Calculation of the Frequencies of the Symmetrical Modes of Vibration for Molecules with Various Types of Symmetry

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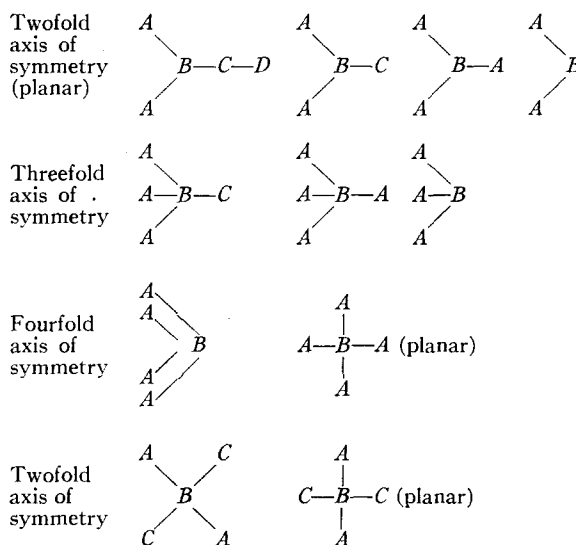
(Received August 1, 1938)

The secular equations for the frequencies of the symmetrical modes of vibration for molecules with various types of symmetry have been developed. The types of symmetry considered include a center of symmetry, and twofold, threefold, and fourfold axes of symmetry. Application to the problem of the configuration of oximes indicates that acetoxime has the following

structural formula: $126°$
$$\begin{array}{c} CH_3 \\ / \quad \backslash \\ C = N - OH. \\ \backslash \quad / \\ CH_3 \end{array}$$
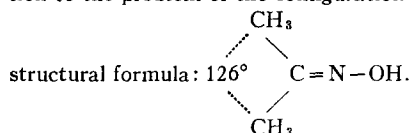
WHEN interpreting Raman spectra in terms of molecular models, it is customary to assume a certain configuration for the molecule, calculate the modes of vibration of such a molecule, and compare the calculated with the observed frequencies. For polyatomic molecules the calculation is very complicated and laborious, although the complete solutions have been given by others[1] for a number of molecular types. When there are a great many lines in the spectrum, it is, moreover, difficult to assign each observed line to a given mode of vibration of the model. The problem is greatly simplified if the data on the polarization of the Raman lines are available, since vibrations with a high degree of symmetry give rise to highly polarized lines (with depolarization factor approaching zero), while vibrations with lesser symmetry give rise to lines with depolarization factors approaching 6/7 as a limiting value.

It is indeed not necessary in most cases to calculate the frequencies of all the possible modes of vibration in order to decide whether an assumed molecular model is satisfactory. It is sufficient to calculate the frequencies of the symmetrical modes since these can be recognized in the spectrum if the depolarization measurements have been made. This calculation is much simpler than the complete calculation. The secular equations involving only the frequencies of the symmetrical vibrations have been developed for the following molecular types:

| Twofold axis of symmetry (planar) | $\begin{array}{c} A \\ \backslash \\ B-C-D \\ / \\ A \end{array}$ | $\begin{array}{c} A \\ \backslash \\ B-C \\ / \\ A \end{array}$ | $\begin{array}{c} A \\ \backslash \\ B-A \\ / \\ A \end{array}$ | $\begin{array}{c} A \\ \backslash \\ B \\ / \\ A \end{array}$ |

| Threefold axis of symmetry | $\begin{array}{c} A \\ \backslash \\ A-B-C \\ / \\ A \end{array}$ | $\begin{array}{c} A \\ \backslash \\ A-B-A \\ / \\ A \end{array}$ | $\begin{array}{c} A \\ \backslash \\ A-B \\ / \\ A \end{array}$ |

| Fourfold axis of symmetry | $\begin{array}{c} A \\ A \\ \quad \backslash \\ \quad\quad B \\ A \; / \\ A \end{array}$ | $\begin{array}{c} A \\ | \\ A-B-A \;\text{(planar)} \\ | \\ A \end{array}$ |

| Twofold axis of symmetry | $\begin{array}{c} A \quad\quad C \\ \backslash \;\; / \\ B \\ / \;\; \backslash \\ C \quad\quad A \end{array}$ | $\begin{array}{c} A \\ | \\ C-B-C \;\text{(planar)} \\ | \\ A \end{array}$ |

The equations will be developed for the first member of each of the above symmetry groups, and the equations for the special cases derived by simplification.

