

The General Solution of the Secular Equation of Second Degree, with Application to the Class A 1 Vibrations of the Symmetrical Triatomic Molecule

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Citation: [The Journal of Chemical Physics](#) **17**, 357 (1949); doi: 10.1063/1.1747260

View online: <http://dx.doi.org/10.1063/1.1747260>

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vided that the activated cyclopropane molecule had a very long life. It is pertinent to note here that Phibbs, Darwent, and Steacie²⁰ found it necessary to postulate an activated molecule followed by ring opening in the mercury photosensitized decomposition of ethylene oxide, which is structurally somewhat similar to cyclopropane. In the present state of our knowledge, no definite choice can be made between the two mechanisms.

CONCLUSIONS

The reaction of cyclopropane with $\text{Hg}(^3P_1)$ atoms is in remarkable contrast to its thermal behavior, where isomerization to propylene seems to be the principal reaction occurring during the decomposition.¹⁵ Furthermore, the cyclopropane reaction is unique among all the mercury photosensitized reactions of the hydrocarbons which have been investigated to date.²¹ While it is not possible at the

²⁰ M. K. Phibbs, B. de B. Darwent, and E. W. R. Steacie, *J. Chem. Phys.* **16**, 39 (1948).

²¹ For discussions of the mercury photosensitized reactions of the hydrocarbons, see: E. W. R. Steacie, *Atomic and Free Radical Reactions* (Reinhold Publishing Corporation, New

York, 1946); Keith J. Laidler, *J. Chem. Phys.* **15**, 712 (1947); E. W. R. Steacie, *Research*, in press.

present time to decide whether the collision of an $\text{Hg}(^3P_1)$ atom with a cyclopropane molecule results in the formation of activated molecule or a trimethylene biradical, it seems fairly certain that the polymer chain is propagated by the successive formation of higher and higher biradicals.

Further work is now under way on the cyclopropane reaction in the laboratories of one of us (H.E.G.), together with investigations of the mercury photosensitized decompositions of the higher cyclic paraffins and olefins.

ACKNOWLEDGMENT

It is a great pleasure for the authors to acknowledge their indebtedness to Dr. Fred L. Mohler of the Mass Spectrometry Section of the National Bureau of Standards for performing the mass spectrometric analyses reported in this paper.

Our thanks are also due Mr. Yves Lupien for assistance in some of the measurements and Mr. Burton Dearing for his assistance in the infra-red measurements.

York, 1946); Keith J. Laidler, *J. Chem. Phys.* **15**, 712 (1947); E. W. R. Steacie, *Research*, in press.

The General Solution of the Secular Equation of Second Degree, with Application to the Class A_1 Vibrations of the Symmetrical Triatomic Molecule

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(Received July 8, 1948)

Various solutions of the secular equation of second degree, giving the force constants, normal coordinates, and potential energy distributions in terms of the fundamental vibration frequencies and molecular constants, have been found and their significance discussed. General formulas are obtained for certain critical solutions and illustrative numerical results given for a series of eight symmetrical triatomic molecules, with curves covering all possible solutions in three typical cases. The solution in which the ratios of the contributions to the potential energy from the two square terms in the valence-force potential energy expression are mutually reciprocal in the two normal modes is shown to be universally applicable; that in which the normal coordinate for the vibration of higher frequency is identical with the corresponding valence-force symmetry coordinate is also quite satisfactory. Both always give real results. Alternative solutions are suggested for use when the difference in frequency of the two modes is small.

I. THE SECULAR EQUATION

IF the motion of a displaced system specified by two coordinates Δ_1 and Δ_2 is simple harmonic, the potential energy, V , contains only quadratic terms and has the following general form

$$2V = d_{11}\Delta_1^2 + d_{22}\Delta_2^2 + (d_{12} + d_{21})\Delta_1\Delta_2, \quad (1)$$

where the d_{ij} 's are the force constants, ($d_{12} = d_{21}$). It is assumed in this paper that Δ_1 and Δ_2 are valence-type coordinates of the required symmetry class. It is usually convenient to express them in terms of

further coordinates z_1 to z_N , as follows

$$\Delta_i = \sum_{k=1}^N a_{ik}z_k, \quad (2)$$

where the coefficients a_{ik} are determined by the geometry of the system. The secular equation giving the normal vibration frequencies of the system described by the force field (1) can then be written¹

$$\begin{vmatrix} A_{11}d_{11} + A_{12}d_{12} - \lambda & A_{21}d_{11} + A_{22}d_{12} \\ A_{11}d_{21} + A_{12}d_{22} & A_{21}d_{21} + A_{22}d_{22} - \lambda \end{vmatrix} = 0, \quad (3)$$

¹ E. Bright Wilson, Jr., *J. Chem. Phys.* **7**, 1047 (1939).

where

$$A_{ij} = A_{ji} = \sum_{k=1}^N a_{ik} a_{jk} (M/m_k), \quad (4)$$

and

$$\lambda = 4\pi^2 \nu^2 c^2 M, \quad (5)$$

ν being the vibration frequency in cm^{-1} , c the velocity of light in cm sec^{-1} , and M some mass, usually related to one of the m_k 's, (which are the masses conjugate to the coordinates z_k), introduced in order that the A_{ij} shall be pure numbers.

An unambiguous solution for the force constants d_{ij} in terms of the vibration frequencies is not possible unless some arbitrary assumption is made as to the nature of the force field, equivalent to postulating a relationship between two of the constants. A possible exception to the above situation occurs when isotopic molecules are available for study; but, with the exception of the hydrogen-deuterium pair, the isotopic shifts are too small to be of much value. We shall examine the range of values allowed to each constant in the general problem and investi-

gate the corresponding variation in the geometrical form and energy properties of the normal vibrations.

II. THE SOLUTION FOR THE CONSTANTS

By elimination of d_{22} from Eq. (3) we obtain the following second-degree equation in d_{11} and d_{12}

$$A_{11}d_{11}^2 + 2A_{12}d_{11}d_{12} + A_{22}d_{12}^2 - (\lambda_1 + \lambda_2)d_{11} + (A_{22}/D)\lambda_1\lambda_2 = 0, \quad (6)$$

where $D = (A_{11}A_{22} - A_{12}^2)$, and λ_1 and λ_2 are the two solutions of (3) corresponding to ν_1 and ν_2 . It can be shown that $(D/A_{11}^2) > 0$, and that consequently Eq. (6) is that of an ellipse.² The center is found at $d_{11} = (A_{22}/2D)(\lambda_1 + \lambda_2)$, $d_{12} = -(A_{12}/2D)(\lambda_1 + \lambda_2)$, the major axis is inclined to the d_{11} axis at an angle $\theta = (1/2) \arctan[2A_{12}/(A_{11} - A_{22})]$, and the semi-axes a and b are given by the following expressions

$$\left. \begin{aligned} a^2 &= (A_{22}/4D) [A_{11} \cos^2 \theta + 2A_{12} \sin \theta \cos \theta + A_{22} \sin^2 \theta]^{-1} (\lambda_1 - \lambda_2)^2 \\ b^2 &= (A_{22}/4D) [A_{11} \sin^2 \theta - 2A_{12} \sin \theta \cos \theta + A_{22} \cos^2 \theta]^{-1} (\lambda_1 - \lambda_2)^2 \end{aligned} \right\}, \quad (7)$$

TABLE I. General solution of the secular equation of second degree.

	d_{12}	d_{11}	d_{22}	i	ρ_i	$V_{11}(\nu_i)$	$V_{22}(\nu_i)$	$V_{12}(\nu_i)$
Mean d_{12} (IV)	$-A_{12}''$	$A_{22}'' \pm a_1 D'$	$A_{11}'' \mp (D'/a_1)$	1	$(a_2 P_1)^{-1}$	$(B_1 + A_{\mu 1})/4$	$(B_2 + A_{\mu 1})/4$	$-(A_{\epsilon 1})/2$
				2	$a_2 P_2$	$(B_2 + A_{\mu 2})/4$	$(B_1 + A_{\mu 2})/4$	$-(A_{\epsilon 2})/2$
Mean d_{11} (V)	$-A_{12}'' \pm D'$	A_{22}''	$A_{11}'' \mp 2a' D'$	1	$a' Q_1$	$(C_1 \epsilon_1)/4$	$(C_2 + C_{1\mu 1})/4$	$-(C + C_{1\mu 1})/2$
				2	$(a' Q_2)^{-1}$	$(C_2 \epsilon_2)/4$	$(C_1 + C_{2\mu 2})/4$	$-(C + C_{2\mu 2})/2$
Mean d_{22} (VI)		$A_{22}'' \mp 2a_2 D'$	A_{11}''	1	$(a_2 Q_1)^{-1}$	$(C_2 + C_{1\mu 1})/4$	$(C_1 \epsilon_1)/4$	$-(C + C_{1\mu 1})/2$
				2	$a_2 Q_2$	$(C_1 + C_{2\mu 2})/4$	$(C_2 \epsilon_2)/4$	$-(C + C_{2\mu 2})/2$
Min. (III) & Max. d_{12}	$-(A_{12}'' \pm A' D')$	$A_{22}'' \pm a_1 D''$	$A_{11}'' \pm (D''/a_1)$	1	$\mp (1/a_1)$	$(1 + K_{1\mu 1})/4$		$(1 - K_{1\mu 1})/2$
				2	$\pm a_1$	$(1 + K_{2\mu 2})/4$		$(1 - K_{2\mu 2})/2$
Min. d_{22} (VII)	$-A_{12}' \lambda_2$	$\lambda_1' + A \lambda_2'$	$A_{11}' \lambda_2$	1	$(1/a_2)$	$1 + A_{\mu 1}$	$A_{\mu 1}$	$-2A_{\mu 1}$
				2	∞	0	1	0
Min. d_{11}		$A_{22}' \lambda_2$	$\lambda_1'' + A \lambda_2''$	1	a'	$A_{\mu 1}$	$1 + A_{\mu 1}$	$-2A_{\mu 1}$
				2	0	1	0	0
Max. d_{11} (VIII)	$-A_{12}' \lambda_1$	$A_{22}' \lambda_1$	$\lambda_2'' + A \lambda_1''$	1	∞	1	0	0
				2	$(1/a')$	$A_{\mu 2}$	$1 + A_{\mu 2}$	$-2A_{\mu 2}$
Max. d_{22}		$\lambda_2' + A \lambda_1'$	$A_{11}' \lambda_1$	1	0	0	1	0
				2	a_2	$1 + A_{\mu 2}$	$A_{\mu 2}$	$-2A_{\mu 2}$
$V_{12} = 0$ (I)	0	$L_1' \pm E'$	$L_1'' \mp E''$	1	*	$(1 \pm E)/2$	$(1 \mp E)/2$	0
				2	*	$(1 \mp E)/2$	$(1 \pm E)/2$	
$V_{11}(\nu_1) = V_{22}(\nu_2)$ (II)	$-2A_{12}' L_3$	$F'(F \pm L_2)$	$F''(F \mp L_2)$	1	*	$F(F \pm 1)/2$	$F(F \mp 1)/2$	$-4A(L_3/L_1)$
				2	*	$F(F \mp 1)/2$	$F(F \pm 1)/2$	

See reference *, Section IV.

