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The Normal Frequencies of Vibration of Symmetrical Pyramidal Molecules AB_3 with Application to the Raman Spectra of Trihalides*

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The symmetrical pyramidal molecule AB_3 is treated by a general normal-coordinate method, six force constants being required. The convenience of the use of "symmetry coordinates" is illustrated in obtaining the formulas for the normal frequencies for several types of potential functions. It is found that with two constants the central force treatment and valence force treatments fit the data equally well. The four constants K , H , K' and H' of the potential function

$$2V = K \sum_i \Delta R_i^2 + \frac{1}{2} H R_0^2 \sum_{ij} \Delta \alpha_{ij}^2 + K' \sum_{ij} \Delta R_i \Delta R_j + 2H' R_0^2 (\Delta \alpha_{12} \Delta \alpha_{23} + \Delta \alpha_{23} \Delta \alpha_{31} + \Delta \alpha_{31} \Delta \alpha_{12})$$

for certain trihalides are obtained from Raman data. The interatomic distances calculated using these values of K in the empirical relation found by Badger for diatomic molecules agree with the distances obtained by other methods to within about 0.1 Å.

THE normal coordinate treatment for symmetrical pyramidal molecules of the type AB_3 has been carried out by Dennison,¹ using central forces, and by Lechner,² using valence forces, both treatments involving two force constants. The latter formulas have not previously been applied to any actual molecules. We have treated this problem from a general viewpoint and have then considered several valence-type approximate potential functions. In order to obtain a set of force constants which might be of use in the interpretation of the spectra of more complicated molecules we have applied one of these treatments, involving four force constants, to the observed spectra of trihalides.

SYMMETRY CONSIDERATIONS

Table I summarizes the facts which may be obtained from the symmetry of the molecule concerning the normal modes of vibration. The numbers under E , $2C_3$, $3\sigma_v$ are the characters of the normal modes corresponding to the operations identity (E), rotation by $\pm 2\pi/3$ ($2C_3$), and reflection through the planes of symmetry ($3\sigma_v$).

TABLE I. Characters for the normal modes of vibration (Point group C_{3v}).

	E	$2C_3$	$3\sigma_v$	Number of modes
A_1	1	1	1	2
E_1	2	-1	0	4

* Contribution No. 424.

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

² F. Lechner, *Wien. Bericht* **141**, 633 (1932).

The symbols A_1 and E_1 refer to the two types of normal modes which occur in this molecule. The last column gives the number of modes belonging to each symmetry type. Two normal modes of vibration occur in the symmetry type A_1 , each of which is completely symmetric and non-degenerate. There are two pairs of modes in the class E_1 , the two members of each pair having the same frequency and being related to each other by rotation about the threefold axis in the manner shown by the characters of Table I.³ The four fundamental frequencies are allowed in both the Raman and infrared spectra. Table II gives

TABLE II. Degeneracy, symmetry type, depolarization of Raman lines, and infrared rotational band character for the four fundamental frequencies.

	Deg.	Sym.	Depol.	Band type
ν_1	1	A_1	$< \frac{3}{4}$	
ν_2	1	A_1	$< \frac{3}{4}$	
ν_3	2	E_1	$\frac{3}{4}$	\perp
ν_4	2	E_1	$\frac{3}{4}$	\perp

further information concerning their properties.

The symmetry also enables us to factor the secular equation into three quadratic factors, two of which are identical. In order to carry out this factorization, it is only necessary to express the potential and kinetic energies in terms of the

³ These results, which are of course well known for this molecule, are best obtained by the group-theory methods of Wigner, *Gött. Nachrichten*, p. 133 (1930). For other discussions of this method see L. Tisza, *Zeits. f. Physik* **82**, 48 (1933); G. Placzek, *Rayleigh-Streuung und Raman Effekt*, Leipzig, 1934; R. S. Mulliken, *Phys. Rev.* **43**, 279 (1933); E. Bright Wilson, Jr., *Phys. Rev.* **45**, 706 (1934).

