases as the angle di-

TABLE II. *Calculated values of perpendicular end isotope effects.*

	$10^2(\Delta\omega_3/\omega_3)$				
2α, degrees	180	120	90	60	0
$CS_2^{(32)}$, $CS^{(32)}S^{(33)}$	−0.121	−0.154	−0.210	−0.340	−0.769
$MgCl_2^{(35)}$, $MgCl^{(35)}Cl^{(37)}$	−0.354	−0.436	−0.565	−0.802	−1.40
$HgCl_2^{(35)}$, $HgCl^{(35)}Cl^{(37)}$	−1.01	−1.08	−1.17	−1.27	−1.40

minishes, attaining its maximum value, for $\alpha=0$ of

$$(\Delta\omega_3/\omega_3)_{\text{max.}} = -\Delta m/2(2m+\Delta m).$$

The observation of the perpendicular isotope effect will be favored by a molecule with a small angle and heavy central atom.

By replacing m by $m+\Delta m$ in Eqs. (8), the normal vibrations of molecules $Y^{(M)}X_2^{(m+\Delta m)}$ are obtained. The isotope effects $\Delta\omega_i/\omega_i$ between these molecules and molecules $Y^{(M)}X_2^{(m)}$ are, to the first approximation, twice the value of the corresponding effects between molecules $Y^{(M)}X^{(m)}X^{(m+\Delta m)}$ and $Y^{(M)}X_2^{(m)}$.

II. TETRATOMIC MOLECULES

We consider a molecule composed of four atoms occupying, at equilibrium the corners of a regular pyramid of altitude c and length of side of triangular base a. We consider the Y atom, of mass M, at the apex, and denote its positions by subscript 4; we consider atoms X^*, X, X, with masses $m+\Delta m$, m, m, at the base, denoting their positions by subscripts 1, 2, 3, respectively.

Let p_1, p_2, p_3, q_1, q_2, q_3 be the changes in relative displacements of the respective particles, assumed small quantities of the first order, and write $f=(c^2+a^2/3)^{1/2}$. Then, assuming that the potential energy has the geometrical configuration of the system, we have

$$\begin{aligned} V = \tfrac{1}{2}\{&K_1(q_1^2+q_2^2+q_3^2)+K_2(q_1q_2+q_1q_3+q_2q_3)+K_3(f^2/a^2)(p_1^2+p_2^2\\ &+p_3^2)+K_4(f^2/a^2)(p_1p_2+p_1p_3+p_2p_3)+K_5(f/a)(p_1q_1+p_2q_2\\ &+p_3q_3)+K_6(f/a)[p_1(q_2+q_3)+p_2(q_1+q_3)+p_3(q_1+q_2)]\}\end{aligned} \tag{17}$$

where the K's are undetermined constants.

We now choose a system of axes, x, y, z with origin at the molecular center of mass and moving with the molecule, with x axis parallel to the 2–3 axis and x, y plane parallel to the 1, 2, 3 plane.

Then let

$$\left.\begin{aligned} &\delta x_4-\tfrac{1}{3}(\delta x_1+\delta x_2+\delta x_3)=x;\ \delta x_1-\tfrac{1}{2}(\delta x_2+\delta x_3)=u;\ \delta x_3-\delta x_2=q_1\\ &\delta y_4-\tfrac{1}{3}(\delta y_1+\delta y_2+\delta y_3)=y;\ \delta y_1-\tfrac{1}{2}(\delta y_2+\delta y_3)=v;\ \delta y_3-\delta y_2=0\\ &\delta z_4-\tfrac{1}{3}(\delta z_1+\delta z_2+\delta z_3)=z;\ \delta z_1-\tfrac{1}{2}(\delta z_2+\delta z_3)=0;\ \delta z_3-\delta z_2=0\end{aligned}\right\} \tag{18}$$

and at equilibrium, we have

$$\left.\begin{aligned} &x_4^0-\tfrac{1}{3}(x_3^0+x_2^0+x_1^0)=0;\ x_1^0-\tfrac{1}{2}(x_2^0+x_3^0)=0;\ x_3^0-x_2^0=a\\ &y_4^0-\tfrac{1}{3}(y_3^0+y_2^0+y_1^0)=0;\ y_1^0-\tfrac{1}{2}(y_2^0+y_3^0)=a(3)^{1/2}/2;\\ &y_3^0-y_2^0=0\\ &z_4^0-\tfrac{1}{3}(z_3^0+z_2^0+z_1^0)=c;\ \ z_1^0-\tfrac{1}{2}(z_2^0+z_3^0)=0;\ \ z_3^0-z_2^0=0\end{aligned}\right\} \tag{19}$$

