Molecular Vibrations of Three Particle Systems with Special Applications to the Ethyl Halides and Ethyl Alcohol

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The vibrational potential of polyatomic molecules is discussed in the light of the theory of directed valence. Andrews' assumptions of "valence forces" are seen to be rather special, but at the same time are fairly good approximations under certain conditions. The normal vibrations of three body systems are calculated for the potential function

$$V = \tfrac{1}{2}[k_1(\Delta r_1)^2 + k_2(\Delta r_2)^2 + k_3(r_1^{0^2} + r_2^{0^2})(\Delta \gamma)^2]$$

with r_1, r_2 radial coordinates and γ an angular one. The potential terms proportional to $\Delta r_1 \Delta r_2$, etc., are treated as perturbations. These calculations are applied to the ethyl halide and ethyl alcohol molecules by considering the CH_3, CH_2 and OH groups as dynamic units. Force constants were determined which gave approximately the experimental frequencies. The calculation of the normal modes of vibration illustrate the approximate validity of the designation of the modes of vibration of *unsymmetrical* three body systems as two independent radial motions and an angular motion.

I. Introduction: Relation of Directed Valence to Vibrational Potentials

IN a recent study of the infrared absorption spectra of the ethyl halides (CH_3CH_2Cl, CH_3CH_2Br, CH_3CH_2I) Cross and Daniels[1] suggested for each of the fundamental bands a type of motion which was believed to represent the chief characteristic of the normal modes of vibration involved. Three of these types of motion (types F_5, F_7, F_8 of reference 1) may be considered as the characteristic modes of a three body system in which the units are the halogen atom, the CH_3 group, and the CH_2 group. These were given as illustrated in Fig. 1. The experi-
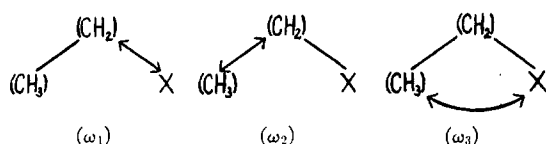

FIG. 1.

mental evidence for each may be summarized briefly as: (1), the occurrence of a characteristic frequency whenever the group $-CH_2X$ is present; (2), the occurrence in all the ethyl halides of a frequency nearly equal to that of a strong Raman line of ethane; and (3), the low value of the bending frequency in the ethyl halides and the fact that no such low frequency is found in the methyl halides.

Cross and Daniels also noted the apparent absence of the frequency characteristic of the H_3C-CH_2 bond in the case of ethyl alcohol (CH_3CH_2OH). They suggested that the symmetry of the molecule resulted in a strong interaction between the different types of motion in such a way that a given frequency could not be assigned to a type of motion involving only a part of the molecule. (The word symmetry, as used here, applies to the equality of the masses attached by the central atom. In ethyl alcohol the attached masses are 15 and 17 on the atomic weight scale.) The same should, incidentally, be true for ethyl fluoride.

The purpose of this paper is to calculate the normal modes of vibration of three body systems analogous to each of the ethyl halides and to ethyl alcohol. The masses, dimensions and normal frequencies shall correspond to those of the molecules, considering the CH_3 group and the CH_2 group as units (Fig. 1). It is reasonable to assume that the hydrogen atoms, by virtue of their small mass and the strong forces holding them to the carbon atoms, do not produce any first order deviations in the dynamical behavior of the molecules from that of three body systems in the vibrations we are considering. Hence the

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[1] P. C. Cross and F. Daniels, J. Chem. Phys. **1**, 48 (1933).

results of this calculation should be a qualitative test of the accuracy of the above suggestions.

Most of the previous work on the small vibrations of triatomic molecules has dealt with symmetrical systems, i.e., systems of the type XY_2.[2, 3, 4, 5] Radakovic[6] has, however, given a general solution for the potential function

$$V = \tfrac{1}{2}[c_{13}(\Delta r_{13})^2 + c_{23}(\Delta r_{23})^2 + c_{12}(\Delta r_{12})^2], \quad (1)$$

in which Δr_{ij} is the displacement of the distance between the particles i and j from the equilibrium distance. Instead of (1) we shall use the potential function

$$V = \tfrac{1}{2}[k_1(\Delta r_1)^2 + k_2(\Delta r_2)^2 + k_3(r_1^{0^2} + r_2^{0^2})(\Delta \gamma)^2]. \quad (2)$$