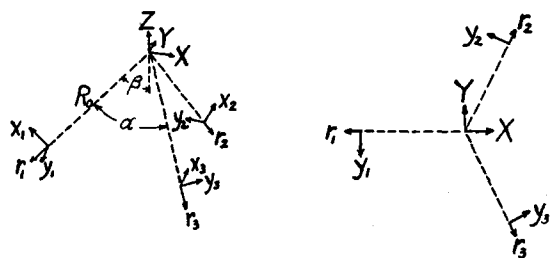


FIG. 1. Perspective view and projection on plane B_3 of coordinate system for molecule AB_3 . r_i points along $A-B_i$. x_i lies in plane formed by axis and bond AB_i . y_i is perpendicular to this plane.

proper kind of coordinates. We shall for convenience call such a set of coordinates, which factors the secular equation to the maximum extent possible from symmetry considerations alone, a set of *symmetry coordinates*. There will usually be an infinite number of such coordinate sets possible; convenience dictates which one to choose. The symmetry coordinates we have used for this molecule are represented graphically in Fig. 2, the component along a given coordinate direction q_i of the arrow attached to the related atom being the coefficient of the corresponding symmetry coordinate S_k in the transformation for q_i ,

$$q_i = \sum_{(k)} S_{ik} S_k, \quad (1)$$

in which q_i is one of the original coordinates, such as r_1 , shown in Fig. 1.

The criteria by which these coordinates are constructed are as follows: Each symmetry coordinate must belong to one of the symmetry types (irreducible representations) allowed for the modes of vibration; i.e., it must transform in one of the ways given in Table I. There must be as many independent symmetry coordinates of each type as there are modes of vibration of that type. Each symmetry coordinate indicates a motion which conserves angular and linear momentum. The symmetry coordinates corresponding to degenerate symmetry types are constructed so that the members of a given degenerate pair are mutually orthogonal. With these rules it is usually not difficult to construct a set of symmetry coordinates. In the present case it is evident from Fig. 2 that S_1 and S_2 are both completely symmetric as required of the two symmetry coordinates associated with A_1 while it

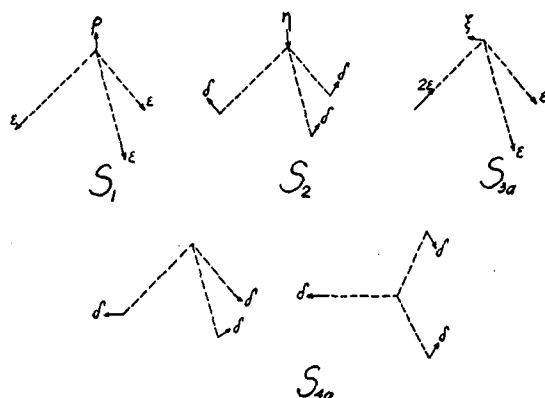


FIG. 2. Graphical representation of symmetry coordinates. In S_{4a} the B atoms all move in plane B_3 in the manner shown by the projection on this plane. $\rho = 3\epsilon(m/M) \cos \beta$; $\eta = 3\delta(m/M) \sin \beta$, $\xi = 3\epsilon(m/M) \sin \beta$.

is easy to show that S_{3a} , S_{3b} , S_{4a} and S_{4b} transform as required for type E_1 . It is also evident from inspection of the figure that they all conserve momentum.

CALCULATION OF FREQUENCIES FROM SYMMETRY COORDINATES

It can be shown that a set of coordinates which satisfies the above conditions will make it possible to express the potential and kinetic energies (assuming, of course, a homogeneous, quadratic potential function) as quadratic functions of the S 's and \dot{S} 's without the appearance of any cross terms except between S 's or \dot{S} 's of the same symmetry type. Thus, in our case, the expressions are

$$2V = a_{11}S_1^2 + 2a_{12}S_1S_2 + a_{22}S_2^2 + a_{33}(S_{3a}^2 + S_{3b}^2) + 2a_{34}(S_{3a}S_{4a} + S_{3b}S_{4b}) + a_{44}(S_{4a}^2 + S_{4b}^2) \quad (2)$$

and

$$2T = b_{11}\dot{S}_1^2 + 2b_{12}\dot{S}_1\dot{S}_2 + b_{22}\dot{S}_2^2 + b_{33}(\dot{S}_{3a}^2 + \dot{S}_{3b}^2) + 2b_{34}(\dot{S}_{3a}\dot{S}_{4a} + \dot{S}_{3b}\dot{S}_{4b}) + b_{44}(\dot{S}_{4a}^2 + \dot{S}_{4b}^2). \quad (3)$$

