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Pauli's principle one can calculate the splitting patterns for these various states. In the sulphate the agreement with excited states was not good even though it was excellent for the lowest state. There were always too many lines in the multiplet, and usually the intervals and over-all separations were wrong. In a few cases, e.g., in the 14,600 multiplet the splitting pattern of five of the six lines could be considered in very fair agreement with some of the possible states (${}^2K_{15/2}$ or ${}^2L_{15/2}$ or ${}^2L_{17/2}$) but the sixth line which had to be neglected was one of the most intense in the group and differed in no way from the others. Also, the matrix coefficients q were very different from that required.

The second possibility is that the transition would be of the type $4f^3-4f^25x$. This supposition is attractive for the second type of multiplet as one would expect the vibrational frequencies to couple with the electron frequency more readily if one of the electrons were outside the completed $5s\ 5p$ shells. This idea is further borne out by

the fact that so far we have not found any vibrational states associated with the lower states and that these associated lines are most pronounced in Pr where only two electrons give rise to the multiplets. On the other hand this supposition as pointed out by Van Vleck¹¹ is open to serious objections such as wrong order of intensity of lines, etc.

We shall discuss the problem of the excited states in much more detail in a later paper as we feel that the problem requires more experimental data before it can be discussed profitably. We have photographed a number of salts in which the potential fields are slightly different and by studying how the excited levels vary from salt to salt we hope to be able to learn a good deal more about the nature of these states.

We wish to thank Dr. H. N. McCoy for his generous gift of the Nd salt used in these investigations and Professor Gibbs of the physics department for extending to us the facilities of his department.

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The Normal Vibrations and the Vibrational Spectrum of C_2H_6 *

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An investigation is made of the vibrations, frequencies and selection rules of C_2H_6 , which is assumed to have an internal rotational degree of freedom subject to a restricting potential of an arbitrary magnitude. Making use of the fact that the total potential energy of such a molecule is invariant under a reflection in a plane perpendicular to the threefold symmetry axis, a set of vibrational selection rules is obtained which is more complete than that of Teller and Topley who made use only of the invariance of the potential energy under operations of the point group D_3 . The vibrational selection rules are found to be essen-

tially the same for all degrees of restriction of the internal rotation except for the rules governing the appearance of the degenerate frequencies in the Raman spectrum, so that even in the limit of free rotation only one type of degenerate vibrational frequency is active in the infrared spectrum. A normal coordinate treatment based on a three-constant potential function of the valence force type is found to give a set of frequencies in good agreement on the whole with the observed frequencies. The fundamental region of the vibrational spectrum seems to afford no conclusive evidence for or against free internal rotation.

IN the present paper a theoretical study is made of the vibration spectrum of C_2H_6 in which there is assumed to be a potential of an arbitrary

magnitude restricting the internal rotation. Previous to this, Sutherland and Dennison¹ have calculated the frequencies of the nondegenerate vibrations upon the assumption that forces between distant H atoms can be neglected, and

* A preliminary report of this study was given at the Washington meeting of the American Physical Society, April, 1936 (see Phys. Rev. **49**, 881 (1936)) and in a Letter to the Editor, Phys. Rev. **51**, 53 (1937).

** Society of Fellows, Harvard University.

¹ Sutherland and Dennison, Proc. Roy. Soc. **A148**, 250 (1935).

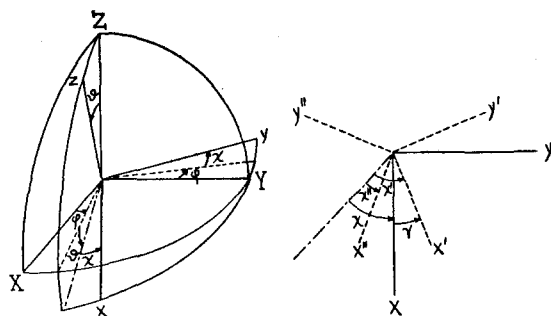


FIG. 1. (a) Diagram of x, y, z axes showing Eulerian angles. (b) Diagram of x, y plane showing relations of x', y' and x'', y'' axes. $\chi = (\chi' + \chi'')/2$ and $\gamma = (\chi' - \chi'')/2$.

Teller and Topley² have assigned frequencies to the normal vibrations in the light of interpretations of the spectra of related molecules and the specific heat of C_2H_6 . In the paper following, which we shall refer to henceforth as II, the rotational structure of the vibration bands is examined and an estimate is made of a lower limit to the potential restricting internal rotation.

COORDINATE SYSTEM

It will first be necessary to specify the rotational and vibrational coordinate systems to be used in the present and the following paper. Figs. 1a and 1b illustrate the rotational coordinates. Single and double primes are used throughout to distinguish coordinates referring to the two CH_3 groups. Two rotating systems of axes x', y', z' and x'', y'', z'' are chosen with a common origin at the center of gravity of the whole molecule, each system defining the equilibrium position of a CH_3 group. Both sets of axes are right-handed systems and the equilibrium configurations of the CH_3 groups, even to the order of the numbering of the H atoms, are identically situated with regard to their own sets of axes. The z' and z'' axes are collinear but point in opposite directions along the symmetry axis of the molecule. The position of the z' axis is given by the polar angle θ and the equatorial angle φ ; the orientation of the x', y' and x'', y'' axes is given by the azimuthal angles χ' and χ'' , respectively, both being measured in the same direction from the same base line in the plane perpendicular to the z' axis. Thus, when $\gamma = 0$

² Teller and Topley, J. Chem. Soc. 885 (1935).