² G. Glockler and Yo-Yun Tung, J. Chem. Phys. **13**, 388 (1945).

both of which are always real and positive. The constant d_{12} varies over the range $(1/2D)[-(A_{12}(\lambda_1+\lambda_2) \pm (A_{11}A_{22})^{1/2}(\lambda_1-\lambda_2))]$ and d_{11} over the range $(A_{22}/2D)[(\lambda_1+\lambda_2) \pm (\lambda_1-\lambda_2)]$.

Similarly, by elimination of d_{11} from Eq. (3), we obtain the second degree equation in d_{22} and d_{12} , corresponding to Eq. (6)

$$A_{22}d_{22}^2 + 2A_{12}d_{22}d_{12} + A_{11}d_{12}^2 - (\lambda_1 + \lambda_2)d_{22} + (A_{11}/D)\lambda_1\lambda_2 = 0. \quad (8)$$

This is also the equation of an ellipse, whose center is at $d_{22} = (A_{11}/2D)(\lambda_1 + \lambda_2)$, $d_{12} = -(A_{12}/2D)(\lambda_1 + \lambda_2)$, whose major axis is inclined to the d_{22} axis at an angle $\theta' = [(\pi/2) - \theta]$ and whose semi-axes are related to a and b in Eq. (7) by $a' = (A_{11}/A_{22})^{1/2}a$, $b' = (A_{11}/A_{22})^{1/2}b$. d_{12} varies as before, and d_{22} over the range $(A_{11}/2D)[(\lambda_1 + \lambda_2) \pm (\lambda_1 - \lambda_2)]$.

The following relations holding at certain singular solutions are of interest:

$$\text{At } (\partial d_{11}/\partial d_{12}) = 0, \quad A_{21}d_{11} + A_{22}d_{12} = 0. \quad (9)$$

$$\text{At } (\partial d_{22}/\partial d_{12}) = 0, \quad A_{11}d_{21} + A_{12}d_{22} = 0. \quad (10)$$

$$\text{At } (\partial d_{12}/\partial d_{11}) = (\partial d_{12}/\partial d_{22}) = 0, \quad (11)$$

$$A_{11}d_{11} + A_{12}d_{12} = A_{21}d_{21} + A_{22}d_{22} = \frac{1}{2}(\lambda_1 + \lambda_2).$$

Eqs. (9) and (10) lead to the factorization of Eq. (3) into two linear equations, and Eq. (11) requires the two diagonal terms to be equal, and the subsidiary elements to be equal but opposite in sign. It is found that real solutions of d_{11} and d_{22} , with $d_{12} = 0$, are only possible if the following condition is satisfied,

$$(A_{11}A_{22}/A_{12}^2)[(\lambda_1 - \lambda_2)/(\lambda_1 + \lambda_2)]^2 \geq 1. \quad (12)$$

It may be noted that in the case $\lambda_1 = \lambda_2$, (degeneracy), Eqs. (6) and (8) each represent two imaginary straight lines, and the only real solution for the constants is $d_{12} = -(A_{12}/D)\lambda$, $d_{11} = (A_{22}/D)\lambda$, and $d_{22} = (A_{11}/D)\lambda$. Conditions (9), (10), and (11) then all hold simultaneously, and all possible linear combinations of Δ_1 and Δ_2 are allowed as normal coordinates.

III. THE NORMAL COORDINATES

It is found that the displacements $z_n(\nu_{1,2})$ associated with the normal modes $\nu_{1,2}$ are related to the (unnormalized) normal coordinates $\eta_{1,2}$ as follows,

$$\begin{aligned} z_n(\nu_{1,2}) &= (M/m_n)[(a_{1n}A_{21} - a_{2n}A_{11})d_{21} \\ &\quad + (a_{1n}A_{22} - a_{2n}A_{12})d_{22} - a_{1n}\lambda_{1,2}]\eta_{1,2}, \\ &= (M/m_n)[(a_{1n}A_{21} - a_{2n}A_{11})d_{11} \\ &\quad + (a_{1n}A_{22} - a_{2n}A_{12})d_{12} + a_{2n}\lambda_{1,2}]\eta_{1,2}, \end{aligned} \quad (13)$$

where the force constants d_{ij} are any set satisfying the original Eq. (3). In terms of the coordinates Δ_1 and Δ_2 , the geometrical form of the normal vibrations is described by the following relations

$$\begin{aligned} (\Delta_1/\Delta_2)(\nu_{1,2}) &= [(A_{11}\lambda_{1,2} - Dd_{22})/(A_{12}\lambda_{1,2} + Dd_{12})] \\ &= [(A_{12}\lambda_{1,2} + Dd_{12})/(A_{22}\lambda_{1,2} - Dd_{11})] \end{aligned} \quad (14)$$

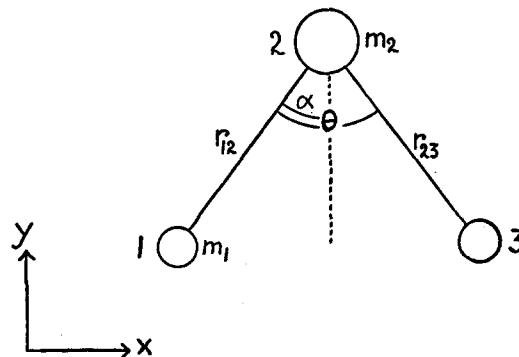


FIG. 1. Coordinates for the symmetrical triatomic molecule.

It is convenient to define two parameters

$$\rho_1 = (\Delta_1/\Delta_2)(\nu_1), \quad \rho_2 = (\Delta_2/\Delta_1)(\nu_2). \quad (15)$$

The normal coordinates define the directions and relative magnitudes of the atomic displacement vectors in the two modes; the alternative, energy description³ requires a knowledge of the relative contributions to the potential energy from each of the three terms in Eq. (1), in each mode. If we write $V_{11} = \frac{1}{2}(d_{11}\Delta_1^2/V)$, $V_{22} = \frac{1}{2}(d_{22}\Delta_2^2/V)$ and $V_{12} = (d_{12}\Delta_1\Delta_2/V)$, so that $V_{11} + V_{22} + V_{12} = 1$, then it can be shown that

$$\begin{aligned} V_{11}(\nu_{1,2}) &= \pm (d_{11}/\lambda_{1,2}) \\ &\quad \times [(A_{11}\lambda_{1,2} - Dd_{22})/(\lambda_1 - \lambda_2)] \\ V_{22}(\nu_{1,2}) &= \pm (d_{22}/\lambda_{1,2}) [(A_{12}\lambda_{1,2} + Dd_{12})/ \\ &\quad \{(\lambda_1 - \lambda_2)(A_{11}\lambda_{1,2} - Dd_{22})\}] \\ V_{12}(\nu_{1,2}) &= \pm (2d_{12}/\lambda_{1,2}) \\ &\quad \times [(A_{12}\lambda_{1,2} + Dd_{12})/(\lambda_1 - \lambda_2)] \end{aligned} \quad (16)$$

where the positive sign refers to ν_1 and the negative to ν_2 .

The plot of (Δ_1/Δ_2) against d_{12} for all possible solutions, for both ν_1 and ν_2 , is symmetrical about $d_{12} = -(A_{12}/2D)(\lambda_1 + \lambda_2)$. At $d_{12} = -(A_{12}/D)\lambda_{1,2}$ the curve has roots at 0 and at $\pm \infty$ (asymptotic), and $[\partial(\Delta_1/\Delta_2)/\partial d_{12}]$ is infinite at the four points corresponding to maximum and minimum values of d_{12} ; i.e., the curve is in two continuous halves. (See Fig. 4.) If ν_i^+ is the normal mode determined by the greater of the two roots for d_{11} corresponding to a given value of d_{12} , and ν_i^- that determined by the smaller, then if $\nu_1 > \nu_2$ those portions of the curve representing ν_1^+ lie at the two extremities of one half, the central region corresponding to ν_1^- ; reflection of the segments for ν_1^+ and ν_1^- at the plane of symmetry through $d_{12} = -(A_{12}/2D)(\lambda_1 + \lambda_2)$ gives the segments for ν_2^- and ν_2^+ , the curves intersecting at the above value of d_{12} . $[\partial(\Delta_1/\Delta_2)/\partial d_{12}]$ changes sign in passing from $\nu_{1,2}^+$ to $\nu_{1,2}^-$.