For this molecule the most general quadratic potential function compatible with the symmetry of the molecule has thus only six independent constants.⁴ Using the coordinates S , we may set

⁴ This simple method of finding the number of independent constants in the quadratic potential function for a molecule of a given symmetry is generally applicable. The group theory considerations, which are very easy to apply, give directly the number and degrees of the factors of the secular equation. For each distinct linear factor there will

up the equations of motion and solve them in the usual manner, obtaining a secular determinant which, when factored, leads to the equations

$$\begin{vmatrix} a_{11} - b_{11}\lambda & a_{12} - b_{12}\lambda \\ a_{12} - b_{12}\lambda & a_{22} - b_{22}\lambda \end{vmatrix} = 0$$

and

$$\begin{vmatrix} a_{33} - b_{33}\lambda & a_{34} - b_{34}\lambda \\ a_{34} - b_{34}\lambda & a_{44} - b_{44}\lambda \end{vmatrix} = 0, \quad (4)$$

the second factor occurring twice. $\lambda = 4\pi^2\nu^2$. ν_1 and ν_2 are the roots of the first equation, while ν_3 and ν_4 are the roots of the second.

The constants b_{ij} depend on the symmetry coordinates selected, the masses of the atoms, and the geometry of the molecule. In our case we obtain

$$2T = 3m\{\dot{N}\dot{S}_1^2 + 2\dot{P}\dot{S}_1\dot{S}_2 + \dot{C}\dot{S}_2^2 + (C+1)(\dot{S}_{3a}^2 + \dot{S}_{3b}^2) - 2\mu(\dot{S}_{3a}\dot{S}_{4a} + \dot{S}_{3b}\dot{S}_{4b}) + (\dot{S}_{4a}^2 + \dot{S}_{4b}^2)\}, \quad (5)$$

so that

$$b_{11} = 3mN, \quad b_{12} = 3mP, \quad b_{22} = 3mC, \\ b_{33} = 3m(C+1), \quad b_{34} = -3m\mu, \quad b_{44} = 3m, \quad (6)$$

with $N = (3m/M)\cos^2\beta + 1$, $C = (3m/M)\sin^2\beta + 1$, $P = -(3m/M)\sin\beta\cos\beta$, $\mu = \sin\beta$. M and m are the masses of A and B , respectively, while β is the angle shown in Fig. 1.

The constants a_{ij} of the potential energy are what we are seeking to find by using the observed spectra. Since, however, there are only four fundamentals, we cannot evaluate the six independent force constants and it is necessary to make some physical assumptions.⁵

POTENTIAL ENERGY FUNCTION

One type of physical assumption which has been used to reduce the number of force constants is the assumption of central forces used by

be one, for each distinct quadratic factor three, for each distinct cubic six, and in general for each distinct factor of the k 'th degree there will be $k(k+1)/2$ independent constants in the most general quadratic potential function for the molecule. One of us (E. Bright Wilson, Jr., *J. Chem. Phys.* **2**, 432 (1934)) has given tables summarizing the results of group-theory considerations as applied to a large class of molecules. The numbers in the last column of Tables I-VII of this paper give the degrees of the factors of the secular equation so that these tables may be used as indicated above to find the number of independent force constants.