THE SECULAR EQUATION FOR THE SYMMETRICAL VIBRATIONS OF THE PLANAR CONFIGURATION

$$\begin{array}{c} A \\ \backslash \\ \theta\text{-----}B - C - D \\ / \\ A \end{array}$$
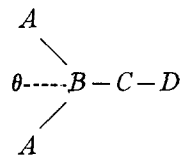
Since the discussion is limited to the symmetrical vibrations, it is sufficient to take one atom A as representative of the two.[2] The

[1] Dennison, Astrophys. J. **62**, 84 (1925).

[2] Glockler and Wall, J. Chem. Phys. **5**, 813 (1937).

atoms B, C, D are not to move out of the axis joining the three.

If m_a, m_b, m_c, m_d are the masses of the atoms A, B, C, D, respectively, and x_a, x_b, x_c, x_d their relative displacements in the x direction, then the kinetic and potential energies are given by

$$T = 2/2 m_a(\dot{x}_a{}^2 + \dot{y}_a{}^2) + \tfrac{1}{2} m_b \dot{x}_b{}^2 + \tfrac{1}{2} m_c \dot{x}_c{}^2 + \tfrac{1}{2} m_d \dot{x}_d{}^2,$$

$$V = 2/2 K_1 \xi_{ab}{}^2 + \tfrac{1}{2} K_2 \xi_{bc}{}^2 + \tfrac{1}{2} K_3 \xi_{cd}{}^2 + 2(2/2) d (r_{ab}\eta)^2,$$

where ξ_{ab}, ξ_{bc}, ξ_{cd} are the relative displacements of A with respect to B, B to C, C to D, respectively; $\eta = \theta - \theta_0$ (the displacement of the angle θ); K_1, K_2, K_3 are the force constants of the bonds $A-B$, $B-C$, $C-D$, respectively; and d is the

deformation constant of the $\begin{matrix} A \\ \diagdown \\ B- \\ \diagup \\ A \end{matrix}$ group.

Since there are two atoms A, the first terms of the kinetic and potential energy expressions contain the factor 2. Since B, C, and D move in the x direction only, the expressions have no terms in y_b, y_c, y_d. The factor 2 is introduced into the last term of the potential energy expression since there are two angles (ABA and ABC) changing for each atom A—see treatment of Glockler and Wall.[2] If the configuration of the

group $\begin{matrix} A \\ \diagdown \\ B-C- \\ \diagup \\ A \end{matrix}$ is approximately equilateral
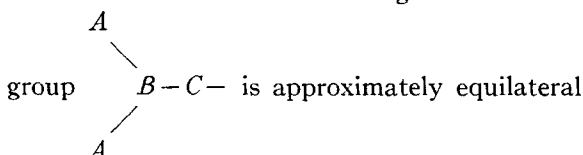
in the equilibrium position, the factor 2 can be used since for a small change in one of the angles there is an equal change in the other.

There exist linear relationships between the x's and y_a and the ξ's and η. From the geometry of the system it follows that

$$\xi_{ab} = (x_b - x_a) \cos\theta - y_a \sin\theta,$$

$$r_{ab}\eta = (x_b - x_a) \sin\theta + y_a \cos\theta,$$

$$\xi_{bc} = (x_c - x_b) \text{ etc.}$$

The secular equation is then

$$\begin{vmatrix} \alpha - 2m_a\omega^2 & -\alpha & \beta & 0 & 0 \\ -\alpha & \alpha + K_2 - m_b\omega^2 & -\beta & -K_2 & 0 \\ \beta & -\beta & \delta - 2m_a\omega^2 & 0 & 0 \\ 0 & -K_2 & 0 & K_2 + K_3 - m_c\omega^2 & -K_3 \\ 0 & 0 & 0 & -K_3 & K_3 - m_d\omega^2 \end{vmatrix} = 0,$$

where
$$\alpha = 2K_1 \cos^2\theta + 4d \sin^2\theta,$$
$$\beta = 2(K_1 - 2d) \sin\theta \cos\theta,$$
$$\delta = 2K_1 \sin^2\theta + 4d \cos^2\theta.$$