If the energy fractions V_{ij} are plotted against d_{12} , for all possible solutions, it is found that the contributions from the two square terms form one

³ See for example O. Burkard, Proc. Ind. Acad. 8, 365 (1938); J. Wagner, Zeits. f. physik. Chemie B45, 69 (1939).

closed curve for each normal mode, $V_{11}(\nu_{1,2}^+)$ coinciding with $V_{22}(\nu_{1,2}^-)$, and $V_{22}(\nu_{1,2}^+)$ with $V_{11}(\nu_{1,2}^-)$. (See Fig. 6.) $(\partial V_{ii}/\partial d_{12})$ is infinite at the two extreme values of d_{12} , where $V_{11}(\nu_i^\pm) = V_{22}(\nu_i^\pm)$; at the minimum of d_{12} , $V_{ii}(\nu_1) \geq V_{ii}(\nu_2)$, according as $d_{12}(\text{min.}) \geq 0$; if $d_{12}(\text{min.}) = 0$, then $V_{ii}(\nu_1) = V_{ii}(\nu_2) = \frac{1}{2}$. V and $(\partial V/\partial d_{12})$ become zero for $V_{ii}(\nu_j^\pm)$ at $d_{12} = -(A_{12}/D)\lambda_j$. The curves for $V_{12}(\nu_i^\pm)$ are both parabolas, with axes parallel to the V axis, vertices at $d_{12} = -(A_{12}/2D)\lambda_i$, $V_{12} = (-1)^i(A_{12}^2/2D) \times [\lambda_i/(\lambda_1 - \lambda_2)]$, ($i=1$, minimum; $i=2$, maximum), and latus rectum $(-1)^{i+1}(\lambda_i/2D)(\lambda_1 - \lambda_2)$. Both curves, produced if necessary, pass through the origin, and $V_{12}(\nu_i) = 0$ at $d_{12} = -(A_{12}/D)\lambda_i$. The points of intersection of the various curves are of interest; at $d_{12} = 0$ and $-(2A_{12}/D)[\lambda_1\lambda_2/(\lambda_1 + \lambda_2)]$, $V_{11}(\nu_1^\pm) = V_{22}(\nu_2^\pm)$, $V_{11}(\nu_2^\pm) = V_{22}(\nu_1^\pm)$, and $V_{12}(\nu_1^\pm) = V_{12}(\nu_2^\pm)$, while at $d_{12} = [-(2A_{12}/D)\lambda_1\lambda_2 \pm (\lambda_1\lambda_2/D)^{\frac{1}{2}}(\lambda_1 - \lambda_2)]/(\lambda_1 + \lambda_2)$, (corresponding to

$d_{11} = (2A_{22}/D)[\lambda_1\lambda_2/(\lambda_1 + \lambda_2)]$, $d_{22} = (2A_{11}/D) \times [\lambda_1\lambda_2/(\lambda_1 + \lambda_2)]$, $V_{ii}(\nu_1) = V_{ii}(\nu_2)$. The exact nature of these intersections depends on the sign of $d_{12}(\text{min.})$; at the upper value of d_{12} in the expression above, $V_{11}(\nu_1^+) = V_{11}(\nu_2^+)$, and, at the lower value, $V_{11}(\nu_1^+) = V_{11}(\nu_2^-)$, if $d_{12}(\text{min.}) < 0$, and $V_{22}(\nu_1^+) = V_{22}(\nu_2^+)$ if $d_{12}(\text{min.}) > 0$. Finally, $V_{ij}(\nu_i) = V_{jj}(\nu_i) = 0$ at $d_{12} = -(A_{12}/D)\lambda_i$.

It follows from the above discussion that the two alternative sets of constants allowed at each possible value of d_{12} correspond to alternative assignments of the fundamental vibration frequencies to the two normal modes; at the extreme values of d_{12} the two solutions coincide. General solutions for singular and related points are given in Table I. The Roman numerals in the first column refer to solutions discussed in the text; where alternatives exist, the numeral refers to $\nu_{1,2}^+$. The additional symbols used in Table I are defined as follows:

$$\lambda_1' = \lambda_1/A_{11} \quad \lambda_1'' = \lambda_1/A_{22} \quad \mu_1 = \lambda_2/\lambda_1 \quad \epsilon_1 = (1 + \mu_1) \\ \lambda_2' = \lambda_2/A_{11} \quad \lambda_2'' = \lambda_2/A_{22} \quad \mu_2 = \lambda_1/\lambda_2 \quad \epsilon_2 = (1 + \mu_2)$$

$$L_1 = (\lambda_1 + \lambda_2) \quad L_1' = \frac{1}{2}(\lambda_1' + \lambda_2') \quad L_1'' = \frac{1}{2}(\lambda_1'' + \lambda_2'') \\ L_2 = (\lambda_1 - \lambda_2)/L_1 \quad L_2' = \frac{1}{2}(\lambda_1' - \lambda_2') \quad L_2'' = \frac{1}{2}(\lambda_1'' - \lambda_2'') \\ L_3 = \lambda_1\lambda_2/L_1$$

$$\left. \begin{aligned} A_{12}' &= A_{12}/D & A_{12}'' &= \frac{1}{2}L_1A_{12}' & A' &= (A_{11}A_{22}/D)^{\frac{1}{2}} \\ A_{11}' &= A_{11}/D & A_{11}'' &= \frac{1}{2}L_1A_{11}' & A &= (A'')^2 \\ A_{22}' &= A_{22}/D & A_{22}'' &= \frac{1}{2}L_1A_{22}' & D' &= (\lambda_1 - \lambda_2)/2D^{\frac{1}{2}} \\ & & & & D'' &= A''D' \end{aligned} \right\} \text{where } A'' = A_{12}/D^{\frac{1}{2}}.$$

$$a_1 = (A_{22}/A_{11})^{\frac{1}{2}} \quad E = [(A')^2 - (A''/L_3)^2]^{\frac{1}{2}} \quad E' = EL_2' \quad E'' = EL_2'' \\ a_2 = A_{12}/A_{11} \quad F = [(A')^2 - (A''/L_2)^2]^{\frac{1}{2}} \quad F' = FL_1' \quad F'' = FL_1'' \\ a' = a_2/a_1^2$$

$$B_1 = (A' + 1)^2 \quad C_1 = (A'' + 1)^2 \quad P_1 = [1 + (1/A')]^{-1} \quad Q_1 = [1 + (1/A'')]^{-1} \\ B_2 = (A' - 1)^2 \quad C_2 = (A'' - 1)^2 \quad P_2 = [1 - (1/A')]^{-1} \quad Q_2 = [1 - (1/A'')]^{-1} \\ C = (C_1C_2)^{\frac{1}{2}}$$

$$K_1 = [(A' - A'')/(A' + A'')] \\ K_2 = (1/K_1)$$

Where there are alternative values for the force constants, but only one for any of the quantities in

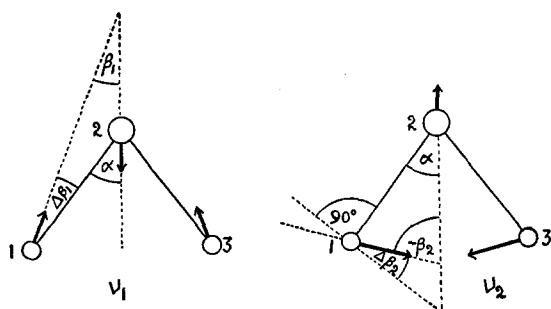


FIG. 2. Directions of displacement vectors in the class A_1 vibrations of the symmetrical triatomic molecule.

the last four columns, the latter is associated with the upper of the alternative signs in the expressions for the constants; the alternative values are obtained by interchanging the subscripts 1 and 2 in the quantities B , C , K , P , and Q .

IV. PARTICULAR SOLUTIONS

It is required to find one or more particular sets of constants, giving satisfactory normal coordinates and potential energy distributions, which can be used whenever there is no evidence as to the nature of the magnitude of the interaction constant d_{12} . If we define ν_i as the mode whose normal coordinate is in practice determined by Δ_i (cf., the terms "C-H stretching," "CCl₂ bending," etc., used in the de-

TABLE II. Directions of displacement vectors in certain singular solutions for the symmetrical triatomic molecule.

	Minimum d_{22} (VII)	Minimum d_{11}	Maximum d_{11} (VIII)	Maximum d_{22}
$\tan\beta_1$	$\tan\alpha$	$-\cot\alpha$	$M \tan\alpha$	$-M \cot\alpha$
$\tan\beta_2$	$-M \cot\alpha$	$M \tan\alpha$	$-\cot\alpha$	$\tan\alpha$
	$(M = [1 + 2(m_1/m_2)])$			

scription of normal modes), and if the subscripts are ordered so that $\nu_1 > \nu_2$, then those solutions corresponding to ν_i^- , as defined in Section III, can be immediately discarded, i.e., only half the total range of solutions need be considered. As a starting point we take the case $d_{12} = 0$ (solution I in Table I), which corresponds to an idealized force field containing only square terms. This is not a general solution, as real values of the other constants cannot be obtained unless the condition (12) holds. But it may be possible to find some characteristic property of the normal modes associated with this solution which can be applied to determine a more general one, applicable to every case yet comparable with the ideal. Such a property has been found in the relation between the energy contributions from the two square terms in Eq. (1); they are mutually reciprocal in the two modes. If we impose this property as a necessary condition, we find that there is a solution II, corresponding to $d_{12} = -(2A_{12}/D)[\lambda_1\lambda_2/(\lambda_1 + \lambda_2)]$ (see Section III). It is to be noted that here the fraction of the potential energy in the cross term in Eq. (1) is the same in both modes, i.e., the solution II is characterized by the relations $V_{11}(\nu_1) = V_{22}(\nu_2)$, $V_{22}(\nu_1) = V_{11}(\nu_2)$, $V_{12}(\nu_1) = V_{12}(\nu_2)$, holding simultaneously.