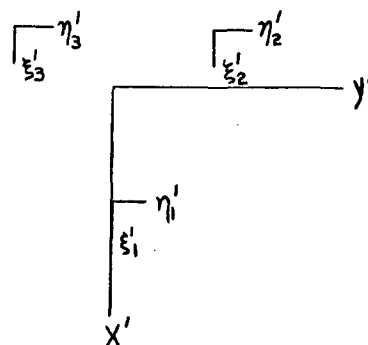


FIG. 2. Projection of H' (H'') plane onto x', y' (x'', y'') plane showing vibrational coordinates.

(see below), the x' and x'' axes are parallel and the y' and y'' axes are antiparallel. Two other coordinates are defined: $\gamma = (\chi' - \chi'')/2$, the internal angle; and $\chi = (\chi' + \chi'')/2$, which is used to help define a third system of axes x, y, z which is coincident with the x', y', z' system when $\gamma = 0$. The positive x axis always bisects the angle between the x' and x'' axes and the z axis is always coincident with the z' axis. (See Fig. 1.)

The displacements of the i th atom relative to the x', y', z' (x'', y'', z'') axes are measured along the Cartesian axes $\xi'_i, \eta'_i, \zeta'_i$ ($\xi''_i, \eta''_i, \zeta''_i$) which have their origin at the equilibrium positions of the i th atom and which are oriented parallel to the x', y', z' (x'', y'', z'') axes. The position chosen for the equilibrium configuration of a CH_3 group is suggested by Fig. 2.

POINT GROUP

Regardless of the magnitude of the forces restricting internal rotation, it is evident that for an arbitrary value of the internal angle, the potential energy of a displacement of C_2H_6 from its equilibrium configuration will be unchanged by a reflection of the molecule in a plane perpendicular to the threefold symmetry axis. The transformation, in terms of the internal angle and the displacement coordinates, corresponding to this operation is

$$\gamma \rightarrow -\gamma, \quad \zeta' \leftrightarrow \xi'', \quad \eta' \leftrightarrow -\eta'', \quad \zeta' \leftrightarrow \zeta'', \\ 1' \leftrightarrow 1'', \quad 2' \leftrightarrow 3'', \quad 3' \leftrightarrow 2'' \quad (1)$$

(see Figs. 1 and 2; under the reflection the internal angle behaves as a vector directed along the threefold axis). The abstract group under

which the potential energy of C_2H_6 , with any sort of restriction on the internal motion, is invariant is thus D_{3h} , i.e., the direct product group formed from D_3 and the group of order two consisting of the identity operation and the reflection in a plane perpendicular to the threefold axis. Only when $\gamma=0$, however, does the above transformation (1) reduce to the transformation which describes a reflection of the displacement coordinates alone and which is a point group transformation for a rigid C_2H_6 molecule having a plane of symmetry perpendicular to the threefold axis. Because of this distinction in the transformations which describe the reflection we shall designate as D'_{3h} the point group of C_2H_6 with an arbitrary value of the internal angle³ to distinguish the present more general case from that of a rigid symmetrical C_2H_6 molecule with point group D_{3h} . The derivation given by Teller and Topley² of the selection rules for C_2H_6 with free internal rotation makes use of the invariance of the potential energy under only the operations of the point group D_3 . The point group D_3 , whereas it describes the symmetry of the molecule in the ordinary sense, i.e., gives the complete set of independent physical operations which transform the *equilibrium* configuration of the molecule into a physically *indistinguishable* configuration, does not take full cognizance of the operations under which the potential energy is invariant, i.e., the operations which transform a *displaced* configuration of the molecule into a physically *equivalent* configuration. In other words, the point group D_3 , although it describes the symmetry of the molecule, does not fully describe the symmetry of the normal modes of vibration.

By virtue of the transformation (1) the displacement coordinates form the basis for a representation of the group D'_{3h} . By standard

³ We may equally well have made use of the invariance of the potential of C_2H_6 , with an arbitrary restriction on internal rotation, under a reflection in the center of gravity of the molecule. We would then have built up a point group D'_{3d} whose operations are described by transformations which reduce to those of D_{3d} when $\gamma=\pi/2$. The transformation (1) does not reduce to the operation of inversion of D_{3d} when $\gamma=\pi/2$ and the molecule has a center of symmetry because the former transformation involves a reorientation of the x, y axes with respect to the molecule.

methods⁴ for reducing the representation we find that the fully reduced representation is⁵

$$\Gamma = 3A_1 + A_2 + \bar{A}_1 + 3\bar{A}_2 + 4E + 4\bar{E}.$$

SYMMETRY COORDINATES

Our next step is to find a set of coordinates having the symmetry properties revealed in the last section. The normal coordinates are defined by the transformation

$$\xi'_i = \sum_k l'_{ik} Q_k, \quad \eta'_i = \sum_k m'_{ik} Q_k, \quad \zeta'_i = \sum_k n'_{ik} Q_k \quad (2)$$

with similar expressions in $l''_{ik}, m''_{ik}, n''_{ik}$ for $\xi''_i, \eta''_i, \zeta''_i$.