The significance of the coordinates is clear from Fig. 2. The coordinate γ is an angle rather than
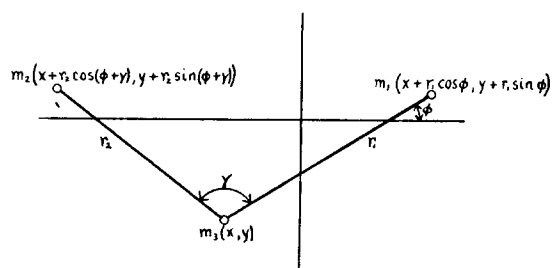

FIG. 2.

a distance, while r_1 and r_2 are identical with r_{13} and r_{23} of (1). The equilibrium values of r_1, r_2 are denoted by r_1^0, r_2^0. The factor $r_1^{0^2} + r_2^{0^2}$ is inserted in (2) to make k_3 dimensionally similar to k_1, k_2; otherwise no direct significance could be attached to comparison of the numerical values of the various force constants.

A system obeying (2) is often called a "valence force system" in the literature. Eq. (2) has a more reasonable form of the potential function than (1) if the directional valence of the central atom is more important than the repulsion between the attached atoms.

The most general form of the potential function for small, i.e., harmonic, vibrations would include terms proportional to $\Delta r_1 \Delta r_2$, $\Delta r_1 \Delta \gamma$, and $\Delta r_2 \Delta \gamma$ (or terms proportional to $\Delta r_{12} \Delta r_{13}$, etc., in (1)). In writing (1) and (2) we have assumed only three atoms, but the extensions to molecules with an arbitrary number of atoms are obvious, and our discussion on cross-terms in the next few paragraphs is not restricted to triatomic molecules.

Actually the terms proportional to $\Delta r_1 \Delta \gamma$ and $\Delta r_2 \Delta \gamma$ do not vanish completely. In the first place, the theory of directional valence requires that the angular equilibrium positions be somewhat modified when one of the bonds is stretched or contracted. This has been demonstrated by one of the writers in an article in this journal.[7] It was there shown, for instance, that in tetravalent carbon compounds, quite irrespective of repulsions between the attached atoms, the tetrahedral angles 109.5° should be somewhat modified when the four bonds are not of equal intensity. The bonds must be considered unequal not only when the four attached atoms are not identical, but also in symmetrical molecules such as CX_4 when an atom X is moved radially from its equilibrium position, so that the symmetry is lost. Hence the terms in $\Delta r_1 \Delta \gamma$ and $\Delta r_2 \Delta \gamma$ cannot disappear, for absence of such terms implies that the equilibrium angles are unmodified by small radial displacements. However, it is probably true that the equilibrium angles do not vary greatly from 109.5° even when the bonds are of unequal intensity or even when the central atom is not tetravalent. (Witness, for instance, the equilibrium angle in the neighborhood of 100° in the case H_2O. Of course CO_2 is collinear and so has an angle of 180°, but here there is the complication of double bonds, to which our discussion does not apply.) This is a very happy circumstance, for otherwise any discussion of angular structure in molecules would needs be much more difficult than in reality. The reason why 109.5° is usually not far amiss is the following: for a structure C–X–Y involving a single valence angle X–C–Y the best value of the angle was shown by one of us[7] to

[2] N. Bjerrum, Verh. d. D. Phys. Ges. **16**, 737 (1914).

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

[4] R. C. Yates, Phys. Rev. **36**, 555 (1930).

[5] K. W. F. Kohlrausch, *Der Smekal-Raman-Effekt* (and references therein) Julius Springer, Berlin, 1931.

[6] M. Radakovic, Wien. Ber. **139**, 107 (1930).