where, of course, the superscript zero refers to the equilibrium positions. Then writing:

$$\begin{aligned}
A &= \tfrac{1}{2}(K_3 - K_4/2) \\
B &= 3(c^2/a^2)(K_3 + K_4)\ \text{[8]} \\
C &= \tfrac{1}{4}\left(3K_1 + \frac{3}{2}K_2 + \frac{K_3}{3} + \frac{K_4}{6} + \frac{K_5}{3} + \frac{5K_6}{3}\right) \\
D &= \tfrac{1}{2}\left(K_1 - \frac{K_2}{2} + \frac{K_3}{9} - \frac{K_4}{18} - \frac{K_5}{3} - \frac{K_6}{3}\right) \\
E &= \frac{K_3}{6} - \frac{K_4}{12} - \frac{K_5}{4} + \frac{K_6}{4} \\
F &= (c/a)3^{-1/2}(K_3 + K_4 + (3/2)K_5 + 3K_6)
\end{aligned}$$

the potential energy in these variables become

$$\begin{aligned}
V = \tfrac{1}{2}\{&A(x^2 + y^2) + Bz^2 + (3/2)Cq_1^2 + Du^2 + 2Cv^2 \\
&+ 2[E(ux + (3^{1/2}/2)yq_1 - yv) \\
&+ Fz((3^{1/2}/2)q_1 + v) + 3^{1/2}(C - D)vq_1]\}.
\end{aligned} \tag{20}$$

To obtain the kinetic energy, we first refer to fixed axes X, Y, Z, with same origin as the x, y, z system, and connected by:

$$X = x + \psi y + \theta z; \quad Y = -\psi x + y + \phi z; \quad Z = -\theta x - \phi y + z \tag{21}$$

where ψ, θ, ϕ, are cosines of (X, y), (X, z), and (Y, z), respectively, and the rotation in space is understood to be small.

Neglecting small quantities of the second order, we have

$$\begin{aligned}
\delta X_j &= \delta x_j + \psi y_j^0 + \theta z_j^0 \\
\delta Y_j &= -\psi x_j^0 + \delta y_j + \phi z_j^0 \\
\delta Z_j &= -\theta x_j^0 - \phi y_j^0 + \delta z_j.
\end{aligned}$$

With these relations and Eqs. (18) and (19) and applying the condition for conservation of linear momentum, the kinetic energy becomes

$$\begin{aligned}
T = \tfrac{1}{2}\left(m + \frac{\Delta m}{3}\right)\Big\{&3\rho(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) + \tfrac{2}{3}(1 + \epsilon)(\dot{u}^2 + \dot{v}^2) + \tfrac{1}{2}(1 - \epsilon)\dot{q}_1^2 \\
&- 4\rho\epsilon(\dot{u}\dot{x} + \dot{v}\dot{y}) + (\beta - \epsilon)\frac{a^2}{2}\dot{\theta}^2 + \frac{a^2}{2}(\beta + \epsilon)\dot{\phi}^2 + a^2\dot{\psi}^2 \\
&+ 2\dot{\theta}c\rho(3\dot{x} - 2\epsilon\dot{u}) + 2\dot{\phi}c\rho\left(3\dot{y} - 2\epsilon\dot{v} + 3^{1/2}\epsilon\frac{a}{c}\dot{z}\right) \\
&+ 2\dot{\psi}a\left[-\rho\epsilon(3^{1/2})\dot{x} + \left(\frac{1 + \epsilon}{3^{1/2}}\right)\dot{u}\right] - 2\rho(3^{1/2})ac\epsilon\dot{\psi}\dot{\theta}\Big\}
\end{aligned} \tag{22}$$

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[8] It is assumed that for $c = 0$, $B \neq 0$.

where

$$\left.\begin{aligned}&\mu = \frac{M}{3m + M}, \quad \rho = \frac{M}{3m + \Delta m + M}, \quad \epsilon = \frac{\Delta M}{3m + \Delta m}\\&b = 6\mu(c^2/a^2) + 1, \; \beta = 6\rho(c^2/a^2) + 1\end{aligned}\right\} . \tag{23}$$