We shall find it convenient in obtaining the normal coordinates to make use of two other special systems of coordinates. Let one set of coordinates Z'_m (Z''_m), referring to a single CH_3 group, be given by the transformation

$$\xi'_i = \sum_m \lambda_{im} Z'_m, \quad \eta'_i = \sum_m \mu_{im} Z'_m, \quad \zeta'_i = \sum_m \nu_{im} Z'_m. \quad (3)$$

The transformation from $\xi''_i, \eta''_i, \zeta''_i$ to Z''_m is given by an *identical* set of coefficients $\lambda_{im}, \mu_{im}, \nu_{im}$. The summation over m extends from 1 to $3N/2$ where $N/2$ is the number of atoms in the CH_3 group. Furthermore, it shall be required that the coordinates Z'_m are normalized to $\frac{1}{2}$ and are orthogonal, that they form the basis for a fully reduced representation of the point group C_{3v} of the CH_3 group and that six of them are given by

$$\begin{aligned} (Z'_{6a})Z'_\xi &= N_T \sum \sqrt{m_i} \xi'_i; \\ (Z'_{6b})Z'_\eta &= N_T \sum \sqrt{m_i} \eta'_i; \\ (Z'_1)Z'_\zeta &= N_T \sum \sqrt{m_i} \zeta'_i; \\ (Z'_{6b})Z'_M \xi &= N_R \sum \sqrt{m_i} (-c_i \eta'_i + b_i \zeta'_i); \\ (-Z'_{6a})Z'_M \eta &= N_R \sum \sqrt{m_i} (-a_i \zeta'_i + c_i \xi'_i); \\ (Z'_1)Z'_M \zeta &= N_R \sum \sqrt{m_i} (-b_i \xi'_i + a_i \eta'_i). \end{aligned} \quad (4)$$

The alternative notation for Z'_m given in parentheses may be ignored for the moment. N_T and N_R are normalization factors; m_i is the mass of the i th atom; a_i, b_i, c_i give the equilibrium values of x'_i, y'_i, z'_i for the i th atom; \bar{c}_i is the z' coordinate of the equilibrium position of the i th atom as measured from the center of gravity of the singly-primed CH_3 group but with the positive direction of the z' axis unchanged.

If we let D denote the representation of the point group C_{3v} formed by the $\xi'_i, \eta'_i, \zeta'_i$ coordinates, then we may denote the reduction of D effected by the transformation to the Z'_m coordinates as the direct sum $D = 3a_1 + a_2 + 4e$.⁶ We shall designate the three coordinates belonging to the

⁴ E. Wigner, Gött. Nach. 133 (1930).

⁵ The notation used is based on that of Mulliken, Phys. Rev. 43, 279 (1933). We have used bars where he uses primes (e.g., \bar{A}_1 , instead of A''_1) for his representations of the group D_{3h} .

⁶ In the notation of Mulliken (reference 5) the a_1, a_2, e representations are A_1, A_2, E , respectively.

irreducible representation a_1 by $m=1, 2, 3$, the coordinate belonging to a_2 by $m=4$, and the pairs of coordinates belonging to the degenerate representation e by $m=5, 6, 7, 8$. Among the last type of coordinates we shall distinguish by the additional subscripts a and b the members of a pair of coordinates belonging to the two-dimensional e representation, and shall require that all the coordinates Z'_{ma} have identical transformation properties under operations of the group and that all Z'_{mb} have identical transformation properties. Choosing Z'_ξ and Z'_η as Z'_{5a} and Z'_{5b} , respectively, we thereby determine that Z'_{ma} and Z'_{mb} shall be, respectively, symmetric and antisymmetric with respect to reflection through the x', z' plane (see Fig. 2). Denoting $Z'_{M\xi}$ by Z'_{eb} we see that $Z'_{M\eta}$ corresponds to $-Z'_{5a}$ in order that Z'_{5a} be related to Z'_{5b} as Z'_{5a} is to Z'_{5b} . It is readily verified that $Z'_\xi = Z'_1$ belongs to a_1 and $Z'_\eta = Z'_4$ is the coordinate belonging to a_2 .

The second set of coordinates is given by the following linear combinations of the Z'_m and Z''_m coordinates:

$$S_m = Z'_m + Z''_m, \quad m=1, 2, 3, 4, \quad (5a)$$

$$\tilde{S}_m = Z'_m - Z''_m, \quad \tilde{m}=1, 2, 3, 4, \quad (5b)$$

$$S_{m\alpha} = (Z'_{ma} + Z''_{ma}) \cos \gamma - (Z'_{mb} + Z''_{mb}) \sin \gamma, \quad m=5, 6, 7, 8, \quad (5c)$$

$$S_{m\beta} = (Z'_{ma} - Z''_{ma}) \sin \gamma + (Z'_{mb} - Z''_{mb}) \cos \gamma,$$

$$\tilde{S}_{m\alpha} = (Z'_{ma} + Z''_{ma}) \sin \gamma + (Z'_{mb} + Z''_{mb}) \cos \gamma,$$

$$\tilde{S}_{m\beta} = -(Z'_{ma} - Z''_{ma}) \cos \gamma + (Z'_{mb} - Z''_{mb}) \sin \gamma, \quad \tilde{m}=7, 8,$$

$$\tilde{S}_{5a} = (1+d^2)^{-1} \{ [(Z'_{5a} + Z''_{5a}) \sin \gamma + (Z'_{5b} + Z''_{5b}) \cos \gamma] + d[(Z'_{5a} - Z''_{5a}) \sin \gamma + (Z'_{5b} - Z''_{5b}) \cos \gamma] \},$$

$$\tilde{S}_{5\beta} = (1+d^2)^{-1} \{ [-(Z'_{5a} - Z''_{5a}) \cos \gamma + (Z'_{5b} - Z''_{5b}) \sin \gamma] + d[-(Z'_{5a} - Z''_{5a}) \sin \gamma + (Z'_{5b} - Z''_{5b}) \cos \gamma] \}, \quad (5d)$$

$$\tilde{S}_{6a} = (1+d^2)^{-1} \{ d[(Z'_{6a} + Z''_{6a}) \sin \gamma + (Z'_{6b} + Z''_{6b}) \cos \gamma] - [(Z'_{6a} - Z''_{6a}) \sin \gamma + (Z'_{6b} - Z''_{6b}) \cos \gamma] \},$$

$$\tilde{S}_{6\beta} = (1+d^2)^{-1} \{ d[-(Z'_{6a} - Z''_{6a}) \cos \gamma + (Z'_{6b} - Z''_{6b}) \sin \gamma] - [-(Z'_{6a} - Z''_{6a}) \sin \gamma + (Z'_{6b} - Z''_{6b}) \cos \gamma] \},$$

where $d = N_{RC_0}/N_T$ and c_0 is the distance between the centers of gravity of the CH₃ group and the molecule as a whole in the equilibrium configuration. The subscripts α, β differentiate the members of a pair of coordinates belonging to a two-dimensional representation.

