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The Normal Modes and Frequencies of Vibration of the Regular Plane Hexagon Model of the Benzene Molecule*

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The thirty modes of vibration of the regular plane hexagon model for the benzene molecule, including both the hydrogen and carbon atoms, are derived by the group theory method described by Wigner. From these the twenty frequencies of vibration are calculated in terms of a simple potential function involving six force constants. Selection rules for the Raman and infrared spectra are listed. Seven fundamentals are permitted in the Raman spectrum and four fundamentals in the infrared. Both analytical and graphical descriptions of the modes of vibration are given. These depend largely on the symmetry of the molecule and are only in part influenced by the choice of potential function adopted.

INTRODUCTION

IN interpreting the infrared and Raman spectra of polyatomic molecules, it is customary to assume that the potential function for the forces between the atoms can be represented with sufficient accuracy by retaining only the quadratic terms in its Taylor expansion in powers of the coordinates.[1] With this restriction, which is equivalent from the classical mechanical standpoint to the assumption that the vibrations are of small amplitude compared to the interatomic distances, it is possible to obtain the fundamental frequencies and normal modes of vibration of the molecule as functions of the force constants. This has been done by a straightforward procedure for a number of simple cases,[2] but complicated molecules, even with high symmetry, are very difficult to treat without more powerful methods.

Wigner[3] has shown that group theory greatly simplifies the process of obtaining the normal modes of vibration of symmetric molecules. In this paper I have applied his method to benzene, obtaining the normal vibrations and frequencies; in addition, the selection rules for the infrared and Raman spectra are given.

MATHEMATICAL METHODS

The positions of the atoms in the molecule are described by giving the Cartesian coordinates of each atom referred to the equilibrium position of the atom as origin. It is convenient to change the scale of the coordinates by the relation

$$q_i = m_i^{\frac{1}{2}} q_i', \tag{1}$$

in which q_i' is the ith coordinate in ordinary units, m_i the mass of the atom whose coordinates are concerned, and q_i the new coordinate. For small oscillations, the kinetic and potential energies are

$$2T = \sum_i \dot{q}_i^2, \quad 2V = \sum_{ij} a_{ij} q_i q_j. \tag{2}$$

The problem of finding the normal modes of vibration and frequencies is solved when the transformation

$$q_i = \sum_k l_{ik} Q_k \tag{3}$$

has been obtained which transforms T and V into

$$2T = \sum_k \dot{Q}_k^2, \quad 2V = \sum_k \lambda_k Q_k^2. \tag{4}$$

The Q_k's are the normal coordinates and the λ_k's are related to the frequencies ν_k by the equation

$$\lambda_k = 4\pi^2 \nu_k^2. \tag{5}$$

To obtain the coefficients l_{ik} and the frequencies

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* Contribution No. 396.

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

[2] Some of these are given by K. W. F. Kohlrausch, *Der Smekal-Raman Effekt.* Springer, Berlin, 1931.

[3] E. Wigner, *Göttinger Nachrichten*, p. 133, 1930.

it is necessary to solve the secular equation

$$|a_{ij}-\delta_{ij}\lambda|=0, \tag{6}$$

in which δ_{ij} is unity if i equals j and zero otherwise.

The solution of the secular equation is facilitated by a knowledge of the symmetry of the molecule, which can be specified by giving the *symmetry operations* which transform the molecule into itself. Thus there are twenty-four symmetry operations which transform the regular plane hexagon model of benzene into itself. These include rotations about symmetry axes, reflections in symmetry planes, inversion through a center of symmetry, and rotations about axes combined with reflections in planes perpendicular to the axes. The set of such operations for a molecule forms a *point group*, which has the characteristic group property that the effect of any two operations applied successively is equivalent to the operation of some one member of the group.