This becomes

$$\omega^8 - L\omega^6 + M\omega^4 - N\omega^2 + P = 0, \qquad (1)$$

where

$$L = K_1\left(\frac{1}{m_a} + \frac{2\cos^2\theta}{m_b}\right) + K_2\left(\frac{1}{m_b} + \frac{1}{m_c}\right)$$
$$+ K_3\left(\frac{1}{m_c} + \frac{1}{m_d}\right) + 2d\left(\frac{1}{m_a} + \frac{2\sin^2\theta}{m_b}\right),$$

$$M = K_1 K_2 \frac{2m_a \cos^2\theta + m_b + m_c}{m_a m_b m_c}$$

$$+ K_1 K_3 \frac{m_b m_c + m_b m_d + (2m_a m_c + 2m_a m_d)\cos^2\theta}{m_a m_b m_c m_d}$$

$$+ K_2 K_3 \frac{m_b + m_c + m_d}{m_b m_c m_d} + 2K_1 d \frac{m_b + 2m_a}{m_a{}^2 m_b}$$

$$+ 2K_2 d \frac{2m_a \sin^2\theta + m_b + m_c}{m_a m_b m_c}$$

$$+ 2K_3 d \frac{m_b m_c + m_b m_d + (2m_a m_c + 2m_a m_d)\sin^2\theta}{m_a m_b m_c m_d},$$

$$N = K_1 K_2 K_3 \frac{2m_a \cos^2 \theta + m_b + m_c + m_d}{m_a m_b m_c m_d}$$

$$+ 2K_1 K_2 d \frac{2m_a + m_b + m_c}{m_a{}^2 m_b m_c} -$$

$$+ 2K_1 K_3 d \frac{m_b m_d + m_b m_c + 2m_a m_c + 2m_a m_d}{m_a{}^2 m_b m_c m_d}$$

$$+ 2K_2 K_3 d \frac{2m_a \sin^2 \theta + m_b + m_c + m_d}{m_a m_b m_c m_d},$$

$$P = 2K_1 K_2 K_3 d \frac{2m_a + m_b + m_c + m_d}{m_a{}^2 m_b m_c m_d}.$$

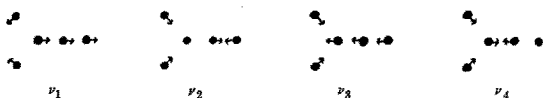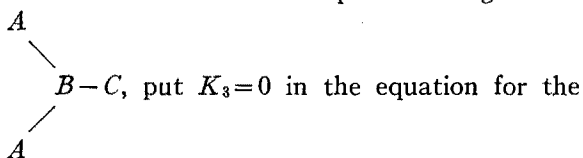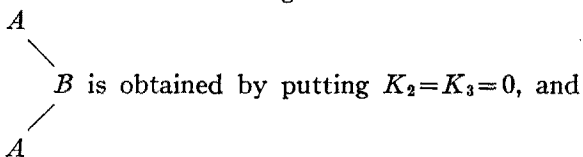This equation gives the frequencies of the symmetrical modes of the model as in Fig. 1.

FIG. 1.

To obtain the secular equation for the symmetrical vibrations of the planar configuration
$$\begin{matrix} A \\ \searrow \\ B-C \\ \nearrow \\ A \end{matrix}$$
, put $K_3 = 0$ in the equation for the pentatomic molecule (Eq. (1)). The equation thus obtained is identical with that obtained by the complete development for the simpler molecule.

The secular equation for the symmetrical vibrations of the triangular triatomic molecule
$$\begin{matrix} A \\ \searrow \\ B \\ \nearrow \\ A \end{matrix}$$
is obtained by putting $K_2 = K_3 = 0$, and by substituting d for $2d$ since there are not two angles changing for each atom A. This gives the equation

$$\omega^4 - \omega^2 \left[K_1 \left(\frac{1}{m_a} + \frac{2 \cos^2 \theta}{m_b} \right) + d \left(\frac{1}{m_a} + \frac{2 \sin^2 \theta}{m_b} \right) \right]$$

$$+ K_1 d \frac{2m_a + m_b}{m_a{}^2 m_b} = 0.$$

The Secular Equation for the Symmetrical Vibrations of the Configuration

$$\begin{matrix} A \\ \searrow \\ A-B-C \\ \nearrow \\ A \end{matrix}$$
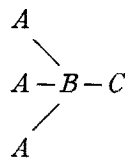
Since the atoms A are symmetrical with respect to the threefold axis of symmetry, it is sufficient to take one of the atoms as representative of the three.
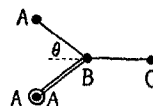
The kinetic and potential energies are given by

$$T = 3 \cdot \tfrac{1}{2} m_a (\dot{x}_a{}^2 + \dot{y}_a{}^2) + \tfrac{1}{2} m_b \dot{x}_b{}^2 + \tfrac{1}{2} m_c \dot{x}_c{}^2,$$

$$V = 3 \cdot \tfrac{1}{2} K_1 \xi_{ab}{}^2 + \tfrac{1}{2} K_2 \xi_{bc}{}^2 + 2 \cdot 3 \cdot \tfrac{1}{2} d (r_{ab} \eta)^2.$$