It may readily be verified that the S coordinates have the transformation properties required by the considerations of the preceding section.⁷ The coordinates with $m=1, 2, 3, 4$

belong to the A_1 and A_2 irreducible representations of D'_{3h} , those with $\tilde{m}=1, 2, 3, 4$ to \tilde{A}_1 and \tilde{A}_2 , those with $m=5, 6, 7, 8$ to E and those with $\tilde{m}=5, 6, 7, 8$ to \tilde{E} . The physical nature of these coordinates is suggested by the diagrams of Fig. 2 in the paper of Stitt and Yost.⁸

The number of S coordinates is $3N$ whereas the number of degrees of vibrational freedom is $3N-7$. In II it is shown that by setting identically equal to zero certain linear combinations of the displacement coordinates, ξ'_i, η'_i , etc., which correspond to incipient translations, over-all rotations and internal rotation of the molecule, the vibrational and rotational kinetic energies can be separated to a first approximation.⁹ Comparing the expressions in question (Eqs. (21) of II) with the S coordinates, we note the following identities:

$$\tilde{S}_1 = Q_z, \quad S_4 = Q_{M\gamma}, \quad \tilde{S}_4 = Q_{Mz}, \quad S_{5a} = Q_z,$$

$$S_{5\beta} = Q_y, \quad \tilde{S}_{5a} = Q_{Mz}, \quad \tilde{S}_{5\beta} = Q_{My}$$

where the Q 's are the Wigner⁴ normal coordinates of over-all rotation, translation and internal rotation, relative to the x, y, z axes. By making these seven S coordinates identically zero we completely define our system of displacement coordinates. We shall call the remaining seventeen coordinates symmetry coordinates.¹⁰ They form the following representation of D'_{3h} : $\Gamma = 3A_1 + 2\tilde{A}_2 + 3E + 3\tilde{E}$. The normal coordinate of internal rotation $Q_{M\gamma}$ belongs to the representation \tilde{A}_1 .

NORMAL COORDINATES

The seventeen normal coordinates defined by the transformation (2) have the same transformation properties as the symmetry coordinates and the normal coordinates belonging to

⁷ In performing the symmetry operations it is convenient to note that the transformation (1) has the following effect: $Z'_m \leftrightarrow Z''_m$ for nondegenerate coordinates; $Z'_{ma} \leftrightarrow Z''_{ma}$, $Z'_{mb} \leftrightarrow -Z''_{mb}$ for degenerate coordinates; $\gamma \rightarrow -\gamma$. It may be objected that inasmuch as the coefficients of the transformation from the displacement coordinates ξ'_i, η'_i , etc., to the S coordinates are not all constant under the operations of the group D'_{3h} , the standard methods of reducing the representation formed by the displacement coordinates do not apply. By setting $\gamma=0$, however, in the expressions (5) for the S coordinates, we have a set of coordinates which are obtained from the original displacement coordinates by a transformation with constant coefficients and

which fully reduce the representation. The further transformation involving γ does not change the number of coordinates belonging to each irreducible representation of D'_{3h} .

⁸ F. Stitt and D. M. Yost, J. Chem. Phys. **5**, 90 (1937). We are indebted to Dr. Stitt for allowing us to see the manuscript of his paper before publication. He has pointed out to us two errors in his diagrams. In $\delta(\sigma)$ of XY_3 an arrow has been omitted and in $\nu_a(\sigma)$ of X_2Y_6 an arrow points in the wrong direction.

⁹ See reference 4; also C. Eckart, Phys. Rev. **47**, 552 (1935) and Wilson and Howard, J. Chem. Phys. **4**, 260 (1936).

¹⁰ Howard and Wilson, J. Chem. Phys. **2**, 630 (1934).

a certain irreducible representation will be formed out of orthogonal linear combinations of the symmetry coordinates of that representation. If the transformation from the symmetry coordinates to the normal coordinates does not involve γ the dependence of both sets of coordinates on γ will consequently be of the same nature. The transformation in question depends on γ only if the coefficients in the potential energy expressed in terms of the symmetry coordinates are functions of γ . We shall show in the following section that in the case of free internal rotation these coefficients are independent of γ . Consequently, we may, by virtue of Eqs. (5), write the coefficients of the transformation (2) to the normal coordinates for the case of free internal rotation in the following way, allowing s'_{ik} to denote l'_{ik} , m'_{ik} or n'_{ik} and s''_{ik} to denote l''_{ik} , m''_{ik} or n''_{ik} ,

$$s'_{ik} = s_{ik}; \quad s''_{ik} = s_{ik}, \quad k = 1, 2, 3, \quad (6a)$$

$$s'_{ik} = s_{ik}; \quad s''_{ik} = -s_{ik}, \quad k = 4, 5, \quad (6b)$$

$$\begin{aligned} s'_{ik\alpha} &= s_{ika} \cos \gamma - s_{ikb} \sin \gamma, \\ s'_{ik\beta} &= s_{ika} \sin \gamma + s_{ikb} \cos \gamma, \end{aligned} \quad k = 6, 7, 8, \quad (6c)$$