Since the application of a symmetry operation R of the undistorted molecule leaves the molecule in a condition indistinguishable from its original position, the potential and kinetic energies are invariant under all such operations. As may be seen by considering Eq. (4), this restricts the possible modes of vibration Q_k. If Q_k is a non-degenerate vibration; i.e., if λ_k has a value distinct from the other λ's, then Q_k must be either symmetric or antisymmetric with respect to the symmetry operations of the point group G of the molecule. If Q_k is degenerate; i.e., if there are several vibrations, say Q_1, Q_2, Q_3, with the same frequency, then the application of a symmetry operation will transform each of these degenerate vibrations into a linear combination of the three.

$$RQ_k\rightarrow Q_k \quad (Q_k \text{ is symmetric to } R), \tag{7}$$

$$RQ_k\rightarrow -Q_k \quad (Q_k \text{ is antisymmetric to } R), \tag{8}$$

$$RQ_k\rightarrow \sum_n R_{kn}Q_n \quad (\text{degenerate}). \tag{9}$$

The sum is over all the Q_n's with the same λ.

The symmetry of the molecule restricts still further the normal coordinates. In the theory of groups it is proved that each group G has only a certain number of *irreducible representations*[4] Γ_1, Γ_2, $\cdots\Gamma_r$, each of which represents a type of symmetry which is allowed for the normal coordinates of a molecule with point group G. Every Q_k must belong to a symmetry type which is correlated with one of the Γ_i's belonging to G, but for a given molecule every symmetry type Γ_i may not be represented among the Q_k's and more than one Q_k may have the same symmetry.[3]

The sum of the diagonal coefficients R_{kk} in the transformation of Eq. (9) is called the *character* χ_R of the operation R when applied to the set Q_k which have the same λ.

$$\chi_R=\sum_k R_{kk}. \tag{10}$$

From this definition and Eqs. (7) and (8) it is clear that the character of an operation for a non-degenerate Q_k must be equal to $+1$ or -1. The manner in which the symmetry of a given normal coordinate is restricted by the knowledge of the Γ_i to which it belongs is illustrated by Table I. The numbers in this table are the characters $\chi_R^{(i)}$ for each symmetry operation R when applied to a Q_k or set of Q_k's with the same λ which belong to the symmetry type of Γ_i. Table I is for the point group D_{6h} to which benzene is assumed to belong. Wigner[3] has published such tables for each of the crystallographic point groups and their construction is described in standard works on group theory.[4]

TABLE I. *Values of $\chi_j^{(i)}$ for the point group D_{6h} and of χ_j' for benzene.*

$R=$	E	C_2	C_3	C_6	C_2'	C_2''	i	σ_h	S_6	S_3	σ_v''	σ_v'
A_{1g} Γ_1	1	1	1	1	1	1	1	1	1	1	1	1
A_{2g} Γ_2	1	1	1	1	−1	−1	1	1	1	1	−1	−1
B_{1g} Γ_3	1	−1	1	−1	1	−1	1	−1	1	−1	1	−1
B_{2g} Γ_4	1	−1	1	−1	−1	1	1	−1	1	−1	−1	1
E_{2g} Γ_5	2	2	−1	−1	0	0	2	2	−1	−1	0	0
E_{1g} Γ_6	2	−2	−1	1	0	0	2	−2	−1	1	0	0
A_{1u} Γ_7	1	1	1	1	1	1	−1	−1	−1	−1	−1	−1
A_{2u} Γ_8	1	1	1	1	−1	−1	−1	−1	−1	−1	1	1
B_{1u} Γ_9	1	−1	1	−1	1	−1	−1	1	−1	1	−1	1
B_{2u} Γ_{10}	1	−1	1	−1	−1	1	−1	1	−1	1	1	−1
E_{2u} Γ_{11}	2	2	−1	−1	0	0	−2	−2	1	1	0	0
E_{1u} Γ_{12}	2	−2	−1	1	0	0	−2	2	1	−1	0	0
h_j	1	1	2	2	3	3	1	1	2	2	3	3
χ_j'	36	0	0	0	−4	0	0	12	0	0	0	4
$h_j\chi_j'$	36	0	0	0	−12	0	0	12	0	0	0	12

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[4] A. Speiser, *Theorie der Gruppen von endlicher Ordnung.* Springer, Berlin, 1927.