Where solution I is found to give complex values for the constants d_{11} and d_{22} , perhaps an obvious first alternative is solution III, with d_{12} a minimum. But this cannot be generally applicable, since here $V_{11}(\nu_i) = V_{22}(\nu_i)$. Where the frequency-difference

$(\nu_1 - \nu_2)$ is small, so that on general grounds it would be regarded as difficult to assign either frequency to a definite mode of vibration, the above energy relationship is clearly the ideal one with which to define the force constants. Where $(\nu_1 - \nu_2)$ is small but there is sufficient evidence for a definite assignment to be made, one of the three solutions IV to VI, corresponding to mean values of the constants, may be used; in these solutions the ratios $(V_{ii}/V_{jj})(\nu_i)$ will be somewhat greater than unity, in agreement with the favored assignment.* In the general case, none of these solutions is as satisfactory as II. Solutions VII and VIII, in which d_{22} and d_{11} take minimum and maximum values, respectively, are of some interest, since they correspond to the secular determinant in Eq. (3) splitting into two linear factors. (See Section II.) In VII, the (unnormalized) normal coordinate η_1' is identical with Δ_1 , and $V_{12}(\nu_1) = -2V_{22}(\nu_1)$, while in VIII η_2' is identical with Δ_2 , and $V_{12}(\nu_2) = -2V_{11}(\nu_2)$. VIII cannot be generally applicable, since it leads to an unsatisfactory distribution of the potential energy in ν_2 when (λ_1/λ_2) is large; the fraction $V_{12}(\nu_2)$ would be expected to decrease with (λ_2/λ_1) , as $V_{12}(\nu_1)$ does in VII, while here the reverse is true. (See Table I.) As an actual example, the results for the symmetrical vibrations of the chlorine monoxide molecule are given below,

$$d_{12} = 1.809, \quad d_{11} = 3.519, \\ d_{22} = 1.213, \quad \times 10^5 \text{ dynes/cm},$$

$$V_{11}(\nu_2) = 3.293, \quad V_{22}(\nu_2) = 4.293, \quad V_{12}(\nu_2) = -6.585.$$

The fractional contributions to the potential energy are most unlikely, and the interaction constant d_{12} seems improbably large (cf., Tables VII and VIII). It will be shown that solution VII gives quite satisfactory results. The general relationship between the three solutions I, II, and VII is indicated below; the superscripts, here and subsequently, refer to

TABLE III. Solutions for the symmetrical triatomic molecule in which the displacement vectors of the terminal atoms have only x or y components.

	d_{12}	d_{11}	d_{22}	i	β_i	ρ_i	$V_{11}(\nu_i)$	$V_{22}(\nu_i)$	$V_{12}(\nu_i)$
$\beta_1^- = 0$	$(\sigma_2'' - \sigma_1')cs$	$c^2\sigma_1' + s^2\sigma_2''$	$c^2\sigma_2'' + s^2\sigma_1'$	1	0	$-(1/t)$	$(c^2 + s^2\sigma_1)c^2$	$(s^2 + c^2\sigma_1)s^2$	$2(1 - \sigma_1)c^2s^2$
				2	$(\pi/2)$	$(1/t)$	$[s^2 + (c^2/\sigma_1)]s^2$	$[c^2 + (s^2/\sigma_1)]c^2$	$2[1 - (1/\sigma_1)]c^2s^2$
$\beta_2^+ = 0$	$(\sigma_1'' - \sigma_2')cs$	$c^2\sigma_2' + s^2\sigma_1''$	$c^2\sigma_1'' + s^2\sigma_2'$	1	$(\pi/2)$	t	$(s^2 + c^2\sigma_2)s^2$	$(c^2 + s^2\sigma_2)c^2$	$2(1 - \sigma_2)c^2s^2$
				2	0	$-t$	$[c^2 + (s^2/\sigma_2)]c^2$	$[s^2 + (c^2/\sigma_2)]s^2$	$2[1 - (1/\sigma_2)]c^2s^2$
$(\sigma_{1,2}' = \lambda_{1,2}/[2\{2 + (m_2/m_1)\}], \quad \sigma_{1,2}'' = \lambda_{1,2}/2(m_2/m_1), \quad \sigma_1 = (\sigma_2''/\sigma_1'), \quad \sigma_2 = (\sigma_2'/\sigma_1''), \quad c = \cos\alpha, \quad s = \sin\alpha, \quad t = \tan\alpha.)$									

* The situation in mind would resemble that in the vinyl halides (H. W. Thompson and P. Torkington, Proc. Roy. Soc. A 184, 1, 21 (1945); Trans. Faraday Soc. 41, 236 (1945); J. Chem. Soc., 303 (1944)) where there is a pair of Class A'' fundamentals with frequencies ~ 900 and 940 cm^{-1} ; evidence from related molecules suggests that they are essentially CH_2 and CH bending modes, respectively. But here there is a third Class A'' (twisting) mode. There seems to be no example of a similar situation arising where the secular equation is only of the second degree; an ideal case would be the pair of parallel vibrations of the linear molecule BAB^* , where B and B^* are isotopes, but there are no certain data available.

TABLE IV. Fundamental vibration frequencies and angles of symmetrical triatomic molecules.

	H ₂ O	D ₂ O	ClO ₂	SO ₂	O ₃	NO ₂	F ₂ O	Cl ₂ O	
ν_1	^a 3652	^b 2666	^c 954	^e 1151.2	^f 1043.4	ⁱ 1320	^h 830	^l 680	cm ⁻¹
ν_2	1595	1179	529	519	710	648	490	330	
ν_3	3756	2789	1105	1358	1740	1621	1110	973	
α	[*] 52° 30'	[*] 52° 30'	^d 68° 30'	^f 60° 30'	^h 63° 30'	ⁱ 65° 0'	^d 52° 0'	^d 55° 30'	

^{*} G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. van Nostrand Company, Inc., New York 1945), gives $2\alpha = 105^\circ 3'$, for the lowest vibrational level.

^a Earle K. Plyler, *Phys. Rev.* **39**, 77 (1932); Rank, Larsen, and Bordner, *J. Chem. Phys.* **2**, 464 (1934); Harold H. Nielsen, *Phys. Rev.* **62**, 422 (1942).

^b E. F. Barker and W. W. Sleator, *J. Chem. Phys.* **3**, 660 (1935); B. T. Darling and D. M. Dennison, *Phys. Rev.* **57**, 128 (1940).

^c C. R. Bailey and A. B. D. Cassie, *Proc. Roy. Soc. A* **137**, 622 (1932); **140**, 605 (1933); **142**, 129 (1933); Z. W. Ku, *Phys. Rev.* **44**, 376 (1933); T. Y. Wu, *Vibrational Spectra and Structure of Polyatomic Molecules* (Edwards Brothers, Inc., Ann Arbor, 1946).

^d L. O. Brockway, *Rev. Mod. Phys.* **8**, 231 (1936).

^e Ernest F. Barker, *Rev. Mod. Phys.* **14**, 198 (1942); H. Gerding and W. J. Nijveld, *Nature*, **137**, 1070 (1936); Bailey, Cassie, and Angus, *Proc. Roy. Soc.* **130**, 142 (1930).

^f V. Schomaker and D. P. Stevenson, *J. Am. Chem. Soc.* **62**, 1267 (1940).

^g Hettner, Pohlman, and Schumacher, *Zeits. f. Physik* **91**, 372 (1934); S. L. Gerhard, *Phys. Rev.* **42**, 622 (1932).

^h W. Shand and R. A. Spurr, *J. Am. Chem. Soc.* **65**, 179 (1943).

ⁱ C. R. Bailey and A. B. D. Cassie, *Proc. Roy. Soc. A* **131**, 239, 910 (1933); Roland Schaffert, *J. Chem. Phys.* **1**, 507 (1933); G. B. B. M. Sutherland and W. G. Penney, *Proc. Roy. Soc. A* **156**, 678 (1936).

^j L. R. Maxwell and U. M. Mosley, *J. Chem. Phys.* **8**, 738 (1940).

^k Hettner, Pohlman, and Schumacher, *Zeits. f. Physik* **96**, 203 (1935); G. B. B. M. Sutherland and W. G. Penney, *Proc. Roy. Soc. A* **156**, 678 (1936).

^l C. R. Bailey and A. B. D. Cassie, *Proc. Roy. Soc. A* **142**, 129 (1933); G. B. B. M. Sutherland and W. G. Penney, *Proc. Roy. Soc. A* **156**, 678 (1936); R. Pohlman and H. J. Schumacher, *Zeits. f. Physik* **102**, 678 (1936).

particular solutions.

$$|d_{12}^{II}| > |d_{12}^{VII}| > |d_{12}^I| (=0);$$

(sign opposite to that of A_{12}).

$$d_{11}^{II} > d_{11}^{VII} > d_{11}^I; \quad d_{22}^I > d_{22}^{II} > d_{22}^{VII}.$$

$$|\rho_1^{II}| > |\rho_1^{VII}| > |\rho_1^I|;$$

(sign the same as that of A_{12}).

$$|\rho_2^{VII}| > |\rho_2^{II}| > |\rho_2^I|; \quad (\rho_2^{VII} = \infty,$$

ρ_2^{II} same sign as A_{12} , ρ_2^I of opposite sign).

For ν_i ,

$$V_{ii}^{II} > V_{ii}^{VII} > V_{ii}^I; \quad V_{ij} \leq 0.$$

It is noteworthy that in all the solutions for which explicit expressions are given for $\rho_{1,2}$ in Table I, these are independent of λ_1 and λ_2 , i.e., the vibrational forms are determined solely by the geometry of the system under consideration, and the atomic masses. This is not so for solutions I and II; in these cases the parameters ρ_1 and ρ_2 take the following values

$$\rho_{1,2}^I = \left\{ \frac{1}{2}(\epsilon_{1,2}/a_2) [1 \pm \{(A/L_2) + E\}/(A')^2] \right\}^{\pm 1}, \quad (17)$$

$$\rho_{1,2}^{II} = \left\{ \frac{1}{2}(\epsilon_{1,2}/a_2) [1 \pm (AL_2 + F)/(A')^2] \right\}^{\pm 1}, \quad (18)$$

where the notation of Table I is used, with the addition $\epsilon_{1,2}' = (1 - \mu_{1,2})$, and in each case the positive signs refer to ν_1 and the negative to ν_2 . It seems unlikely that the form of vibration would be quite independent of the vibration frequencies, so solution II must be regarded as more satisfactory than VII in this respect. It should also be observed that in VII the constants d_{12} and d_{22} are independent of ν_1 , while in I and II both frequencies enter into the expressions for all three constants. VII can therefore be regarded as an approximation to II, which only holds rigidly when the frequency-difference ($\nu_1 - \nu_2$)

is large; since it corresponds to factorization of the secular equation, it enables a complete solution to be obtained very rapidly. Solutions with maximum d_{22} and minimum d_{11} , which also lead to factorization, correspond to a reversed assignment of the vibration frequencies.