$$\begin{aligned} s''_{ik\alpha} &= s_{ika} \cos \gamma - s_{ikb} \sin \gamma, \\ s''_{ik\beta} &= -s_{ika} \sin \gamma - s_{ikb} \cos \gamma, \\ \bar{s}'_{ik\alpha} &= \bar{s}_{ika} \sin \gamma + \bar{s}_{ikb} \cos \gamma, \\ \bar{s}'_{ik\beta} &= -\bar{s}_{ika} \cos \gamma + \bar{s}_{ikb} \sin \gamma, \end{aligned} \quad \bar{k} = 9, 10, 11, \quad (6d)$$

$$\begin{aligned} \bar{s}''_{ik\alpha} &= \bar{s}_{ika} \sin \gamma + \bar{s}_{ikb} \cos \gamma, \\ \bar{s}''_{ik\beta} &= \bar{s}_{ika} \cos \gamma - \bar{s}_{ikb} \sin \gamma. \end{aligned}$$

The unprimed coefficients s_{ik} , s_{ika} , s_{ikb} are constants and show the relation between the singly and doubly primed coefficients. The numbering used above has been discarded but the distinction between the coordinates of the two types E and \bar{E} is still made by using k and \bar{k} to denote coordinates of different types. The above coefficients will be used in II in evaluating the kinetic energy.

POTENTIAL ENERGY

In terms of the symmetry coordinates, Eqs. (5), the most general quadratic potential function may be expressed as $V = \frac{1}{2} \sum C_{mn}(\gamma) S_m S_n + \Phi(\gamma)$. The force constants C_{mn} are functions

of γ , and Φ is the potential energy governing the internal rotation of the equilibrium framework. The only assumptions underlying this expression are that the equilibrium positions of the atoms do not change as γ changes and that for all values of γ the vibrations are of infinitesimal amplitude. Since the potential energy is invariant under the operations of the point group D_3 , which do not involve γ , there will be no cross terms between S_m 's of the A_1 and \bar{A}_2 types or between either of these and the degenerate type. The question arises as to whether there are cross terms between the E and \bar{E} coordinates. An investigation of the degenerate coordinates, Eqs. (5c, d), reveals that when one or more are excited, an internal rotation by $\pm 2\pi/6$ produces a vibration configuration physically equivalent to the initial configuration. Consequently, $C_{mn}(\gamma)$ must be such that if we expand it in a Fourier series about the position $\gamma = 0$

$$C_{mn} = A^0_{mn} + A'_{mn} \cos 6\gamma + A''_{mn} \cos 12\gamma + \dots \quad (7a)$$

$$\text{or } C_{mn} = B'_{mn} \sin 6\gamma + B''_{mn} \sin 12\gamma + \dots \quad (7b)$$

Since under the reflection (1), $S_m \rightarrow +S_m$ or $-S_m$ according as S_m belongs to the E or \bar{E} type, whereas the potential energy must be invariant, it is clear that between degenerate coordinates of the same type C_{mn} has the form (7a) and between degenerate coordinates of different types C_{mn} has the form (7b). The coefficients C_{mn} of the nondegenerate coordinates will have the form (7a).

Case of free internal rotation¹¹

If there is no interaction between H atoms of different groups and consequently no cross

¹¹ We shall speak of a molecule as having free internal rotation if the molecule in its *equilibrium* configuration undergoes internal rotation without a change in potential energy. If a change in potential energy is involved the molecule will be said to have restricted internal rotation; if the potential is of such magnitude that the internal motion is for practical purposes entirely a torsional vibration, the internal rotation will be said to be completely restricted. This conception of free internal rotation, which seems to be the common one and implies the absence of direct forces between H atoms in different CH_3 groups, does not necessarily imply that the classical vibration frequencies are independent of the internal angle. Although the latter is found to be true in the case of C_2H_6 with free internal rotation, molecules in which the rotating parts are not symmetrical tops will have vibrations whose reduced

terms between the displacement of such atoms in the potential function, it can be shown by direct substitution of the expressions (5) for the S coordinates in the potential energy that the coefficients of the symmetry coordinates in the resulting expression do not involve the internal angle γ . Although the interaction energy of a C atom of one group with the atoms of the other group depends upon the projection of the displacements of the former onto the coordinate system of the latter and thus depends upon γ , this explicit appearance of γ is removed when the symmetry coordinates are introduced.

The normal coordinates for free internal rotation will thus have the same dependence on γ as do the symmetry coordinates, Eqs. (5). The normal vibrations for any value of the internal angle will be the same as for a molecule restricted to an internal torsion-vibration about that value of the angle.¹² In the nondegenerate vibrations the motion of the atoms of a CH₃ group with reference to the rotating axis system (x' , y' , z' or x'' , y'' , z'') of that group does not change as the molecule undergoes internal rotation. With the degenerate vibrations, however, it is otherwise. In these the two C atoms, which move in parallel or antiparallel directions, continue to move in the same direction relative to the x , y axes (see Fig. 1b), despite the relative motion of the two CH₃ groups.¹³ Furthermore, if we hold a degenerate normal coordinate at a fixed non-zero

value and vary the internal angle, the displaced H atoms in the groups will pulsate with the frequency of internal rotation, preserving at each moment translational and rotational momenta of the molecule as a whole. A characteristic difference between the E and \bar{E} vibrations is that in the former the C atoms move in parallel directions, in the latter they move in antiparallel directions.