The number n_i of Q_k's which have the characters corresponding to Γ_i is given by the group theory formula

$$n_i = (1/N)\sum_R \chi_R^{(i)}\chi_R'. \tag{11}$$

Here N is the number of symmetry operations of G, $\chi_R^{(i)}$ is the character of R in Γ_i, and χ_R' is a new quantity, the character of R when applied to the original set of coordinates q_i. Thus if

$$Rq_i = \sum_j \tau_{ij}q_j \tag{12}$$

summed over all the q_j's, then

$$\chi_R' = \sum_i \tau_{ii}. \tag{13}$$

There is a simple theorem which shortens the labor of the calculation: the symmetry operations of a group G can be divided into *classes* such that χ_R for every member R of the same class is the same. This applies both to $\chi_R^{(i)}$ and to χ_R'. If h_j is the number of operations and χ_j is the character of the operations in the jth class, then Eq. (11) becomes

$$n_i = (1/N)\sum_j h_j\chi_j^{(i)}\chi_j' \tag{14}$$

and we need to calculate χ_j' for only one member of each class. The n_i's give the number of Q_k's which have the symmetry properties $(\chi_R^{(i)})$ of Γ_i. We may symbolize this by writing:

$$\Gamma_{\text{benzene}} = \sum_i n_i\Gamma_i. \tag{15}$$

Six Q_k's will correspond to translation and rotation of the molecule as a whole. The symmetry classes to which these belong may be found by inspection, and a new set of numbers n_i' obtained which gives the number of purely internal motions of each symmetry class.

By using the symmetry of the molecule it is possible to factor the secular Eq. (6) into a number of equations of lower degree. Group theory provides the theorem: the degree of the factor of the secular equation from which the Q_k's belonging to Γ_i are obtained is n_i' and this factor is repeated $\chi_E^{(i)}$ times, where $\chi_E^{(i)}$ is the character of the identity operation E for Γ_i. A corollary is, therefore, that the roots λ_k of this factor will have a multiplicity $\chi_E^{(i)}$.

APPLICATION TO BENZENE

The model assumed for benzene is the usual regular plane hexagon with the carbon and hydrogen atoms lying in the same plane as is shown in Fig. 1. The thirty-six q's are shown in Fig. 2 and form systems of rectangular coordinates with origin at the equilibrium position of each atom. R_i, Y_i, Z_i and r_i, y_i, z_i are the coordinates of the ith carbon and the ith hydrogen atom, respectively. The R_i, r_i point radially outward as shown in Fig. 2, while the Z_i, z_i are perpendicular to the plane of the ring.

The symmetry operations of this model are also shown in Fig. 2; they fall into the following twelve classes. $E(h_1=1)$ identity; $C_2(h_2=1)$ rotation by π about the six-fold axis; $C_3(h_3=2)$ rotation by $\pm 2\pi/3$ about the six-fold axis; $C_6(h_4=2)$ rotation by $\pm\pi/3$ about the six-fold axis; $C_2'(h_5=3)$ rotation by π about axes P, Q, R; $C_2''(h_6=3)$ rotation by π about axes T, U, V; $i(h_7=1)$ inversion through the center of symmetry; $\sigma_h(h_8=1)$ reflection through the plane of symmetry in the XY plane; $S_6(h_9=2)$ rotatory-reflection about the six-fold axis by $\pm\pi/3$; $S_3(h_{10}=2)$ rotatory-reflection about the six-fold axis by $\pm 2\pi/3$; $\sigma_V''(h_{11}=3)$ reflection through planes D, F, G; $\sigma_V'(h_{12}=3)$ reflection through planes A, B, C. These operations form the point group D_{6h}.