[7] J. H. Van Vleck, J. Chem. Phys. **1**, 219 (1933); (cf. especially Sections 5 and 6).

vary from 90° to 180° depending on the relative importance of the bonds emanating from the $2s$ and $2p$ states of the C atom. If the $s-p$ interplay were the only important thing, the best angle would be 180°, while 90° would be required for pure p-bonding. Actually, the p-bonding is perhaps dominant, so that the best angle is nearer 90° than 180°. In a compound of the form CWXYZ, each angle W–C–X, W–C–Y, . . . Y–C–Z has an optimum value between 90° and 180° as far as its own particular directional valence is concerned. These values are in general not compatible, and so must be somewhat modified, with the most powerful directional valences, of course, in general favored at the expense of the others. The important thing, however, is that the best value for any individual angle is between 90° and 180°, and so never extremely different from 110° even when the bonds are of unequal intensity. Hence the alteration in equilibrium angle upon stretching or contracting a bond is probably very small, and so the terms in $\Delta r_1 \Delta \gamma$ and $\Delta r_2 \Delta \gamma$ originating from this cause are probably subordinate. A term in $\Delta r_1 \Delta r_2$ is, in principle, required because the configuration of the C atom is somewhat modified by any alterations in position of the attached atoms, so that when one bond is stretched, the equilibrium radial values for other bonds are altered. Such terms, however, are probably very small. Otherwise particular bonds would not have nearly invariant vibration frequencies in a wide range of compounds.

In the preceding paragraph we have considered only the effect of the valences emanating from the central atom. A more important cause of the "cross-terms" proportional to $\Delta r_1 \Delta r_2$, $\Delta r_1 \Delta \gamma$, $\Delta r_2 \Delta \gamma$ is perhaps the repulsions between the attached atoms. If r_{12} be the distance between the attached atoms, this repulsive energy is a function of the single argument r_{12}, and will generate cross-terms since $(\Delta r_{12})^2 = [a\Delta r_1 + b\Delta r_2 + c\Delta \gamma]^2$. The cross-terms originating from this cause will be computed in the next paper for the H_2O molecule. It will be found that these terms are sufficiently small to let (2) be the dominant part of the potential energy, but are at the same time by no means negligible, and are sufficiently

great to make purely fortuitous any exact agreement with experiment achieved by using a potential of the form (2). For this reason, it has seemed desirable to give in Section V a theory for treating the cross-terms as a perturbation superposed on (2).

When the specification of the molecule requires several angular coordinates γ_1, γ_2, $\cdots$, the vibrational potential will in general contain cross-terms proportional to $\Delta \gamma_1 \Delta \gamma_2$, etc., because the equilibrium position of any given valence angle is modified by angular displacements in other bonds. Such cross-terms do not arise in the cases treated in this or the following paper, because we restrict our attention to effectively triatomic molecules, where only one angular coordinate is necessary. The well-known assumptions of Andrews[8] concerning molecular vibrations appear to be tantamount to assuming that all the various types of cross-terms are negligible. Hence his hypotheses are rather restrictive. We have seen that the quantum mechanics of directed valence requires that the cross-terms, at least in $\Delta r \Delta \gamma$, are not excessive, and this probably explains why Andrews' theory has been attended with some qualitative success.

After our calculations were completed an article by Lechner[9] appeared, likewise giving the derivation of the characteristic frequencies for the potential function (2). His paper does not give the details of his derivation or analyze the perturbing effect of cross-terms and so it seems advisable to include the mathematical analysis which we used, as well as the applications, which are to different molecules than those studied by Lechner. Also, we believe the Lagrangian function (6) which we give may be useful for other three body problems besides the ones which we consider. In particular the kinetic energy terms of (6) would be useful if one desired to carry through a calculation in which the oscillations were not infinitesimal, so that the method of normal coordinates could not be used.

[8] D. H. Andrews, Phys. Rev. **36**, 544 (1930).
[9] F. Lechner, Monatshefte f. Chemie **61**, 385 (1932).

II. THE PROBLEM OF THE THREE BODY SYSTEMS

The kinetic energy in the Cartesian coordinate system is

$$T = \tfrac{1}{2}m_1[\{\dot{x}+\dot{r}_1\cos\phi - r_1\dot\phi\sin\phi\}^2 + \{\dot{y}+\dot{r}_1\sin\phi + r_1\dot\phi\cos\phi\}^2]$$

$$+\tfrac{1}{2}m_2[\{\dot{x}+\dot{r}_2\cos(\phi+\gamma) - r_2(\dot\phi+\dot\gamma)\sin(\phi+\gamma)\}^2 + \{\dot{y}+\dot{r}_2\sin(\phi+\gamma)+r_2(\dot\phi+\dot\gamma)\cos(\phi+\gamma)\}^2]$$