Case of restricted internal rotation

When interaction terms between H atoms of different CH₃ groups are introduced the potential energy coefficients of symmetry coordinates belonging to the same irreducible representation of D'_{3h} become of the form (7a). Let us imagine that we have chosen a set of coordinates Q^0_k such that $2V^0 = \sum A^0_{mn} S_m S_n = \sum \lambda_k (Q^0_k)^2$. If the potential restricting internal rotation is small we may treat $V' = (1/2) \cos 6\gamma \sum A'_{mn} S_m S_n = (1/2) \cos 6\gamma \sum \lambda'_k Q^0_k Q^0_l$ as a perturbation. The most important terms in the perturbation will be the squared terms, since the fundamental frequencies of vibrations of the same symmetry are widely separated. The restricting potential $\Phi(\gamma)$ may be represented by $B \cos 6\gamma$. Consequently, choosing an arbitrary vibrational state specified by the vibrational quantum numbers n_k , we may express the perturbation as one in γ alone, namely, as

$$V = \cos 6\gamma \{ (1/2) \sum \lambda'_{kk} [(Q^0_k)^2]_{n_k n_k} + B \} \\ = B' \cos 6\gamma, \quad (8)$$

in which $[(Q^0_k)^2]_{n_k n_k}$ is the average value of $(Q^0_k)^2$ in the vibrational state n_k . The problem of calculating the energy levels of the internal motion for a given vibrational state is thus reduced to the same problem as that for the case of rigid CH₃ groups.¹⁴ A calculation in which it is assumed that the forces between H atoms in different groups are repulsive and can be represented by a fraction¹⁵ of a Morse potential function shows that the value of $\sum \lambda'_{kk} [(Q^0_k)^2]_{n_k n_k}$ with all n_k 's equal to zero is less than 10 percent of the value of B . The percentage is independent of the fraction of the Morse curve chosen. The

masses contain the internal angles (L. S. Kassel, J. Chem. Phys. 3, 326 (1935)). Even though in this case there is, dynamically speaking, never actually free internal rotation, even in the ground vibrational state, it seems to us that it will avoid confusion if we retain the initial meaning of the term free internal rotation.

¹² The normal mode $Q_{M\gamma}$ is the sole representative of the \bar{A}_1 representation and hence cannot mix with any of the other normal modes.

¹³ The motion of the two C atoms in the same direction makes the frequency of vibration independent of the internal angle. The symmetry coordinates S_{6a} , S_{6b} , \bar{S}_{6a} , \bar{S}_{6b} , Eq. (5), necessarily entail this sort of motion since otherwise the vibration would give rise to an over-all translation or rotation. In the remaining symmetry coordinates of the degenerate type, translation and rotation are conserved by the CH₃ groups separately. Nevertheless, only when S_{6a} , S_{6b} , \bar{S}_{6a} , \bar{S}_{6b} are correct normal coordinates and when we can neglect the difference in energy between motions of the C atoms in parallel and antiparallel directions, in which case corresponding E and \bar{E} vibrations become accidentally degenerate, is it permissible for the C atoms to move in independent directions in a normal vibration. The proper vibrations for the lifting of the four-fold E , \bar{E} degeneracy are those in which the C atoms move in parallel and antiparallel directions. Only the former of these motions involves a resultant electric moment.

¹⁴ See Nielsen, Phys. Rev. 40, 445 (1932).

¹⁵ This is the assumption made by Eyring, J. Am. Chem. Soc. 54, 3191 (1932), and by Van Vleck and Cross, J. Chem. Phys. 1, 357 (1933).

TABLE I. Table of characters for the irreducible representations of the abstract group D'_{3h} and the distribution of the components of electric moment and polarizability and of the normal vibrations among the irreducible representations.

D'_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	I.R.	R	ν
A_1	1	1	1	1	1	1		$\alpha_{zz}, \alpha_x + \alpha_{yy}$	$\nu_1 \nu_2 \nu_3$
A_2	1	1	-1	1	1	-1			
\bar{A}_1	1	1	1	-1	-1	1			
\bar{A}_2	1	1	-1	-1	-1	-1	μ_z	$(-\alpha_{zz} + \alpha_{yy}, \alpha_{xy})^*$	$\nu_4 \nu_5$
E	2	-1	0	2	-1	0	μ_x, μ_y	α_{xz}, α_{yz}	$\nu_6 \nu_7 \nu_8$
\bar{E}	2	-1	0	-2	1	0			$\nu_9 \nu_{10} \nu_{11}$

* Consult the text.

energy levels of the internal motion are discussed further in II.

There is also a perturbation potential of the form

$$V' = (1/2) \sin 6\gamma \sum B'_{mn} S_m \bar{S}_n \\ = (1/2) \sin 6\gamma \sum \lambda_{kl} Q^0_k \bar{Q}^0_l \quad (9)$$

between E and \bar{E} coordinates which is important only when the E and \bar{E} vibrations are almost degenerate.

SELECTION RULES

In deriving the selection rules we shall assume that the electric moment and the polarizability of each CH_3 group depend only on the coordinates of that group and that the electric moment and the polarizability of the molecule are the sums of the moments and polarizabilities of the two groups. It is convenient to focus one's attention on the x, y, z system of axes since it is found that the components of electric moment relative to these axes involve only the normal coordinates and not the internal angle, and that the same is true with two exceptions in the case of the components of the polarizability tensor.