⁵ The use of isotopic molecules theoretically gives more

Dennison.¹ His potential function is

$$2V = K_1(\Delta R_1^2 + \Delta R_2^2 + \Delta R_3^2) + K_2(\Delta r_{12}^2 + \Delta r_{13}^2 + \Delta r_{23}^2), \quad (7)$$

in which ΔR_i is the change in the distance $A-B_i$ while Δr_{ij} is the change in distance B_i-B_j . K_1 and K_2 are the force constants. This is easily expressed in terms of the coordinates S by using Fig. 2, and by inspection expressions for the a_{ij} are determined. Substitution of these in Eq. (4) gives Dennison's results.

If, on the other hand, we assume that there are no direct forces acting between the non-bonded atoms but that the atoms are held in place by the rigidity, both lateral and extentional, of the chemical bonds, we might assume that a reasonable form for the potential function is

$$2V = K(\Delta R_1^2 + \Delta R_2^2 + \Delta R_3^2) + HR_0^2(\Delta\alpha_{12}^2 + \Delta\alpha_{13}^2 + \Delta\alpha_{23}^2), \quad (8)$$

in which α_{ij} is the angle B_i-A-B_j and R_0 the distance $A-B$ at equilibrium. K and H are the force constants. By writing this in terms of the symmetry coordinates S , we get expressions for the a_{ij} 's from which we may obtain Lechner's² results.

A more extreme valence type of potential function is obtained from a consideration of Pauling's ideas concerning the chemical bond.⁶ From this viewpoint, the stability of a molecule is due to the overlapping of the bond eigenfunctions of the bonded atoms. In our example the central atom A is assumed to have three eigenfunctions whose directions of maximum value are the bond directions. We shall assume that these retain their relative positions but that when the molecule is distorted from the equilibrium position in any manner the whole figure formed by these eigenfunctions rotates until the overlapping with the eigenfunctions from the B atoms is as large as possible, thus giving the molecule the lowest energy for that configuration of the atoms. The potential function corresponding to this picture of the molecule is

$$2V = K(\Delta R_1^2 + \Delta R_2^2 + \Delta R_3^2) + HR_0^2(\Delta\sigma_1^2 + \Delta\sigma_2^2 + \Delta\sigma_3^2), \quad (9)$$

data with which to calculate the six force constants, but practically the shifts are so small for all but the hydrogen isotope that they are not of much use.

⁶ Linus Pauling, *J. Am. Chem. Soc.* **53**, 1367 (1931).

where $\Delta\sigma_i$ is the angle between the direction of the maximum of the bond eigenfunction for the atom A and the direction of the line $A-B_i$. The mutual directions of the three bond eigenfunctions are kept fixed but their absolute orientation relative to the B atoms is varied until for each configuration of the molecule $\Delta\sigma_1^2 + \Delta\sigma_2^2 + \Delta\sigma_3^2$ is a minimum. This potential function leads to the equations

$$\begin{aligned} m^2\lambda^2 - [KN + HC]m\lambda + KH\gamma &= 0, \\ m^2\lambda^2 - [\tfrac{1}{2}K(C+1) + HGW]m\lambda + KHGD &= 0, \end{aligned} \quad (10)$$

in which N and C have been given above with Eq. (6), and

$$\begin{aligned} \gamma &= 3m/M + 1, \quad G = (8 - 7 \sin^2 \beta) / (4 - 3 \sin^2 \beta)^2, \\ W &= ((3m/2M) \sin^2 \beta - 1) \sin^2 \beta + 2, \\ D &= (3m/M - 1) \sin^2 \beta + 2. \end{aligned}$$

Finally we have considered a potential function of the type used by Lechner with the addition of two more constants, which we have chosen in the following way

$$\begin{aligned} 2V &= K(\Delta R_1^2 + \Delta R_2^2 + \Delta R_3^2) \\ &\quad + HR_0^2(\Delta\alpha_{12}^2 + \Delta\alpha_{23}^2 + \Delta\alpha_{31}^2) \\ &\quad + 2K'(\Delta R_1\Delta R_2 + \Delta R_2\Delta R_3 + \Delta R_3\Delta R_1) \\ &\quad + 2H'R_0^2(\Delta\alpha_{12}\Delta\alpha_{23} + \Delta\alpha_{23}\Delta\alpha_{31} + \Delta\alpha_{12}\Delta\alpha_{31}). \end{aligned} \quad (11)$$