$$+\tfrac{1}{2}m_3[\dot{x}^2+\dot{y}^2]. \tag{3}$$

Let us take the origin of these coordinates at the center of mass, which we may suppose to be stationary. Then x and y may be eliminated through the relations

$$\sum m_i x_i = \sum m_i y_i = 0, \tag{4}$$

and the resulting Lagrangian function is

$$L = T - V = \tfrac{1}{2}\mu_1[\dot{r}_1^2 + r_1^2\dot\phi^2] + \tfrac{1}{2}\mu_2[\dot{r}_2^2 + r_2^2\dot\phi^2 + 2r_2^2\dot\phi\dot\gamma + r_2^2\dot\gamma^2]$$

$$-\mu_3[\dot{r}_1\dot{r}_2\cos\gamma + r_1\dot{r}_2\dot\phi\sin\gamma - r_2\dot{r}_1(\dot\phi+\dot\gamma)\sin\gamma + r_1r_2(\dot\phi^2+\dot\phi\dot\gamma)\cos\gamma]$$

$$-\tfrac{1}{2}[k_1(\Delta r_1)^2 + k_2(\Delta r_2)^2 + k_3(r_1^{0^2}+r_2^{0^2})(\Delta\gamma)^2], \tag{5}$$

where

$$\mu_1 = \frac{m_1m_2 + m_1m_3}{m_1+m_2+m_3}, \quad \mu_2 = \frac{m_1m_2+m_2m_3}{m_1+m_2+m_3}, \quad \mu_3 = \frac{m_1m_2}{m_1+m_2+m_3}.$$

Since ϕ does not occur explicitly in L, it is ignorable and $\dot\phi$ may be eliminated by solving $\partial L/\partial\dot\phi = P$ for $\dot\phi$ and substituting this value of $\dot\phi$ in the function[10] $R = L - \dot\phi(\partial L/\partial\dot\phi)$. Since P is the angular momentum of the system, it will be taken as zero inasmuch as, for our purposes, the system may be considered devoid of rotation. This gives

$$R = \tfrac{1}{2}[\mu_1 - \rho\mu_3^2 r_2^2\sin^2\gamma]\dot{r}_1^2 + \tfrac{1}{2}[\mu_2 - \rho\mu_3^2 r_1^2\sin^2\gamma]\dot{r}_2^2 + \tfrac{1}{2}\rho r_1^2 r_2^2[\mu_1\mu_2 - \mu_3^2\cos^2\gamma]\dot\gamma^2$$

$$+[-\mu_3\cos\gamma + \rho\mu_3^2 r_1 r_2\sin^2\gamma]\dot{r}_1\dot{r}_2 + \rho\mu_3 r_1 r_2\sin\gamma\{[\mu_1 r_1 - \mu_3 r_2\cos\gamma]\dot{r}_1\dot\gamma + [\mu_2 r_2 - \mu_3 r_1\cos\gamma]\dot{r}_2\dot\gamma\}$$

$$-\tfrac{1}{2}[k_1(\Delta r_1)^2 + k_2(\Delta r_2)^2 + k_3(r_1^{0^2}+r_2^{0^2})(\Delta\gamma)^2], \tag{6}$$

in which $1/\rho = \mu_1 r_1^2 + \mu_2 r_2^2 - 2\mu_3 r_1 r_2\cos\gamma$.

Since the vibrations are small, the equilibrium values r_1^0, r_2^0, γ^0 of r_1, r_2, γ, respectively, may be substituted in the coefficients of the velocity terms in (6). Then if we introduce new coordinates $q_1 = \Delta r_1$, $q_2 = \Delta r_2$, $q_3 = (r_1^{0^2}+r_2^{0^2})^{\frac{1}{2}}\Delta\gamma$, we have

$$R = \tfrac{1}{2}\sum_i\sum_j a_{ij}\dot{q}_i\dot{q}_j - \tfrac{1}{2}\sum_i k_i q_i^2, \quad (a_{ij}=a_{ji}). \tag{7}$$

The values of the constants a_{ij} are immediately obtained from Eq. (6). The three equations of motion obtained from the Lagrangian function (7) are

$$a_{i1}\ddot{q}_1 + a_{i2}\ddot{q}_2 + a_{i3}\ddot{q}_3 + k_i q_i = 0, \quad (i=1, 2, 3). \tag{8}$$