Table I shows the essential facts regarding the vibrational transitions in the infrared and Raman spectra for the case of *free internal rotation*. The column under I.R. contains the allocation of μ_x, μ_y, μ_z the components of electric moment, to the irreducible representations of D'_{3h} . Thus \bar{A}_2 vibrations will give rise to parallel type bands and E vibrations to perpendicular type bands in the infrared.¹⁶ In the column R is

¹⁶ Teller and Topley (reference 2) on the basis of the selection rules for a molecule with point group D_3 , which does not sufficiently describe the symmetry of the normal vibrations, concluded that all degenerate frequencies were active in the infrared.

the corresponding distribution of the components of the polarizability tensor relative to the x, y, z axes among the representations, indicating that the A_1, E and \bar{E} vibrations are Raman active. An unusual feature is presented by the components of the polarizability which fall into the E representation. The situation may be represented as follows if we expand polarizability components in terms of the normal coordinates and retain only the linear terms:

$$-\alpha_{zz} + \alpha_{yy} = \cos 3\gamma \sum \tau_k Q_{k\alpha} + \sin 3\gamma \sum \bar{\tau}_k \bar{Q}_{k\alpha}, \quad (10) \\ 2\alpha_{xy} = \cos 3\gamma \sum \tau_k Q_{k\beta} + \sin 3\gamma \sum \bar{\tau}_k \bar{Q}_{k\beta}.$$

In the last column of Table I the distribution of the normal vibrations among the representations is given in terms of the frequencies.

When a potential restricting internal rotation is introduced the vibrational selection rules remain unaltered except for the Raman activity of the E vibrations in the limit of complete restriction. This exception arises through the appearance of γ in the polarizability components of Eq. (10). If, in the limit of complete restriction of the internal rotation, $\gamma = 0, \pi/3$ or $2\pi/3$ and the molecule has a plane of symmetry perpendicular to the C—C axis, the E vibrations are active; they alone contribute to the components (10). If, on the other hand, $\gamma = \pi/6, \pi/2$ or $5\pi/6$ and the molecule has a center of symmetry, the E vibrations are inactive in the Raman spectrum since only the \bar{E} vibrations contribute to the polarizability. The selection rules for the internal motion are discussed in the subsequent paper. Since the frequencies of the degenerate vibrations do not actually appear in the Raman spectrum, probably because of too low intensity, the Raman vibrational spectrum offers no clue as to whether there is small or large restriction of internal rotation.

The statement that the vibrational selection rules remain unaltered with the exception just discussed requires amplification inasmuch as the perturbation (9), which appears only when there are forces restricting the internal rotation, would seem to couple E and \bar{E} vibrations. The coupling, however, involves the eigenfunctions for the internal rotation and transitions to \bar{E} vibrations from the ground vibrational state may occur only when accompanied by changes in the quantum

number of the internal rotation. Further discussion of this point is postponed until II. It is concluded there that the infrared vibrational spectrum also offers no conclusive evidence regarding internal rotation.

FUNDAMENTAL FREQUENCIES

There is a twofold purpose in attempting to apply a normal coordinate treatment with a simple potential function to such a complex molecule as C₂H₆. One of these is to determine an approximate set of normal coordinates with which the vibrational angular momenta may be estimated; these quantities have an important use in II. The other purpose is to compute a set of vibration frequencies which may serve as a guide in the interpretation of regions of the vibrational spectrum where assignments of frequencies are uncertain.

To calculate the vibrational frequencies we have chosen the following valence-force-type potential function, which is equally well suited to free and restricted internal rotation,

$$2V = K_1 \sum_i (\Delta r'^2_i + \Delta r''^2_i) + K_2 r_0^2 \left\{ \sum_{i,j} (\Delta \alpha'^2_{ij} + \Delta \alpha''^2_{ij}) + \sum_i (\Delta \beta'^2_i + \Delta \beta''^2_i) \right\} + K_3 \Delta R^2. \quad (11)$$

The single and double primes refer to different CH₃ groups and i, j refer to the three H atoms of a group. K_1, K_2, K_3 are force constants; $\Delta r'_i$ is the change in the C'-H'_{*i*} bond distance, $\Delta \alpha'_{ij}$ is the change in H'_{*i*}-C'-H'_{*j*} bond angle, ΔR is the change in the C'-C'' bond distance, $\Delta \beta'_i$ is the change in the H'_{*i*}-C'-C'' bond angle; r_0 is the equilibrium value of the C'-H' bond distance. It is to be noted that the force constants for the distortion of all bond angles are assumed to be the same, an assumption which can, perhaps, be justified only by the agreement with observed frequencies to which it leads. It is also assumed that the tetrahedral angles are preserved in CH₃.

Following are the equations giving the frequencies of vibration in terms of the force constants of (11). The equation for the three A_1 frequencies ν_1, ν_2, ν_3 is

$$\begin{aligned} \omega^3 - \omega^2(K_1 D + K'_2 E + K'_3) \\ + \omega(K_1 K'_2 F + K_1 K'_3 + K'_2 K'_3) \\ - K_1 K'_2 K'_3 = 0, \quad (12) \end{aligned}$$

$$\begin{aligned} \text{where } \omega = 4\pi^2 m \nu^2, \quad D = (3m\tau^2/M) + 1, \\ E = (3m\mu^2/M) + 1, \quad F = (3m/M) + 1, \\ K'_3 = (2m/M)K_3, \quad K'_2 = (Z+1)K_2, \\ Z = 12\tau^2/(4-3\mu^2); \end{aligned}$$

m and M are the masses of the H and C atoms, respectively; $\mu = \sin \beta^0$ and $\tau = \cos \beta^0$ where β^0 is the equilibrium value of the bond angle H'-C'-C''. The equation for the \bar{A}_2 frequencies ν_4, ν_5 may be obtained from Eq. (12) by letting $K'_3 = 0$. The E frequencies ν_6, ν_7, ν_8 are the roots of the equation

$$\begin{aligned} \omega^3 - \omega^2 \{ K_1 L/2 + K''_2 Q/2 + K_2 [2(F+1) \\ + G\tau^2]/2L \} + \omega \{ K_1 K''_2 N + K_1 K_2 (F+1)/2 \\ + K''_2 K_2 [4F+G(1+\tau^2)]/2L \} \\ - K_1 K''_2 K_2 F = 0, \quad (13) \end{aligned}$$

where $L = E + 1$, $Q = [(3m\mu^2/M) - 2]\mu^2 + 4$,

$$G = (3m\mu/M)^2, \quad N = L - \mu^2, \quad K''_2 = 3K_2/(4-3\mu^2)$$

and the other quantities are given above. The equation for the \bar{E} frequencies $\nu_9, \nu_{10}, \nu_{11}$ is too complicated to be reproduced here.