The secular equation is

$$\begin{vmatrix} \alpha - 3m_a \omega^2 & -\alpha & \beta & 0 \\ -\alpha & \alpha + K_2 - m_b \omega^2 & -\beta & -K_2 \\ \beta & -\beta & \delta - 3m_a \omega^2 & 0 \\ 0 & -K_2 & 0 & K_2 - m_c \omega^2 \end{vmatrix} = 0,$$

where
$$\alpha = 3K_1 \cos^2 \theta + 6d \sin^2 \theta,$$

$$\beta = 3(K_1 - 2d) \sin \theta \cos \theta,$$

$$\delta = 3K_1 \sin^2 \theta + 6d \cos^2 \theta.$$

This equation becomes

$$\omega^6 - M\omega^4 + N\omega^2 - P = 0, \qquad (2)$$

where

$$M = K_1 \left(\frac{1}{m_a} + \frac{3 \cos^2 \theta}{m_b} \right) + K_2 \left(\frac{1}{m_b} + \frac{1}{m_c} \right)$$

$$+ 2d \left(\frac{1}{m_a} + \frac{3 \sin^2 \theta}{m_b} \right),$$

$$N = K_1 K_2 \frac{3m_a \cos^2 \theta + m_b + m_c}{m_a m_b m_c} + 2K_1 d \frac{3m_a + m_b}{m_a{}^2 m_b}$$

$$+ 2K_2 d \frac{3m_a \sin^2 \theta + m_b + m_c}{m_a m_b m_c},$$

$$P = 2K_1 K_2 d \frac{3m_a + m_b + m_c}{m_a{}^2 m_b m_c}.$$

The secular equation for the symmetrical vibrations of a tetrahedral molecule

$$A - B - A$$

with A above and A below (tetrahedral arrangement)

is obtained by putting $K_2 = K_1$ and $m_b = m_a$ in Eq. (2). The secular equation for the symmetrical vibrations of a pyramidal molecule

$$A - B$$

with A above and A below

is obtained by putting $K_2 = 0$ in Eq. (2), and by substituting d for $2d$ since there is only one angle changing for each atom A.

THE SECULAR EQUATION FOR THE SYMMETRICAL VIBRATIONS OF THE MOLECULAR TYPE
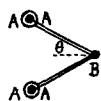
The kinetic and potential energies are given by

$$T = 4 \cdot \tfrac{1}{2} m_a (\dot{x}_a{}^2 + \dot{y}_a{}^2) + \tfrac{1}{2} m_b \dot{x}_b{}^2,$$

$$V = 4 \cdot \tfrac{1}{2} K_1 \xi_{ab}{}^2 + 4 \cdot \tfrac{1}{2} d (r_{ab}\eta)^2.$$

The secular equation is

$$\begin{vmatrix} \alpha - 4m_a\omega^2 & \beta & -\alpha \\ \beta & \delta - 4m_a\omega^2 & -\beta \\ -\alpha & -\beta & \alpha - m_b\omega^2 \end{vmatrix} = 0,$$

where

$$\alpha = 4K_1 \cos^2 \theta + 4d \sin^2 \theta,$$

$$\beta = 4(K_1 - d) \sin \theta \cos \theta,$$

$$\delta = 4K_1 \sin^2 \theta + 4d \cos^2 \theta.$$

The equation is therefore

$$\omega^4 - \omega^2 \left(\frac{K_1 + d}{m_a} + \frac{\alpha}{m_b} \right) + K_1 d \frac{m_b + 4m_a}{m_a{}^2 m_b} = 0.$$
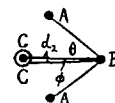
To obtain the secular equation for the planar configuration

$$A - B - A$$

with A above and A below

we need only put

$\theta = \pi/2$. In this case $\alpha = 4d$, and the equation reduces to

$$\left(\omega^2 - \frac{K_1}{m_a} \right)\left(\omega^2 - d \frac{4m_a + m_b}{m_a m_b} \right) = 0.$$