Recapitulating, we have shown that there is a solution, II, of the second-degree secular equation in which the fractional contributions to the potential energy from the two square terms are mutually reciprocal in the two modes of vibration, as in the solution for the case of no cross term, I; and a solution, VII, in which the (unnormalized) normal coordinate for the higher frequency is identical with the corresponding valence-type coordinate in the potential energy expression. Both are in principle universally applicable. For the special case of small frequency-difference ($\nu_1 - \nu_2$), it is suggested that the solution III, corresponding to minimum d_{12} and to equal potential energy fractions V_{11} and V_{22} , would be most satisfactory where the two observed fundamental frequencies cannot be definitely assigned, and solutions IV, V, or VI, corresponding to mean values of the constants, where there is evidence for an assignment one way or the other.

V. THE SYMMETRICAL TRIATOMIC MOLECULE

We shall apply the above general results to the class A_1 (symmetrical) vibrations of the non-linear triatomic system AB_2 . The coordinates and various coefficients defined in Eqs. (2) and (4) take the following values. (See Fig. 1.)

$$\left. \begin{aligned} z_1 &= x_3 - x_1 \\ z_2 &= 2y_2 - y_1 - y_3 \end{aligned} \right\} \quad (19)$$

$$\left. \begin{aligned} m_{z1} &= (m_1/2) \\ m_{z2} &= [m_1 m_2 / 2(m_2 + 2m_1)] \end{aligned} \right\}. \quad (20)$$

$$\left. \begin{aligned} a_{11} &= -a_{22} = \sin \alpha \\ a_{12} &= a_{21} = \cos \alpha \end{aligned} \right\} \quad (21)$$

$$\left. \begin{aligned} A_{11} &= 2[(m_2/m_1) + 2 \cos^2 \alpha] \\ A_{22} &= 2[(m_2/m_1) + 2 \sin^2 \alpha] \\ A_{12} &= -2 \sin 2\alpha \\ M &= m_2 \end{aligned} \right\} \quad (22)$$

$\Delta_1 = (\Delta r_{12} + \Delta r_{23})$ is the coordinate for stretching of

the $A-B$ bonds, and $\Delta_2 = r\Delta\theta$ the coordinate for deformation of the angle \widehat{BAB} . A convenient parameter for the description of the geometrical form of the normal modes in a triatomic molecule is the ratio of the Cartesian displacements of the terminal atoms. This quantity can be expressed as follows:

$$\left. \begin{aligned} (x_1/y_1)^{v_{1,2}} &= [1 + 2(m_1/m_2)](z_1/z_2)^{v_{1,2}} = \frac{\{2[2 + (m_2/m_1)](d_{22} \sin \alpha - d_{12} \cos \alpha) - \lambda_{1,2} \sin \alpha\}}{\{2(m_2/m_1)(d_{12} \sin \alpha + d_{22} \cos \alpha) - \lambda_{1,2} \cos \alpha\}} \\ &= \frac{\{2[2 + (m_2/m_1)](d_{12} \sin \alpha - d_{11} \cos \alpha) + \lambda_{1,2} \cos \alpha\}}{\{2(m_2/m_1)(d_{11} \sin \alpha + d_{12} \cos \alpha) - \lambda_{1,2} \sin \alpha\}} \end{aligned} \right\} \quad (23)$$

where the constants are any set satisfying Eqs. (6) and (8). We shall define angles

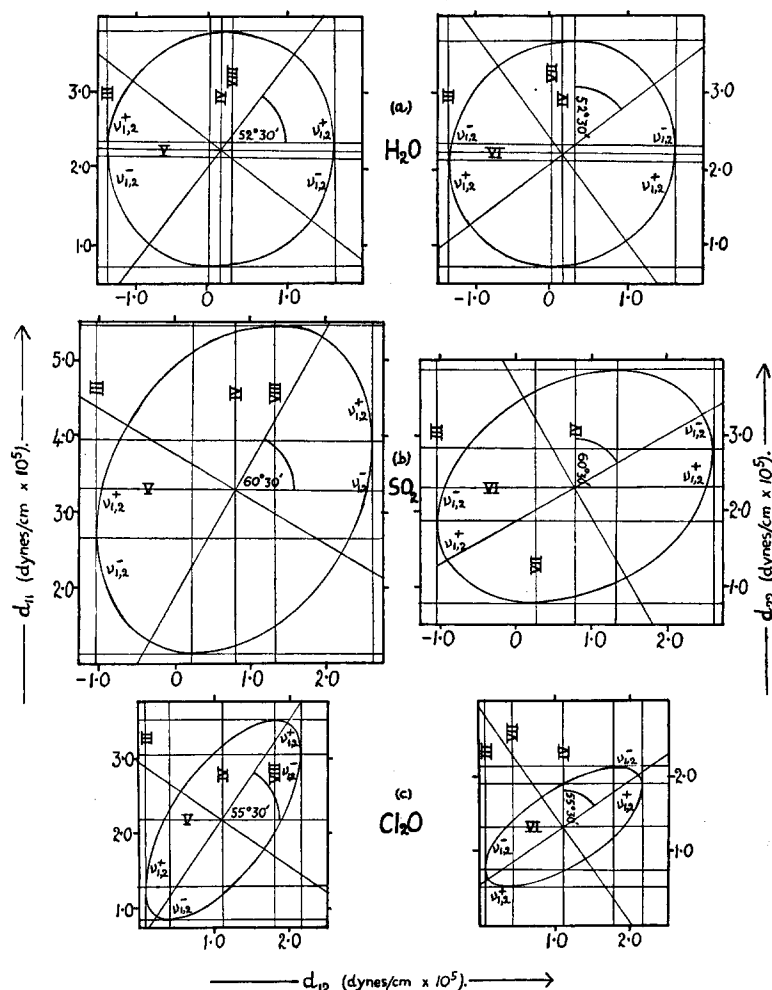
$$\beta_{1,2} = \tan^{-1}(x_1/y_1)^{v_{1,2}}, \quad (24)$$

and two derived angles,

$$\left. \begin{aligned} \Delta\beta_1 &= (\alpha - \beta_1) \\ \Delta\beta_2 &= [\alpha - \{(\pi/2) + \beta_2\}] \end{aligned} \right\} \quad (25)$$

$\Delta\beta_1$ is the angle made by the displacement vector of atom 1 with the valence bond $A-B$, and $\Delta\beta_2$ that between the displacement vector of atom 1 and the normal to the valence bond, the signs of the two angles being such that the vectors in the two modes are mutually perpendicular when $\Delta\beta_1 = \Delta\beta_2$. Clearly, $\Delta\beta_{1,2} = 0$ correspond to idealized stretching and bending modes respectively (see Fig. 2). $\rho_{1,2}$ and

FIG. 3. Allowed solutions for the force constants for the class A_1 vibrations of typical symmetrical triatomic molecules.



$\tan\beta_{1,2}$ are mutually related as follows:

$$\rho_{1,2} = \left\{ \frac{\tan\alpha \tan\beta_{1,2} + [1 + 2(m_1/m_2)]}{\tan\beta_{1,2} - [1 + 2(m_1/m_2)] \tan\alpha} \right\}^{\pm 1}, \quad (26)$$

$$\tan\beta_{1,2} = [1 + 2(m_1/m_2)] \frac{\{(\rho_{1,2})^{\pm 1} \tan\alpha + 1\}}{\{(\rho_{1,2})^{\pm 1} - \tan\alpha\}}, \quad (27)$$

where in each case the positive sign refers to ν_1 , the negative to ν_2 . It is found that in the four solutions corresponding to maximum and minimum values of the constants d_{11} and d_{22} , the angles $\beta_{1,2}$ are simply related to the angle α , as shown in Table II. It will be observed that the simple normal coordinates for ν_1 and ν_2 in solutions VII and VIII, respectively, are associated with idealized displacement vectors. ($\Delta\beta_1^{\text{VII}}=0$, $\Delta\beta_2^{\text{VIII}}=0$.) In solution VII, $\tan\Delta\beta_2 = \{\tan\alpha/[1 + (m_2/2m_1)\sec^2\alpha]\}$; in the limits $(m_1/m_2)=0$ and ∞ $\Delta\beta_2$ takes values 0 and α , respectively. It can be shown that $\Delta\beta_1^{\text{I}} > 0 > \Delta\beta_1^{\text{II}}$, and that $\Delta\beta_2^{\text{I}} > \Delta\beta_2^{\text{VII}} > \Delta\beta_2^{\text{II}} > 0$. It follows from Eqs. (26) and (27) that the plot of $\beta_{1,2}$ against d_{12} , for all possible solutions, is symmetrical about

$d_{12} = -(A_{12}/2D)(\lambda_1 + \lambda_2)$; reflection of the segments for ν_1^+ and ν_1^- (which lie on one continuous curve), give those for ν_2^- and ν_2^+ , respectively. For $\nu_{1,2}^+$, $(\partial\beta/\partial d_{12}) > 0$, and for $\nu_{1,2}^-$, $(\partial\beta/\partial d_{12}) < 0$, while at the extreme values of d_{12} , $(\partial\beta/\partial d_{12}) = \infty$. Where the curves cross the d_{12} axis, the displacement vectors of the terminal atoms in ν_1 and ν_2 are mutually perpendicular; the data for these solutions are summarized in Table III.