Table II gives the results of the calculation. The "calculated" frequencies enclosed in paren-

TABLE II. Observed and calculated frequencies in cm⁻¹ and force constants in dynes/cm for C₂H₆. The observed frequencies were obtained from the following sources: Infrared (gas),¹⁷ Raman (gas),¹⁸ Raman (gas),¹⁹ Raman (liq.).²⁰

	OBS.	CALC.		OBS.	CALC.
ν_1	993	(993)	ν_6	827	840
ν_2	1460	1570	ν_7	1480	1480
	(liq.)	2910	ν_8	3000	3020
ν_3	2927*		ν_9	—	1005
ν_4	1380	(1380)	ν_{10}	—	1515
ν_5	2926†	(2900)	ν_{11}	—	3025
$K_1 = 4.79 \times 10^5$			$K_2 = 0.46 \times 10^5$		
			$K_3 = 5.62 \times 10^5$		

* $\nu_3 = 2927$ cm⁻¹ is the mean of the two Raman frequencies 2899 cm⁻¹ and 2955 cm⁻¹.

† $\nu_5 = 2926$ cm⁻¹ is the mean of the two infrared frequencies 2896 cm⁻¹ and 2955 cm⁻¹.

¹⁷ Levin and Meyer, J. Opt. Soc. Am. **16**, 137 (1928).

¹⁸ Lewis and Houston, Phys. Rev. **44**, 903 (1933).

¹⁹ Bhagavantam, Ind. J. Phys. **6**, 595 (1932).

²⁰ Daure, Ann. de physique **12**, 375 (1929).

theses were used to evaluate K_1 , K_2 , K_3 . The other frequencies calculated with the values of the force constants so obtained agree surprisingly well with the remaining eight observed frequencies except for ν_2 , the calculated value of which is 8 percent higher than the shift of 1460 cm^{-1} observed in the Raman spectrum²⁰ of liquid C_2H_6 . We assign this strong Raman line tentatively to ν_2 following Sutherland and Denison.¹ The pair of Raman frequencies 2899 and 2955 cm^{-1} probably arises from resonance between ν_3 and $2\nu_7$ in close analogy to the resonance proposed by Barker and Adel²¹ for the methyl halides. The overtone corresponding to $2\nu_{10}$ likewise has an A_1 component which could resonate with ν_3 but, lacking other evidence, we shall have to assume there is sufficient difference between the values of $2\nu_7$ and $2\nu_{10}$ to explain the appearance of two rather than three Raman lines. Similarly the pair of infrared frequencies 2896 and 2955 cm^{-1} probably arises from resonance between ν_5 and $\nu_7 + \nu_{10}$. The ν_7 and ν_{10} and also the ν_8 and ν_{11} vibrations are very similar except for a phase difference of π in the vibrations of one CH_3 group, and the vibration corresponding to $\nu_7 + \nu_{10}$ has an \tilde{A}_2 component which may resonate with ν_5 . The correctness of the first interpretation could be tested by polarization measurements on the pair of Raman lines in question. It is possible that the weak Raman line of frequency 975 cm^{-1} found by Bhagavantam¹⁹ corresponds to ν_9 . Kemp and Pitzer²² have found that the heat capacity of C_2H_6 in the range 140 to 400°K is well reproduced with statistical-mechanical calculations based upon a restricting potential of about 3150 cal. and a value of 1160 cm^{-1} for ν_9 .

²¹ Adel and Barker, J. Chem. Phys. 2, 627 (1934).

²² We wish to thank Doctors Kemp and Pitzer for permitting us to see a copy of their paper on the entropy of C_2H_6 before publication.

In the infrared rotation-vibration spectrum obtained by Levin and Meyer¹⁷ there is scarcely more evidence for two perpendicular type bands in the ν_7 (1480) region, differing by about 30 cm^{-1} , than in the very similar band of CH_3F . The same may be said of the band corresponding to $\nu_8 = 3000 \text{ cm}^{-1}$. Yet Bartholomé and Sachsse,²³ using less resolving power, which revealed only the band envelopes, found distinct evidence of two bands of approximately equal intensity at 1465 and 1495 cm^{-1} . We have seen that through the perturbation (9) there may be a coupling of E and \tilde{E} vibrations whereby the latter may become active in the infrared, but the selection rules governing the appearance of the \tilde{E} vibrations involve a change in the quantum number of the internal rotation (or torsion oscillation). A further discussion of this point is deferred to II where it is concluded that the second band found by Bartholomé and Sachsse cannot be satisfactorily explained as a fundamental \tilde{E} frequency.

CONCLUSION

The fundamental region of the vibrational Raman and infrared spectra of C_2H_6 is satisfactorily accounted for with the selection rules of the point group D'_{3h} and the frequencies calculated with a three-constant valence-force type of potential function, without knowledge of the magnitude of the restriction of the internal rotation, except for a doubtful point introduced by the two infrared bands found by Bartholomé and Sachsse in the 1480 cm^{-1} region. This point is discussed in the subsequent paper along with additional evidence bearing on the magnitude of the potential between CH_3 groups.

²³ Bartholomé and Sachsse, Zeits. f. physik. Chemie B30, 40 (1935).