This function would be the general one if we had included two more constants, the interaction of the stretching of each bond with the change of the adjacent angles, and the interaction of the stretching of each bond with the change of the angle opposite. We were guided in deciding to neglect these two rather than any other pair by the discussion which Van Vleck and Cross⁷ have made of the water molecule in which they decided that the interaction of stretching and bending is the least important. With these four constants we obtain a set of expressions for the a_{ij} and find that the frequencies are given by the equations

$$\begin{aligned} m^2\lambda^2 - [(K + 2K')N + (H + 2H')LC]m\lambda \\ + (K + 2K')(H + 2H')L\gamma &= 0, \\ m^2\lambda^2 - [\tfrac{1}{2}(K - K')(C + 1) + (H - H')QW]m\lambda \\ + (K - K')(H - H')QD &= 0, \end{aligned} \quad (12)$$

⁷ J. H. Van Vleck and P. C. Cross, J. Chem. Phys. **1**, 357 (1933).

in which N , C , γ , W and D have been given above with Eq. (10) while

$$Q = 3/(4 - 3 \sin^2 \beta) \quad \text{and} \quad L = 4 \cos^2 \beta \cdot Q.$$

APPLICATION TO TRIHALIDES

These four potential functions have been applied to the observed Raman data for the trihalides of phosphorus, arsenic, antimony and bismuth.⁸ The three two-constant potential functions, Eqs. (7), (8) and (9), fit the data with comparable accuracy, as shown by the examples in Table III. Table IV gives the results for the

TABLE III. Comparison of results of two-constant treatments for PCl_3 and $AsCl_3$.

	ν obs.	a	b	c
PCl_3	ν_1	510	496 (-14)	466 (-44)
	ν_2	257	205 (-52)	231 (-26)
	ν_3	480	497 (+17)	534 (+54)
	ν_4	190	223 (+33)	219 (+29)
	$K \cdot 10^{-5}$		2.01	2.24
	$K_2 \cdot 10^{-5}$		0.867	
$AsCl_3$	$H \cdot 10^{-5}$		0.340	0.565
	ν_1	410	426 (+16)	385 (-25)
	ν_2	193	164 (-29)	183 (-10)
	ν_3	370	383 (+13)	398 (+28)
	ν_4	159	174 (+15)	168 (+9)
	$K \cdot 10^{-5}$		1.80	2.10
	$K_2 \cdot 10^{-5}$		0.600	
	$H \cdot 10^{-5}$		0.234	0.425

Frequencies in cm^{-1} and force constants in dynes/cm, listed under a , b and c , are calculated by the use of the potential function of
(a) Eq. (7) (central forces). $K = K_1$.
(b) Eq. (8) (valence forces).
(c) Eq. (9) (valence forces).

four-constant treatment (Eq. (11)) of these molecules, with which the data can be fitted exactly. The angles for PF_3 , $AsCl_3$ and PCl_3 are from electron diffraction studies.⁹ The other angles were chosen as reasonable in the light of theoretical considerations and crystal structure evidence.⁶ The effect on the force constants of possible inaccuracies in the angles is small compared to the effect due to the inaccuracy of the Raman data.

Using the values of K for these molecules we have calculated the interatomic distances R_0 by

⁸ Bhagavantam, Ind. J. Phys. **5**, 73 (1930) and Trumphy, Zeits. f. Physik **68**, 675 (1931) have published similar computations for a central force treatment of this type of molecule. They use the angle as a third adjustable parameter and obtain values considerably different from those given by electron diffraction experiments.

⁹ We are indebted to Dr. L. O. Brockway for the results for PF_3 and $AsCl_3$.

TABLE IV. Bond angle α , observed Raman frequencies ν_1 , ν_2 , ν_3 and ν_4 in cm^{-1} . Calculated force constants K , H , K' and H' in dynes/cm and calculated interatomic distances in Angstroms for trihalides.