It is found that the angle θ giving the gradient of the major axis of the ellipse (6) is $[(\pi/2) - \alpha]$, and that the semi-axes (7) are as follows:

$$\left. \begin{aligned} a^2 &= (A_{22}/8D)(m_1/m_2)(\lambda_1 - \lambda_2)^2 \\ b^2 &= (A_{22}/8D)[m_1/(2m_1 + m_2)](\lambda_1 - \lambda_2)^2 \end{aligned} \right\}. \quad (28)$$

Hence, the ratio of the semi-axes for both ellipses (6) and (8) is $(a/b) = [(m_2 + 2m_1)/m_2]^{\frac{1}{2}}$, and the eccentricity is $e = [(m_2 + 2m_1)/2m_1]^{-\frac{1}{2}}$. At the limits $(m_1/m_2)=0$ and ∞ , each ellipse degenerates into a circle and a straight line, respectively.

To obtain numerical results, a series of eight symmetrical triatomic molecules representing a convenient range of (m_1/m_2) has been taken. The

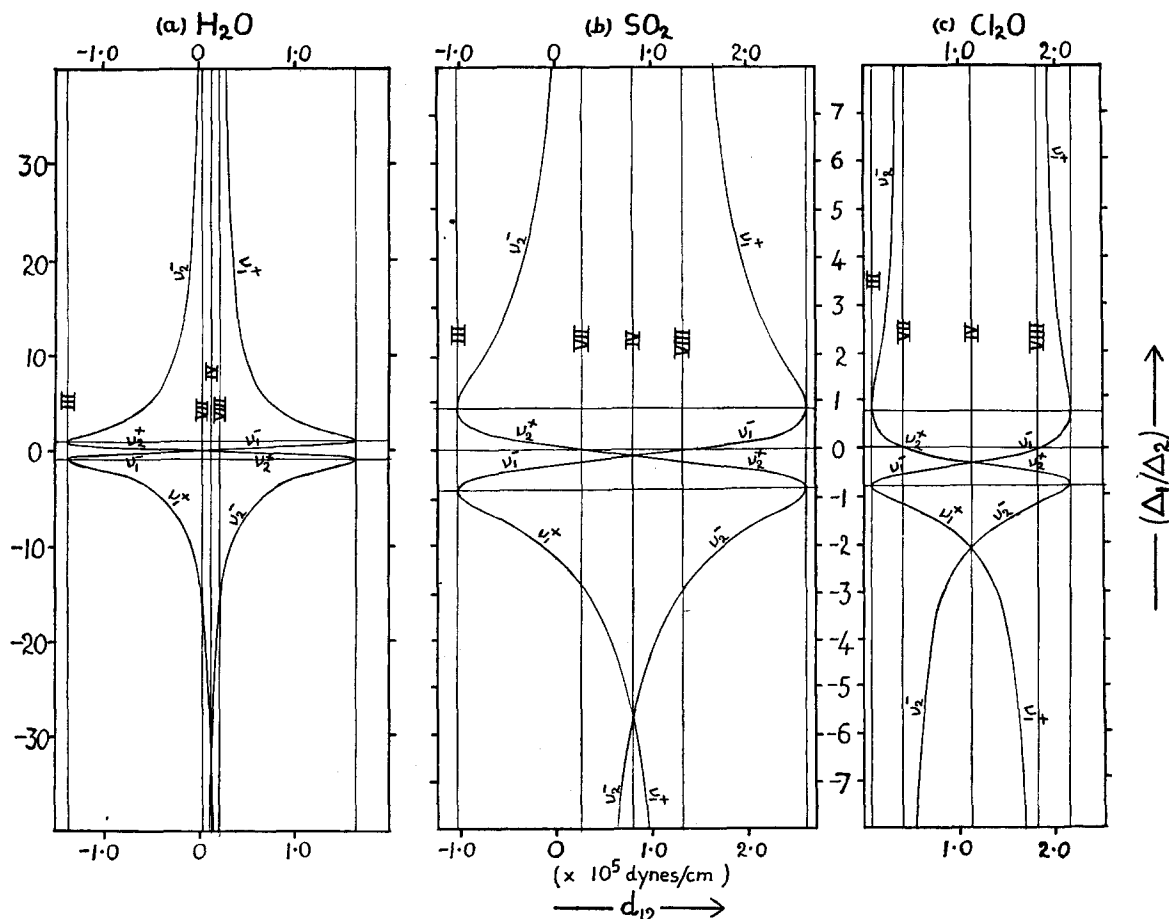


FIG. 4. The composition of the normal coordinates for the class A_1 vibrations of typical symmetrical triatomic molecules, for all allowed solutions of the force constants.

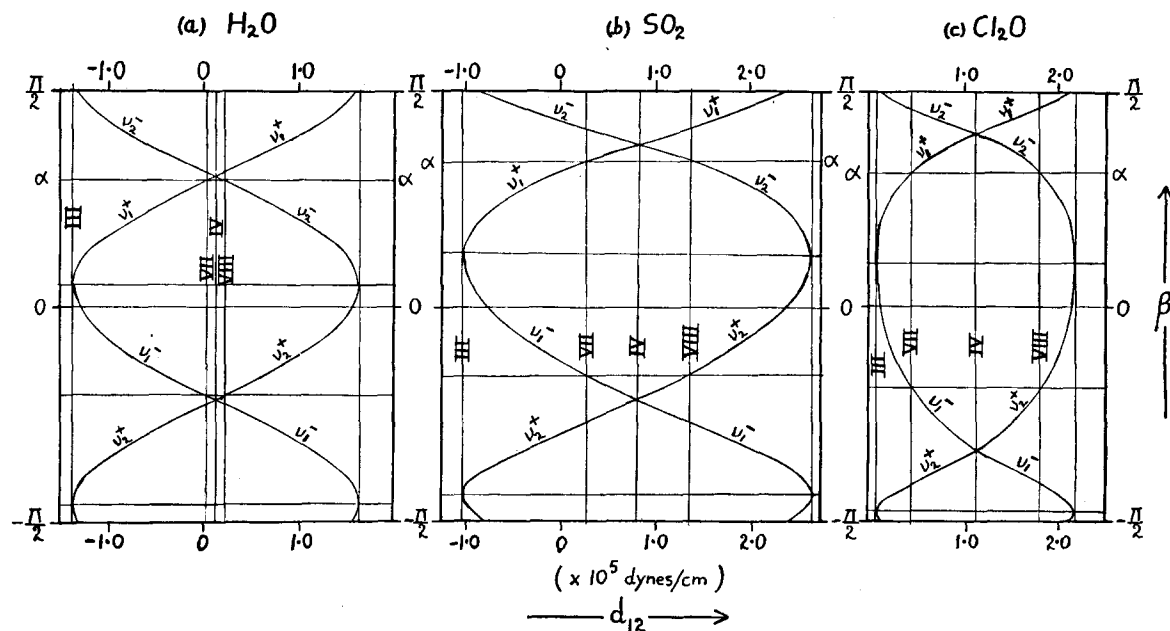


FIG. 5. The direction of the displacement vectors of the terminal atoms in the class A_1 vibrations of typical symmetrical triatomic molecules, for all allowed solutions of the force constants.

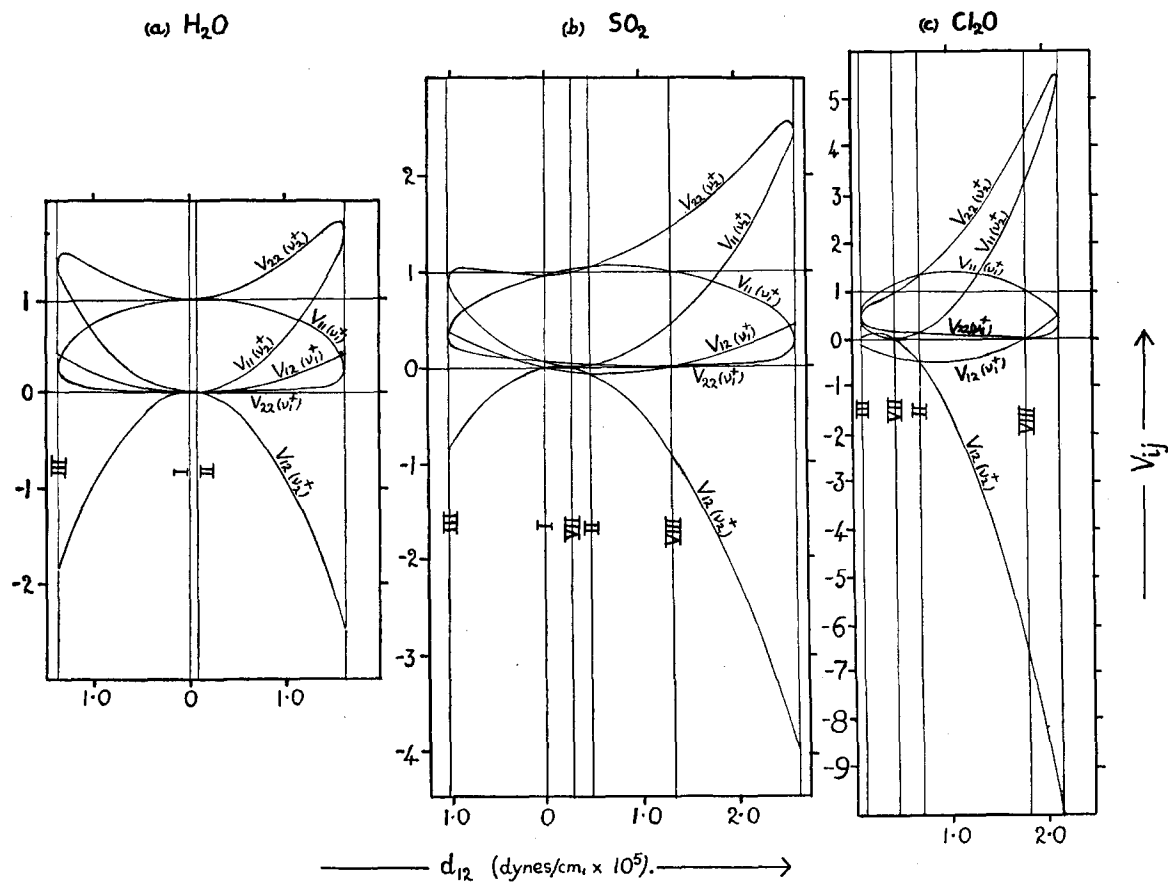


FIG. 6. The distribution of the potential energy in the class A_1 vibrations of typical symmetrical triatomic molecules, for all allowed solutions of the force constants.