From the conservation of angular momentum

$$(\partial T/\partial\dot{\phi} = 0, \; \partial T/\partial\dot{\theta} = 0, \; \partial T/\partial\dot{\psi} = 0)$$

and dropping terms in ϵ^2, we have

$$\begin{aligned}T = \tfrac{1}{2}\left(m + \frac{\Delta m}{3}\right)\Bigg\{&\frac{3\rho}{\beta}\left[1 - \epsilon\left(1 - \frac{1}{\beta}\right)\right]\dot{x}^2 + \frac{3\rho}{\beta}\left[1 + \epsilon\left(1 - \frac{1}{\beta}\right)\right]\dot{y}^2\\&+ 3\rho\dot{z}^2 + \tfrac{1}{2}(1 - \epsilon)\dot{q}_1{}^2 + \tfrac{1}{3}\dot{u}^2 + \tfrac{2}{3}(1 + \epsilon)\dot{v}^2\\&- 2\rho\frac{\epsilon}{\beta}\left(\dot{u}\dot{x} + 2\dot{y}\dot{v} + 6\rho\frac{c}{a}(3^{1/2})\dot{y}\dot{z}\right)\Bigg\}.\end{aligned} \tag{24}$$

Eqs. (I), (20), and (24) then yield the following equations for the vibrations of the molecule $Y^{(M)}X_2{}^{(m)}X^{(m+\Delta m)}$:

$$\begin{aligned}\left(m + \frac{\Delta m}{3}\right)^2\lambda^{*2} - \left(m + \frac{\Delta m}{3}\right)\left(\frac{B}{3\rho} + 6C - 3D\right)\lambda^*&\\+ \frac{2BC - BD - F^2}{\rho} = 0&\end{aligned} \tag{25}$$

$$\begin{aligned}\left(m + \frac{\Delta m}{3}\right)^2\lambda^{*2} - \left(m + \frac{\Delta m}{3}\right)\left\{\frac{\beta A\left[1 - \epsilon(1 - 1/\beta)\right]}{3\rho} + 3D - 2\epsilon E\right\}\lambda^*&\\+ \frac{\beta}{\rho}(AD - E^2)\left[1 - \epsilon(1 - 1/\beta)\right] = 0&\end{aligned} \tag{26}$$

$$\begin{aligned}\left(m + \frac{\Delta m}{3}\right)^2\lambda^{*2} - \left(m + \frac{\Delta m}{3}\right)\left\{\frac{\beta A\left[1 + \epsilon(1 - 1/\beta)\right]}{3\rho} + 3D + 2\epsilon E\right\}\lambda^*&\\+ \frac{\beta}{\rho}(AD - E^2)\left[1 + \epsilon(1 - 1/\beta)\right] = 0.&\end{aligned} \tag{27}$$

We denote the roots of (25) by λ_1^*, λ_3^*, of (26) by λ_2^*, λ_4^* of (27) by λ_5^*, λ_6^*. Each of the roots is distinct, so that the molecule $Y^{(M)}X_2{}^{(m)}X^{(m+\Delta m)}$ has six normal frequencies of vibration. By setting $\Delta m = 0$, these equations reduce to those of the molecule $Y^{(M)}X_3{}^{(m)}$, Eq. (25) becoming

$$m^2\lambda^2 - m(B/3\mu + 6C - 3D)\lambda + (2BC - BD - F^2)/\mu = 0 \tag{28}$$

and Eqs. (26) and (27) giving

$$\left[m^2\lambda^2 - m(bA/3\mu + 3D)\lambda + (b/\mu)(AD - E^2)\right]^2 = 0. \tag{29}$$

Dennison has shown that the vibrations represented by (28) are parallel to the altitude c of the molecular pyramid, that the vibrations represented by (29) are perpendicular to the altitude and that whereas the perpendicular vibrations are four in number, only two are distinct, or, calling the roots of (29) $\lambda_2, \lambda_5, \lambda_4, \lambda_6$, then

$$\lambda_2 = \lambda_5,\ \lambda_4 = \lambda_6 \tag{30}$$

the molecule $Y^{(M)}X_3^{(m)}$ having four distinct normal frequencies of vibration. Thus the substitution of an atom of mass $(m+\Delta m)$ for one of the base atoms of mass m removes the degeneracy of the parallel mode of vibration, and a gas composed of molecules of $Y^{(M)}X_3^{(m)}$ and $Y^{(M)}X_2^{(m)}X^{(m+\Delta m)}$ will show ten fundamental infrared bands (disregarding, of course, the possibility of one or more being inactive in absorption).