	α	ν_1	ν_2	ν_3	ν_4	$K \times 10^{-5}$	$H \times 10^{-5}$	$K' \times 10^{-5}$	$H' \times 10^{-5}$	R_0	$R_0 - R$ (obs)
(a) PF_3	100°	890	531	840	486	4.56	1.07	0.39	0.04	1.64	0.09
(b) PCl_3	102°	510	257	480	190	2.11	0.31	0.28	0.06	2.15	0.12
(c) PBr_3	104°	380	162	400	116	1.62	0.27	0.05	0.07	2.31	0.07*
(d) AsF_3	97°	707	341	644	274	3.90	0.40	0.34	0.06	1.80	0.08
(e) AsCl_3	96°	410	193	370	159	2.01	0.23	0.19	0.02	2.24	0.03
(f) SbCl_3	94°	360	165	320	134	1.75	0.17	0.16	0.02	2.30	-0.10*
(g) BiCl_3	93°	288	130	242	96	1.17	0.10	0.15	0.02	2.46	-0.04*

* $R(\text{obs})$ for these molecules taken from Pauling's tables of covalent radii. These values are probably somewhat high for these molecules.

Source of assignments:

(a) D. M. Yost of this laboratory, unpublished results. (b) and (e) See Kohlrausch, *Der Smekal-Raman-Effekt*, p. 201, Julius Springer, Berlin, 1931. (c) Cabannes and Rousset, *Ann. de physique* **19**, 272 (1933). (d) Yost and Sherborne, *J. Chem. Phys.* **2**, 125 (1934). (f) Braune and Engelbrecht, *Zeits. f. physik. Chemie* **B19**, 303 (1932). (g) Bhagavantam, *Ind. J. Phys.* **5**, 66, 86 (1930).

means of the relation found by Badger¹⁰ connecting the force constant and the interatomic distance in diatomic molecules. The last column

¹⁰ R. M. Badger, *J. Chem. Phys.* **2**, 128 (1934).

of Table IV gives the difference between these values and the distances obtained either from electron diffraction or from Pauling's table of covalent radii.

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A Photographic Method for the Study of Mechanical Models of Vibrating Molecules

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IN the study of the vibrations of complex molecules the mechanical models developed by Kettering, Shutts and Andrews¹ have proved useful as a general aid to the interpretation of spectra and particularly as a means of obtaining suggestions regarding the different possible modes of vibration. One of the chief disadvantages in this method, however, is the difficulty of making certain by means of visual observation just what is taking place when the model vibrates. To overcome this defect a photographic

method has been developed for recording the types of motion, as shown in Fig. 1.

White dots, 2 mm diam., are painted with enamel on the balls B , B , B which represent the atoms. A 300 watt lamp L is placed so that the greater part of the light from it can be thrown on the model with the help of a mirror M and lens. The latter is so arranged that the light beam passes across the reciprocating bar K which runs from the motor P to the model to transmit the energy of agitation, and is reflected back on the model. It is brought to a rough focus at a point about two centimeters above the bar on which a screen S is placed so that at one end of the stroke it cuts down the intensity of the light by 75 percent. The resultant effect is that, when the model is executing a characteristic mode of vibration in phase with the agitating bar, the intensity of the light falling on it at one extreme of the phase is about four times that at the other extreme.

A camera C is placed about five feet from the model and arranged so that a time exposure may be taken while the model is vibrating. With

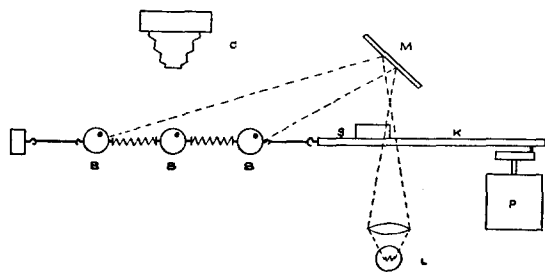


FIG. 1.

¹ C. F. Kettering, L. W. Shutts and D. H. Andrews, *Phys. Rev.* **36**, 531 (1930).