TABLE V. Solution I. ($d_{12}=0$.)

	H ₂ O		D ₂ O		ClO ₂		SC ₂		NO ₂	
d_{11}	3.779		3.845		3.729		4.903		5.345	
d_{22}	0.7025		0.7223		0.7916		0.8078		0.9249	
$\angle i$	1	2	1	2	1	2	1	2	1	2
$\Delta\beta_i$	0° 46'	4° 7'	1° 29'	7° 53'	4° 55'	22° 4'	4° 6'	23° 33'	8° 18'	40° 8'
ρ_i	-13.92	74.86	-7.226	38.47	-2.466	11.62	-2.294	13.92	-1.186	6.855
N_i	0.1724	0.04911	0.2808	0.08092	0.4920	0.1688	0.5076	0.1383	0.9649	0.2812
$V_{11}(\nu_i)$	99.904	0.096	99.642	0.358	96.628	3.372	96.965	3.035	89.049	10.951
$V_{22}(\nu_i)$	0.096	99.904	0.358	99.642	3.372	96.628	3.035	96.965	10.951	89.049

fundamental vibration frequencies and angles are given in Table IV. No attempt has been made to correct for anharmonicity; it seemed more consistent to take the observed fundamentals in every case, since the correction to be applied is in general unknown. The constants for H₂O and D₂O will therefore not be comparable with those given by Dennison,⁴ who includes cubic and quartic terms. In the case of the chlorine oxides, the calculations were carried out for Cl³⁵O₂ and Cl³⁵O, using the observed frequencies. This seemed the best procedure, since we are interested here in the normal coordinates for a given model, and the frequencies cannot be accurately corrected without knowing the force field; the error in any case is small, and does not detract from the use of these molecules as illustrations of the general theory.

The ellipses (6) and (8) are given in Fig. 3 for the three molecules H₂O, SO₂, and Cl₂O; the increase of the eccentricity as (m_1/m_2) increases is an obvious feature. Plots of (Δ_1/Δ_2), β and V_{ij} for the same three molecules are shown in Figs. 4, 5, and 6. It is seen that the general form of each curve is the same in all three cases, as would be expected from the analysis in Section III. The changes encountered in the (Δ_1/Δ_2) and V_{ij} plots in passing from H₂O to Cl₂O can be correlated with the general tendency for the cross term in the potential energy expression to become of increasing importance as (m_1/m_2) increases from a small value. It may be observed that in the

limit (m_1/m_2)=0 the V_{ij} curves are all symmetrical about $d_{12}=0$. Points for some of the general solutions discussed previously are indicated on the figures. These particular solutions are dealt with as follows:

- I.. (for the five molecules which satisfy Eq. (12),) in Table V;
- III. (for the three molecules which do not satisfy Eq. (12),) in Table VI;
- II. (all cases), in Table VII;
- VII. (all cases), in Table VIII.

In the tables, force constants are given in units of 10^{-5} dyne/cm, to four significant figures, the angles $\Delta\beta_i$ to the nearest minute, and the relative energy components V_{ij} as percentages of the total potential energy, to three decimal places. The quantity N_i is a normalizing factor for the amplitudes in the first vibrational level: $N_i\rho_i=\Delta_i\nu_i$ (i.e., $N_i=\Delta_i\nu_i$), in tenths of an Angstrom; except for the case ρ_2^{VII} , ($=\infty$), when the actual magnitude of $\Delta_2\nu_2$ is given, in the same units. For completeness, the constant d_{33} for the class B_1 (asymmetrical stretching), mode, and the corresponding normal coordinate, normalized as above, is given in Table IX; and the solution, IX, of the symmetrical vibrations, in which $d_{11}=d_{33}$, in Table X, for all cases which allow of a real solution. In solution IX, the interaction constant d_{13} associated with the interaction term $\Delta r_{12}\Delta r_{23}$ in the general valence force potential energy function for the triatomic molecule takes the value nought; IX can therefore be regarded as an analog of I (for which $d_{12}=0$), for the special case of the triatomic molecule. The symmetry coordinate for the class B_1 vibration, corresponding to Δ_1 , is $\Delta_3=\Delta r_{12}-\Delta r_{23}$ (see Eqs. (2) and (21)), and the force constant d_{33} is given by the linear equation

$$A_{33}d_{33}-\lambda_3=0, \quad (29)$$

where A_{33} is identical with A_{22} in Eq. (22). The normal coordinate is identical with Δ_3 except for a normalizing factor. It may be observed that solution VII for ν_1 is the geometrical analog of ν_3 .

TABLE VI. Solution III. (d_{12} a minimum.)

	O ₃		F ₂ O		Cl ₂ O	
d_{12}	0.1223		0.08065		0.07123	
d_{11}	2.754		1.417		1.285	
d_{22}	1.480		1.088		0.7778	
$\angle i$	1	2	1	2	1	2
$\Delta\beta_i$	36° 15'	53° 45'	41° 14'	48° 46'	37° 53'	52° 7'
ρ_i	-0.7331	1.364	-0.8762	1.141	-0.7780	1.285
N_i	1.496	0.8507	1.559	0.9836	1.674	0.8450
$V_{11,22}(\nu_i)$	53.253	47.121	53.474	46.950	53.836	46.675
$V_{12}(\nu_i)$	-6.507	5.758	-6.949	6.101	-7.671	6.651

⁴ David M. Dennison, Rev. Mod. Phys. 12, 175 (1940).

TABLE VII. Solution II. ($V_{11}(\nu_1) = V_{22}(\nu_2)$, $V_{11}(\nu_2) = V_{22}(\nu_1)$, $V_{12}(\nu_1) = V_{12}(\nu_2)$.)

	H ₂ O		D ₂ O		ClO ₂		SO ₂	
d_{12}	0.06856		0.1340		0.3285		0.4521	
d_{11}	3.788		3.876		3.934		5.232	
d_{22}	0.7022		0.7211		0.7779		0.7961	
$\backslash i$	1	2	1	2	1	2	1	2
$\Delta\beta_i$	-0° 31'	2° 48'	-1° 0'	5° 19'	-2° 25'	12° 2'	-2° 30'	16° 3'
ρ_i	-20.48	-110.4	-10.74	-57.75	-4.694	-23.73	-3.478	-22.85
N_i	0.1171	0.03333	0.1889	0.05417	0.2596	0.08595	0.3355	0.08787
$V_{11}(\nu_i)$	100.133	0.044	100.485	0.162	102.734	0.922	103.855	1.307
$V_{22}(\nu_i)$	0.044	100.133	0.162	100.485	0.922	102.734	1.307	103.855
$V_{12}(\nu_i)$	-0.177		-0.647		-3.656		-5.162	
	O ₃		NO ₂		F ₂ O		Cl ₂ O	
d_{12}	0.8643		0.8494		0.6803		0.6898	
d_{11}	4.249		6.514		2.534		2.732	
d_{22}	1.131		0.8698		0.7881		0.5382	
$\backslash i$	1	2	1	2	1	2	1	2
$\Delta\beta_i$	-6° 3'	21° 42'	-3° 51'	26° 47'	-8° 9'	24° 42'	-7° 53'	35° 7'
ρ_i	-2.512	-9.434	-1.981	-14.83	-2.174	-6.990	-1.422	-7.217
N_i	0.5131	0.2184	0.5840	0.1495	0.7101	0.3043	0.9941	0.3074
$V_{11}(\nu_i)$	113.604	4.793	110.819	3.772	122.128	8.038	134.725	13.130
$V_{22}(\nu_i)$	4.793	113.604	3.772	110.819	8.038	122.128	13.130	134.725
$V_{12}(\nu_i)$	-18.397		-14.591		-30.166		-47.854	

TABLE VIII. Solution VII. ($\rho_2 = \infty$.)

	H ₂ O		D ₂ O		ClO ₂		SO ₂	
d_{12}	0.04082		0.08012		0.2148		0.2720	
d_{11}	3.785		3.865		3.878		5.118	
d_{22}	0.7020		0.7202		0.7731		0.7882	
$\backslash i$	1	2	1	2	1	2	1	2
$\Delta\beta_i$	0	3° 20'	0	6° 21'	0	15° 32'	0	19° 2'
ρ_i	-17.20	∞	-8.989	∞	-3.600	∞	-2.898	∞
N_i	0.1395	(3.679)	0.2258	(3.123)	0.3389	(2.019)	0.4032	(1.981)
$V_{11}(\nu_i)$	100.063	0	100.231	0	101.563	0	101.868	0
$V_{22}(\nu_i)$	0.063	100	0.231	100	1.563	100	1.868	100
$V_{12}(\nu_i)$	-0.125	0	-0.462	0	-3.125	0	-3.737	0
	O ₃		NO ₂		F ₂ O		Cl ₂ O	
d_{12}	0.6322		0.5270		0.4587		0.4261	
d_{11}	4.029		6.158		2.307		2.344	
d_{22}	1.107		0.8481		0.7564		0.5017	
$\backslash i$	1	2	1	2	1	2	1	2
$\Delta\beta_i$	0	29° 44'	0	31° 52'	0	31° 14'	0	40° 21'
ρ_i	-1.751	∞	-1.609	∞	-1.649	∞	-1.177	∞
N_i	0.7435	(1.955)	0.7217	(2.134)	0.9468	(1.964)	1.214	(1.980)
$V_{11}(\nu_i)$	109.844	0	105.618	0	113.714	0	118.262	0
$V_{22}(\nu_i)$	9.844	100	5.618	100	13.714	100	18.262	100
$V_{12}(\nu_i)$	-19.689	0	-11.235	0	-27.429	0	-36.525	0

TABLE IX. d_{33} . (Class B_1 mode.)