The usual assumption of a periodic solution $q_i = A_i e^{-i\lambda t}$ yields the following relations for determination of the amplitudes.

$$[a_{i1}A_1 + a_{i2}A_2 + a_{i3}A_3]\lambda^2 - k_i A_i = 0, \quad (i=1, 2, 3). \tag{9}$$

The existence of a non-trivial solution of the three Eqs. (9) requires that the determinant of the coefficients vanish, whence

$$\begin{vmatrix} a_{11}\lambda^2 - k_1 & a_{12}\lambda^2 & a_{13}\lambda^2 \\ a_{21}\lambda^2 & a_{22}\lambda^2 - k_2 & a_{23}\lambda^2 \\ a_{31}\lambda^2 & a_{32}\lambda^2 & a_{33}\lambda^2 - k_3 \end{vmatrix} = 0. \tag{10}$$

From this equation the constants necessary to yield solutions of the Eqs. (9) may be determined.

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[10] Cf., for instance, Whittaker, *Analytical Dynamics*, Third edition, page 54, Cambridge, 1927.

III. Evaluation of the Force Constants

The interatomic distances given in Table I were calculated from the values of the atomic radii given by Sigwick and Bowen.[11] The carbon to carbon distance r_2^0 was taken throughout as 1.54A. No experimental values of the angles between the valence directions were available, but as shown in Section I, they cannot vary greatly from the tetrahedral angle.

Values of the force constants, k_1, k_2 and k_3, were determined which made the roots of (10) equal to the experimental values of λ^2, which have the significance $\lambda^2 = 4\pi^2 c^2 \omega^2$ in terms of the

Table I.

	r_1^0(A)	$k_1 \times 10^{-5}$	$k_2 \times 10^{-5}$	$k_3 \times 10^{-5}$	ω_1(cm^{-1}) Calc.	Obs.	ω_2(cm^{-1}) Calc.	Obs.	ω_3(cm^{-1}) Calc.	Obs.
CH_3CH_2Cl	1.74	2.2	3.9	0.22	660	655	980	966	335	335
CH_3CH_2Br	1.9	1.6	3.8	0.22	570	560	970	960	285	290
CH_3CH_2I	2.1	1.2	3.8	0.18	510	500	960	950	245	260
CH_3CH_2OH	1.37	4.1	3.6	0.26	910	885	1020	1045	430	425

wave number ω.[12] In case no reasonable real values of the force constants would give the required roots of (10), values were selected which gave roots nearly the same as those obtained from experimental data. Values of these constants, together with the calculated values of ω and the wave numbers of the corresponding Raman lines, are given in Table I.

As an alternative the force constants of the potential function (1) were calculated, and are as follows:

CH_3CH_2Cl; $c_{13} = 2.5 \times 10^5$, $c_{23} = 3.8 \times 10^5$, $c_{12} = 1.2 \times 10^5$.

CH_3CH_2Br; $c_{13} = 2.25 \times 10^5$, $c_{23} = 3.75 \times 10^5$, $c_{12} = 1.0 \times 10^5$.

CH_3CH_2I; $c_{13} = 1.96 \times 10^5$, $c_{23} = 3.7 \times 10^5$, $c_{12} = 0.78 \times 10^5$.

CH_3CH_2OH; $c_{13} = 4.0 \times 10^5$, $c_{23} = 3.5 \times 10^5$, $c_{12} = 1.7 \times 10^5$.[13]

Insofar as the consistency of the values of the force constants is concerned, there is little basis for a choice between the two potential functions. In particular, the value of k_2 or c_{23} should not vary greatly from molecule to molecule since the the intensity of the $CH_3 - CH_2$ bond should be but little affected by the nature of the other atom attached to the C atom. This condition is seen to be met with either the potential function (2) based on valence forces, or with the less likely alternative (1).

IV. The Normal Modes of Vibration

After determination of the force constants, k_i, the roots of Eq. (10) were substituted in (9) to obtain the ratio $A_1 : A_2 : A_3$ for each frequency. The corresponding values of A_ϕ were obtained from the relation $\partial L/\partial \phi = P = 0$. The resulting normal modes of vibration are shown in Figs. 3 to 6.