Just as in the triatomic case, any particular isotope shift $\Delta\omega_i/\omega_i$ can be calculated only if the force constants are known, but the sum of the relative isotope effects of the parallel frequencies can be calculated from the masses alone, and the sum of the isotope effects of the perpendicular frequencies from the masses and the ratio of the altitude to the length of side of the base. As it must now be obvious, from the triatomic case, how each individual $\Delta\omega_i/\omega_i$ may be written down, merely by applying Eq. (II), we shall not state these, but shall state only the more interesting and useful expressions for the sums of isotope effects.

(a) Central isotope effects, molecules $Y^{(M)}X_3^{(m)}$ and $Y^{(M+\Delta M)}X_3^{(m)}$

These relationships apply to molecules such as $Cl^{(35)}O_3$ and $Cl^{(37)}O_3$, $B^{(10)}I_3$ and $B^{(11)}I_3$.

The normal vibrations of molecules $Y^{(M+\Delta M)}X_3^{(m)}$ are obtained simply by substituting $M+\Delta M$ for M in Eqs. (28) and (29). Then for the parallel vibrations we have

$$\frac{\Delta\omega_1}{\omega_1} + \frac{\Delta\omega_3}{\omega_3} = \frac{(\mu - 1)\Delta M}{2(M + \Delta M)} \tag{31}$$

and for the perpendicular vibrations:

$$\frac{\Delta\omega_2}{\omega_2} + \frac{\Delta\omega_4}{\omega_4} = \frac{(\mu - 1)\Delta M}{2b(M + \Delta M)}\,. \tag{32}$$

For a co-planar molecule, that is, for one where $c = 0$, $b = 1$ and hence

$$\frac{\Delta\omega_1}{\omega_1} + \frac{\Delta\omega_3}{\omega_3} = \frac{\Delta\omega_2}{\omega_2} + \frac{\Delta\omega_4}{\omega_4} = \frac{(\mu - 1)\Delta M}{2(M + \Delta M)}\,. \tag{33}$$

(b) End isotope effects, molecules $Y^{(M)}X_3^{(m)}$ and $Y^{(M)}X_2^{(m)}X^{(m+\Delta m)}$

These relationships apply to molecules such as $PCl_3^{(35)}$ and $PCl_2^{(35)}Cl^{(37)}$. From Eqs. (II), (25) and (28) we get, for the parallel vibrations

$$\frac{\Delta\omega_1}{\omega_1} + \frac{\Delta\omega_3}{\omega_3} = -\frac{(\mu + 1)\Delta m}{2(3m + \Delta m)} \backsimeq -\frac{(\mu + 1)\Delta m}{6m}\,. \tag{34}$$

From (II), (26), (27) and (29) the isotope effects of the perpendicular vibrations are related by:

$$\frac{\Delta\omega_2}{\omega_2}+\frac{\Delta\omega_4}{\omega_4}=-\frac{\Delta m}{6m}\left(\frac{\mu-2}{b}+3\right) \tag{35}$$

$$\frac{\Delta\omega_5}{\omega_5}+\frac{\Delta\omega_6}{\omega_6}=-\frac{\Delta m}{6m}\left(\frac{\mu}{b}+1\right) \tag{36}$$

where, it must be recalled, $\omega_2=\omega_5$, $\omega_4=\omega_6$, but

$$\Delta\omega_2 \neq \Delta\omega_5 \text{ and } \Delta\omega_4 \neq \Delta\omega_6.$$

For co-planar molecules, $b=1$ and hence

$$\frac{\Delta\omega_1}{\omega_1}+\frac{\Delta\omega_3}{\omega_3}=\frac{\Delta\omega_2}{\omega_2}+\frac{\Delta\omega_4}{\omega_4}=\frac{\Delta\omega_5}{\omega_5}+\frac{\Delta\omega_6}{\omega_6}=-\frac{(\mu+1)\Delta m}{6m}\cdot \tag{37}$$

To the first order, the isotope effects of $Y^{(M)}X^{(m)}\,X_2^{(m+\Delta m)}$ are approximately twice the corresponding effects of $Y^{(M)}X_2^{(m)}X^{(m+\Delta m)}$ and isotope effects of $Y^{(M)}X_3^{(m+\Delta m)}$ approximately three times the corresponding effects of the latter.

It is hoped that the above relations for isotope effects may be of use in the analysis of bands of tetratomic molecules.

It may be superfluous to emphasize that the expressions here refer to the frequencies of small vibration and not *exactly* to the (0, 1) bands, but it is expected that the difference in those values may be neglected and our results applied to the (0, 1) bands themselves.

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