	H ₂ O	D ₂ O	ClO ₂	SO ₂	O ₃	NO ₂	F ₂ O	Cl ₂ O
d_{33}	3.880	3.983	3.210	4.942	5.482	4.304	2.786	2.456
Δ_{33}	2.401	2.040	1.432	1.279	1.375	1.498	1.541	1.536

The data summarized in the tables illustrate most of the points dealt with in the general case. Here the coefficient A_{12} is negative, so the interaction constant d_{12} is positive in solutions I, II, and VII. The tendency of the system to reach a minimum potential energy conventionally requires that ρ_1 and ρ_2 be both negative or both positive according as d_{12} is positive or negative; if d_{12} is zero, then ρ_1 and ρ_2 may be either positive or negative. Solutions I, II, and VII satisfy these conditions in all cases. The three cases given for solution III are all unsatisfactory in ν_2 , while in solution IX only F₂O and Cl₂O satisfy the required conditions in both normal modes. Solution IX is in any case not generally applicable; it gives a negative value of d_{12} for ClO₂ and NO₂, and a large positive one for F₂O; for SO₂ and Cl₂O it differs only slightly from II and VII, while for H₂O, D₂O, and O₃, $d_{33} > d_{11}(\text{max.})$ and there is no real solution. The interaction constant d_{13} is given in Table XI for solutions I, II, and VII. With respect to d_{11}^{II} , it is small and negative for H₂O, D₂O, and F₂O, small and positive for SO₂ and Cl₂O, large and negative for O₃, and large and positive for NO₂ and ClO₂. The energy principle does not necessarily require d_{13} to be negative because the product term $\Delta r_{12} \cdot \Delta r_{23}$ is positive in class A_1 modes, or positive because the product term is negative in the class B_1 mode; d_{13} is a subsidiary constant which occurs in

the general valence force field, but which is eliminated when the secular equation is reduced to a product of symmetry factors, and the minimum number of constants employed.

Differences between the solutions I, II, and VII in general increase with (m_1/m_2) ; for H₂O they are very small. For this reason, the molecules H₂S, D₂S, H₂Se, and D₂Se were not included in the series studied. The maximum difference in the constants is $(d_{11}^{\text{II}} - d_{11}^{\text{I}})$ for NO₂, $(1.169 \times 10^5 \text{ dynes/cm} = 21.9 \text{ percent})$; but NO₂ only just satisfies Eq. (12). For Cl₂O, the maximum difference is 16.5 percent, and in all other cases much less. This, of course, is excluding solution III, which will not be satisfactory for any of the cases dealt with here (see Section IV, and the energy principle discussed above), and is given merely to illustrate the general theory in those cases where there is no real solution permitted with $d_{12} = 0$.

A general solution for the force constants of the triatomic molecule has been given by Glockler and Tung,² who extended the results to apply to other second-degree systems. They concluded that at singular points $(\partial d_{13}/\partial d_{22}) = (\partial d_{13}/\partial d_{12}) = 0$ satisfactory sets of constants were obtained. They attempted no analysis of the normal coordinates, but claimed that the results for the isotopic molecules H₂O, D₂O; H₂S, D₂S, supported their choice. Since $d_{13} \equiv (d_{11} - d_{33})$, their solution is identical with the solution VIII of this paper, which corresponds to the singularity $(\partial d_{11}/\partial d_{12}) = 0$, and which, in the limit $(m_1/m_2) = 0$, (more generally $(A_{12}/D) = 0$), is identical with VII $((\partial d_{22}/\partial d_{12}) = 0)$, but becomes less satisfactory as (m_1/m_2) increases. (cf. Section

TABLE X. Solution IX. ($d_{11} = d_{33}$.)

	ClO ₂		SO ₂		NO ₂		F ₂ O		Cl ₂ O	
d_{12}	-0.4136		0.04453		-0.4069		1.095		0.4950	
d_{11}	3.210		4.942		4.304		2.786		2.456	
d_{22}	0.9729		0.8018		1.187		0.9814		0.5046	
i	1	2	1	2	1	2	1	2	1	2
$\Delta\beta_i$	17° 38'	35° 48'	3° 24'	22° 49'	19° 58'	48° 3'	-19° 28'	10° 32'	-2° 25'	38° 58'
ρ_i	-1.386	3.145	-2.378	16.82	-0.8990	2.753	-5.378	-2.829	-1.237	-23.63
N_i	0.8281	0.5549	0.4903	0.1151	1.207	0.5907	0.2662	0.8105	1.155	0.08684
$V_{11}(\nu_i)$	74.426	31.368	97.932	2.118	64.443	38.906	115.475	62.687	123.702	0.942
$V_{22}(\nu_i)$	11.739	94.055	2.810	97.240	22.000	81.349	1.406	176.756	16.614	108.030
$V_{12}(\nu_i)$	13.835	-25.423	-0.742	0.642	13.557	-20.255	-16.881	-139.442	-40.316	-8.972

TABLE XI. Values of the interaction constant d_{13} .

	H ₂ O	D ₂ O	ClO ₂	SO ₂	O ₃	NO ₂	F ₂ O	Cl ₂ O
Solution I	-0.101	-0.138	0.519	-0.039		1.041		
Solution II	-0.092	-0.107	0.724	0.290	-1.233	2.210	-0.252	0.276
Solution VII	-0.095	-0.118	0.668	0.176	-1.453	1.854	-0.479	-0.112

IV.) Solution VIII can be used when (m_1/m_2) is small, as in H_2O , D_2O , H_2S , and D_2S , but is not a general one.

APPENDIX

The following approach to the second-degree equation may be of interest.

In place of the two valence-type coordinates Δ_1 and Δ_2 , we use two linear combinations defined as below.

$$\begin{aligned}\Delta_1' &= \Delta_1 + p_1 \Delta_2, \\ \Delta_2' &= \Delta_2 + p_2 \Delta_1,\end{aligned}$$

where p_1 and p_2 are arbitrary parameters. With these coordinates, the secular equation can be written

$$|d'A' - \lambda I| = 0,$$

where I is the unit matrix, d' is the force constant matrix for the coordinates Δ_1' , Δ_2' , and the elements of A' are

$$\begin{aligned}A_{11}' &= A_{11} + 2p_1 A_{12} + p_1^2 A_{22}, \\ A_{22}' &= A_{22} + 2p_2 A_{12} + p_2^2 A_{11}, \\ A_{12}' &= A_{21}' = A_{12}(1 + p_1 p_2) + p_2 A_{11} + p_1 A_{22},\end{aligned}$$

the A_{ij} referring to the initial coordinates Δ_1 and Δ_2 . The con-

dition for reduction to canonical form is

$$A_{12}' = 0.$$

With values of p_1 and p_2 satisfying this equation, Δ_1' and Δ_2' are the (unnormalized) normal coordinates for the problem. p_2 may be expressed in terms of p_1 , the latter replaced by p , and the solution given in terms of this single parameter. The results, referring to the initial coordinate system, are given by

$$\begin{aligned}d_{12} &= d_{11}'[p - (RS/D)\mu_1], \\ d_{11} &= d_{11}'[1 + (R^2/D)\mu_1], & \rho_1 &= (S/R), \\ d_{22} &= d_{11}'[p^2 + (S^2/D)\mu_1], & \rho_2 &= -(1/p), \\ V_{11}(\nu_1) &= (S/A_{11}')^2[1 + (R^2/D)\mu_1], \\ V_{22}(\nu_1) &= (R/A_{11}')^2[p^2 + (S^2/D)\mu_1], \\ V_{12}(\nu_1) &= [2RS/(A_{11}')^2][p - (RS/D)\mu_1], \\ V_{11}(\nu_2) &= (p/A_{11}')^2[D\mu_2 + R^2], \\ V_{22}(\nu_2) &= (1/A_{11}')^2[p^2 D\mu_2 + S^2], \\ V_{12}(\nu_2) &= -[2p/(A_{11}')^2][p D\mu_2 - RS],\end{aligned}$$

where

$$\begin{aligned}d_{11}' &= (\lambda_1/A_{11}'), \\ R &= A_{12} + pA_{22}, \\ S &= A_{11} + pA_{12},\end{aligned}$$

and other quantities are as defined previously. Solutions VII and VIII correspond to $p=0$ and $-(A_{12}/A_{22})$, (i.e., to $p_1=0$, $p_2=0$), respectively.

Temperature Variation of Ultrasonic Velocity in Liquids

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Measurements have been made of the ultrasonic velocity in thirty-four organic liquids over a temperature range of 0–60°C by use of a variable-path ultrasonic interferometer operating at 500,000 cycles per second. For all of the liquids studied the relation between velocity and temperature was found to be essentially linear. Values of density, adiabatic compressibility, and temperature coefficient ($\Delta V/\Delta T$) are also reported. It was found that the successive substitution of a heavier atom in a molecule leads to successively smaller temperature coefficients. It is pointed out that the temperature coefficient of ultrasonic velocity appears to be inversely proportional to the square root of the molecular weight, to a fair degree of accuracy.

THE variation of the velocity of ultrasonic waves in liquids with changes in temperature has been studied by various workers. Perhaps the earliest work of precision was that of Freyer, Hubbard, and Andrews,¹ who showed that the relation was essentially a linear one for the organic liquids studied by them. Other workers² have confirmed and added to their results, so that we find for

all substances studied, with the exception of water below a certain temperature, that the ultrasonic velocity decreases with increasing temperature; that is, liquids possess a negative temperature coefficient which is of the order of $-3 \times 10^{-3} \text{ C}^{-1}$. Over short ranges of temperature, say 50 centigrade degrees, the velocity-temperature curves appear essentially linear for the substances studied.

On the other hand, Rao³ proposes the relation

$$V = V_0(1 - \theta/\theta_c)^{9/10},$$

where V is the ultrasonic velocity at temperature θ , and θ_c is the critical temperature. This is, of course, very nearly a linear relation. No analysis of the available data was made by Rao to determine whether this relation fits better than one assuming

¹ E. B. Freyer, J. C. Hubbard, and D. H. Andrews, *J. Am. Chem. Soc.* **51**, 759 (1929).

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³ M. R. Rao, *J. Chem. Phys.* **9**, 682 (1941).