Explicit formulas for α, β and γ in terms of the masses, force constants and molecular dimensions have been given by Lechner[9] and so need not be repeated here. Lechner expresses the equations of motion in the form $\ddot{q}_i = \Sigma a_i q_i$ rather than (8), but we have verified that his secular equation is the same as ours.

[11] N. V. Sidgwick and E. J. Bowen, Ann. Rep. Chem. Soc. **28**, 402 (1931).

[12] Eq. (10) is a cubic, $\lambda^6 + \alpha\lambda^4 + \beta\lambda^2 + \gamma = 0$, in λ^2. In the evaluation of its roots λ_1^2, λ_2^2, λ_3^2, it is convenient to utilize the well-known expressions
$\gamma = -\lambda_1^2 - \lambda_2^2 - \lambda_3^2$, $\beta = \lambda_1^2\lambda_2^2 + \lambda_1^2\lambda_3^2 + \lambda_2^2\lambda_3^2$, $\alpha = -\lambda_1^2\lambda_2^2\lambda_3^2$.

[13] There are no real values of c_{ij} which give the experimental values of ω for ethyl alcohol. The values given here correspond roughly to values 1015, 935 and 425 cm^{-1} for ω.
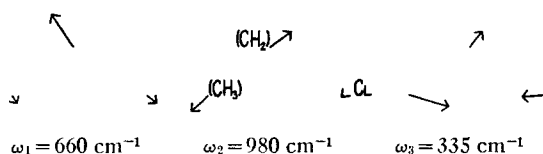
$\omega_1=660$ cm^{-1} $\omega_2=980$ cm^{-1} $\omega_3=335$ cm^{-1}

FIG. 3.

$\omega_1=570$ cm^{-1} $\omega_2=970$ cm^{-1} $\omega_3=285$ cm^{-1}

FIG. 4.

$\omega_1=510$ cm^{-1} $\omega_2=960$ cm^{-1} $\omega_3=245$ cm^{-1}

FIG. 5.

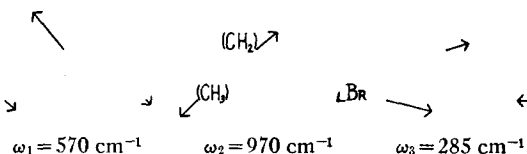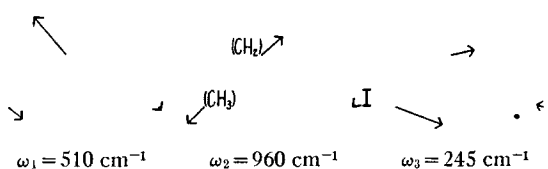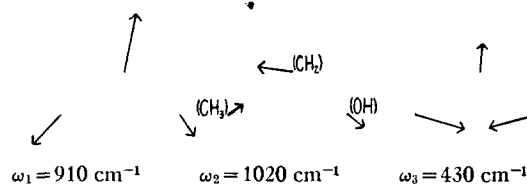$\omega_1=910$ cm^{-1} $\omega_2=1020$ cm^{-1} $\omega_3=430$ cm^{-1}

FIG. 6.

V. THE EFFECT OF CROSS TERMS IN THE POTENTIAL FUNCTION

We shall now consider briefly the effect of adding the cross-terms

$$\tfrac{1}{2}\sum_i\sum_{j(j\neq i)}k_{ij}q_iq_j \quad (k_{ij}=k_{ji}) \tag{11}$$

to the potential function of (7). The existence and origin of these terms was discussed in Section I. The addition of (11) merely introduces into the equations of motion (8) the extra term $\sum_j k_{ij}q_j$. The resulting secular equation is still a cubic, but as it can be solved only numerically, the addition of (11) introduces so many arbitrary constants that the problem ceases to be tractable or significant. Instead, the extent to which (11) influences the frequencies can be more easily studied if one introduces it as a perturbation. The result of the perturbation is perhaps best examined by introducing normal coordinates, $A_1\cdots$, for the unperturbed problem. The coordinates q_1, q_2, q_3 will be linear functions $q_i=\sum_j\alpha_{ij}A_j$ of these coordinates. After addition of (11) these coordinates lose their "normal" property and the Lagrangian function in terms

of the A's may be thrown into the form:

$$R'=\tfrac{1}{2}\sum_i[A_i'^2-\lambda_i^2A_i^2]-\tfrac{1}{2}\sum_i\sum_j\beta_{ij}^2A_iA_j, \tag{12}$$

with

$$\beta_{ij}=\beta_{ji}=\sum_l\sum_{m(l<m)}k_{lm}(\alpha_{li}\alpha_{mj}+\alpha_{lj}\alpha_{mi}).$$