THE SECULAR EQUATION FOR THE SYMMETRICAL VIBRATIONS OF THE MOLECULAR TYPE

The kinetic and potential energies are given by

$$T = 2 \cdot \tfrac{1}{2} m_a (\dot{x}_a{}^2 + \dot{y}_a{}^2) + \tfrac{1}{2} m_b \dot{x}_b{}^2 + 2 \cdot \tfrac{1}{2} m_c (\dot{x}_c{}^2 + \dot{z}_c{}^2),$$

$$V = 2 \cdot \tfrac{1}{2} K_1 \xi_{ab}{}^2 + 2 \cdot \tfrac{1}{2} d_1 (r_{ab}\eta_1)^2 + 2 \cdot \tfrac{1}{2} K_2 \xi_{bc}{}^2$$

$$+ 2 \cdot \tfrac{1}{2} d_2 (r_{bc}\eta_2)^2.$$

To obtain the equation for the planar type it is sufficient to put $\theta = \phi = \pi/2$. The secular equation then becomes $(\omega^2 - K_1/m_a)(\omega^2 - K_2/m_c) = 0$ for the valence vibrations, and for the deformation vibrations

$$\begin{vmatrix} 2d_1 - 2m_a\omega^2 & -2d_1 & 0 \\ -2d_1 & 2d_1 + 2d_2 - m_b\omega^2 & -2d_2 \\ 0 & -2d_2 & 2d_2 - 2m_c\omega^2 \end{vmatrix} = 0.$$

THE STRUCTURE OF ACETOXIME

In a previous investigation by the author[3] the Raman spectra of dimethyl-ketoxime (acetoxime), diethyl-ketoxime, and acetaldoxime were obtained. The spectra were interpreted satisfactorily on the basis of the following configuration for the symmetrical oximes

$$C = N - OH.$$

with R above and R below
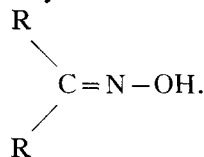
Treating the molecule from the dynamic point of view as of the type

$$B - C - D$$

with A above and A below

(in acetoxime A is the CH_3 group and D the OH group),

[3] Bernstein and Martin, Trans. Roy. Soc. Canada 31, 105 (1937).

TABLE I.

RAMAN FREQUENCIES, cm⁻¹		MODE OF VIBRATION. SEE FIG. 1
CALC.	OBS.	
330	335	ν_1
795	812	ν_2
940	930	ν_3
1712	1682	ν_4

the frequencies of the symmetrical modes of vibration were calculated. The force constants were obtained from molecules in which the same groups appear. For example, the deformation force constant was obtained by calculations on the tetramethyl ethylene molecule, the $N-O$ force constant from the hydroxylamine molecule, and the $C=N$ force constant from the guanidine molecule.

It was necessary to make a decision between two possible lines in the Raman spectrum of acetoxime, which might arise from the deformation vibration. To make this decision we obtained the depolarization factors for these radiations and found that the line at 335 cm⁻¹ was more polarized than the line at 474 cm⁻¹. The first line was therefore taken for the symmetrical deformation vibration.

To make the depolarization measurements two small pieces of polarizing film (Polaroid) were mounted in front of the slit of the spectrograph with their axes at right angles to each other, so that half the slit was covered by each piece.

Thus two spectra are obtained, one immediately above the other, arising from the components of the scattered radiations polarized in directions parallel to and perpendicular to the path of the exciting beam. Density measurements were made with a Moll microphotometer, and the depolarizations obtained. An account of this method for obtaining depolarization data is being published in detail shortly.

The calculated and observed frequencies for the acetoxime molecule are given in Table I.

The closeness of the agreement is somewhat fortuitous, considering the assumptions used. The calculations however appear to assign definitely each of the four observed lines to one of the modes of vibration in Fig. 1. The observed frequencies were then used in Eq. (1) to obtain the force constants and the angle θ. The values are

$$2d = 0.66 \times 10^5 \text{ dynes per cm}$$
$$K_1 = 4.60 \times 10^5 \text{ '' '' ''}$$
$$K_2 = 10.0 \times 10^5 \text{ '' '' ''}$$
$$K_3 = 3.80 \times 10^5 \text{ '' '' ''}$$
$$\theta = 63°.$$

The structure of acetoxime may therefore be represented by the planar configuration

$$
\begin{array}{c}
CH_3 \\
\diagup \quad \diagdown \\
126° \qquad C=N-OH. \\
\diagdown \quad \diagup \\
CH_3
\end{array}
$$