The secular equation is then

$$\begin{vmatrix} \beta_{11}+\lambda_1^2-\lambda'^2 & \beta_{12} & \beta_{13} \\ \beta_{21} & \beta_{22}+\lambda_2^2-\lambda'^2 & \beta_{23} \\ \beta_{31} & \beta_{32} & \beta_{33}+\lambda_3^2-\lambda'^2 \end{vmatrix}=0. \tag{13}$$

Here primes are attached to the λ's when we wish to designate their values as modified by the inclusion of (11). The approximate solution of (13) is

$$\lambda_i'^2=\lambda_i^2+\beta_{ii}-\sum_{j(j\neq i)}\beta_{ij}^2/(\lambda_j^2-\lambda_i^2) \tag{14}$$

if the off-diagonal elements of (13) are small in comparison with the differences $\lambda_j^2-\lambda_i^2$.

The effect of the introduction of the cross-terms may best be examined by writing down a specific numerical form of (14) for a particular example, ethyl alcohol.

$\lambda_1'^2-\lambda_1^2=(0.6k_{12}-1.17k_{13}-1.85k_{23})\times10^{23}$

$\qquad -(0.06k_{12}^2+1.15k_{13}^2+0.47k_{23}^2-0.62k_{12}k_{13}+0.35k_{12}k_{23}-2.34k_{13}k_{23})\times10^{18}.$

$\lambda_2'^2-\lambda_2^2=(-0.94k_{12}-0.1k_{13}+0.08k_{23})\times10^{23}$

$\qquad +(0.06k_{12}^2+1.65k_{13}^2+1.06k_{23}^2-0.54k_{12}k_{13}+0.41k_{12}k_{23}-2.64k_{13}k_{23})\times10^{18}.$

$\lambda_3'^2-\lambda_3^2=(0.03k_{12}+0.31k_{13}+0.37k_{23})\times10^{23}$

$\qquad -(0.01k_{12}^2+0.47k_{13}^2+0.64k_{23}^2+0.08k_{12}k_{13}+0.08k_{12}k_{23}-0.3k_{13}k_{23})\times10^{18}. \tag{15}$

A rough estimate of the k_{ij}'s by a procedure similar to that used in evaluating $g(r_{12})$ in the following paper yields the values $k_{12} = 0.13 \times 10^5$, $k_{13} = 0.039 \times 10^5$, $k_{23} = 0.044 \times 10^5$. Introduction of these terms gives the values $\lambda_1'^2 = 2.9 \times 10^{28}$, $\lambda_2'^2 = 3.58 \times 10^{28}$, $\lambda_3'^2 = 0.685 \times 10^{28}$ for the perturbed frequencies. The unperturbed values are $\lambda_1^2 = 2.95 \times 10^{28}$, $\lambda_2^2 = 3.7 \times 10^{28}$, $\lambda_3^2 = 0.655 \times 10^{28}$. These values could be altered by choosing other values for the constants k_1, k_2, k_3 in the unperturbed system, but it appears unlikely that the separation of λ_1^2 and λ_2^2 could be made great enough to agree with the experimental data. The separation is probably partly due to certain factors that have been neglected, such as the effect of the hydrogen atoms on the potential function and on the effective masses of the units, or to errors in the dimensions of the molecules. Despite this discrepancy, however, the approximate validity of the calculations is retained.

VI. CONCLUSION

It is apparent from the normal modes of vibration of the systems studied that the designation of a type of motion involving only a part of the molecule to account for certain frequencies is justified under certain conditions of dissymmetry. This may in a large measure be responsible for the well-established fact that certain chemical bonds are accompanied by frequencies which vary but little from a mean value as drastic changes are made in other parts of the molecule. However, as was suggested by Cross and Daniels, the presence of certain types of symmetry, such as the approximate mass symmetry of ethyl alcohol, may cause an interaction of the different types of motion in such a way as to largely obliterate the characteristic features of the separate types of motion.