Table I gives the characters $\chi_j^{(i)}$ for the twelve irreducible representations of D_{6h}, which has twenty-four operations as listed above. In addi-

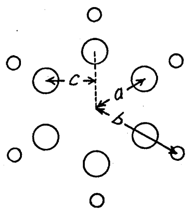

FIG. 1. Model of benzene.

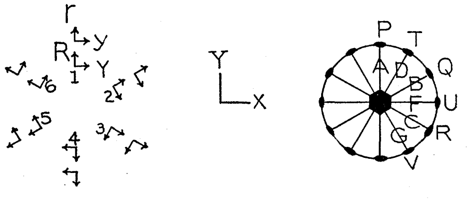

FIG. 2. Coordinates and symmetry of benzene.

tion to the symbols Γ_1, Γ_2, $\cdots\Gamma_{12}$ for the irreducible representations which were used in the general discussion, Tisza's[5] symbols, A_g, A_u, etc., are given. These are more useful for specific applications since they are more descriptive. Thus A and B refer to non-degenerate, E_1, E_2 to degenerate types of vibration. The subscript g means that the vibration is symmetric with respect to the inversion i, while u means that it is anti-symmetric to i. A refers to vibrations that are symmetric to rotation by $2\pi/n$ about the n-fold axis; B labels vibrations which are anti-symmetric to this operation. Table I also gives the characters χ_j' of the *reducible representation;* i.e., the q_i's or R_i, Y_i, Z_i, r_i, y_i, z_i. The operation of C_2, for example, on the molecule moves every atom to a new position. Therefore, in the transformation Eq. (12), each of the τ_{ii} must be zero so that χ_R' is zero for C_2. The same is true for the operations belonging to the classes C_3, C_6, C_2'', i, S_6, S_3, and σ_V''. This illustrates that it is only the unshifted atoms which contribute to χ_j'. Thus reflection of the molecule through the plane of symmetry A shifts all but the atoms C_1, C_4, H_1, H_4. For these:

$$\begin{aligned} AR_1&\rightarrow R_1, & Ar_1&\rightarrow r_1, \\ AY_1&\rightarrow -Y_1, & Ay_1&\rightarrow -y_1, \\ AZ_1&\rightarrow Z_1, & Az_1&\rightarrow z_1. \end{aligned} \tag{16}$$

with similar equations for C_4, H_4. The sum of the coefficients τ_{ii} is thus $+4$.

When the values of $h_j\chi_j'$ and $\chi_j^{(i)}$ from Table I are substituted in Eq. (14), the result is obtained that:

$$\begin{aligned} \Gamma_{\text{benzene}} = &\underset{(1)}{2\Gamma_1}+\underset{(1)}{2\Gamma_2}+\underset{(1)}{2\Gamma_4}+\underset{(2)}{4\Gamma_5}+\underset{(2)}{2\Gamma_6} \\ &+\underset{(1)}{2\Gamma_8}+\underset{(1)}{2\Gamma_9}+\underset{(1)}{2\Gamma_{10}}+\underset{(2)}{2\Gamma_{11}}+\underset{(2)}{4\Gamma_{12}}. \end{aligned} \tag{17}$$

The figures in parentheses indicate the multiplicities of the frequencies derived from the corresponding Γ_i.

Before interpreting this in terms of frequencies and factors of the secular equation, it is convenient to eliminate the Q_k's which refer to translation and rotation of the molecule as a whole, since they do not enter into the calculation of the frequencies. In Fig. 3, which shows the modes of vibration of benzene, Y, Z, ω_Y, ω_Z represent translation and rotation with respect to the Y and Z axes, and the remaining translation and rotation are of course related to Y and ω_Y by a rotation about the six-fold axis. The symmetry properties of these motions, obtained by inspection, show that Q_z belongs to Γ_8 and Q_{ω_z} to Γ_2, while Q_x, Q_y and Q_{ω_x}, Q_{ω_y} are two sets of degenerate modes belonging to Γ_{12} and Γ_6, respectively. When these are taken out, we obtain:

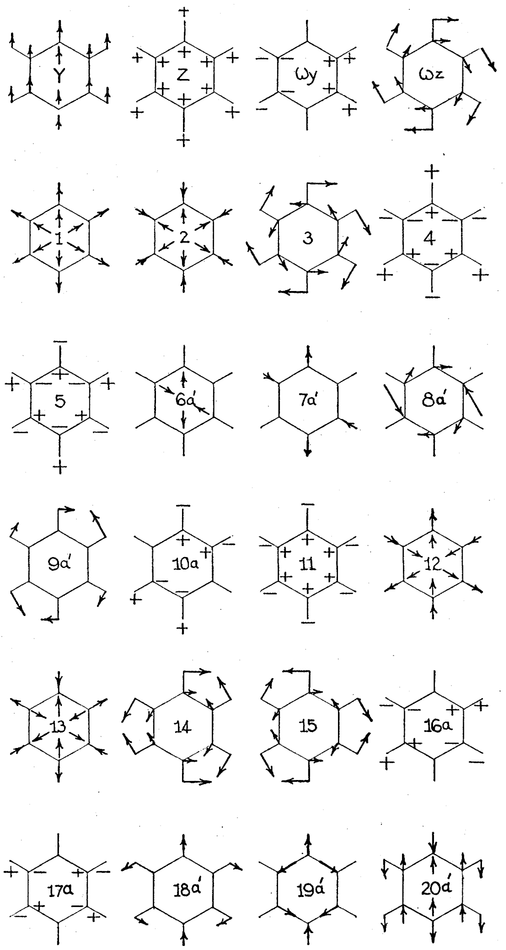

FIG. 3. Modes of vibration of benzene. $6a'$, $7a'$, $8a'$, $9a'$ must be combined to give four true modes, and $18a'$, $19a'$, $20a'$ must be similarly combined.

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[5] L. Tisza, Zeits. f. Physik **82**, 48 (1933).

$$\Gamma'_{\text{benzene}}=2\Gamma_1+\Gamma_2+2\Gamma_4+4\Gamma_5+\Gamma_6+\Gamma_8+2\Gamma_9+2\Gamma_{10}+2\Gamma_{11}+3\Gamma_{12}, \quad (18)$$

or, using the other type of symbols:

$$\Gamma'_{\text{benzene}}=2A_{1g}+A_{2g}+2B_{2g}+4E_{2g}+E_{1g}+A_{2u}+2B_{1u}+2B_{2u}+2E_{2u}+3E_{1u}. \quad (18a)$$

From this we immediately obtain the following information: There are 20 different frequencies, of which 10 are double. The secular equation may be factored by the use of symmetry and without regard to the type of forces involved, into four linear factors of which two are equal (Γ_2, Γ_8, $\Gamma_6(2)$), six quadratic factors of which two are equal (Γ_1, Γ_4, Γ_9, Γ_{10}, $\Gamma_{11}(2)$), two equal cubic factors ($\Gamma_{12}(2)$), and two equal quartic factors ($\Gamma_5(2)$).

TABLE II. *Selection rules for fundamentals in the infrared and Raman spectra.*

Frequencies permitted in Raman spectrum:
ν_1, ν_2, ν_6*, ν_7*, ν_8*, ν_9*, ν_{10}*.
Frequencies permitted in infrared spectrum:
ν_{11}, ν_{18}, ν_{19}, ν_{20}.

* These lines should have a depolarization of $\frac{3}{4}$.

Furthermore, this information is sufficient to determine the modes of vibration shown in Fig. 3 and described in the next section. Additional information which comes from the symmetry discussion is contained in Table II, which gives the selection rules for the Raman and infrared spectra. These were obtained directly from the general table given by Placzek.[5a]

NORMAL COORDINATES FOR BENZENE

The coefficients l_{ki} of the transformation of Eq. (3) have certain properties which assist in their determination, such as, for example,

$$\sum_k l_{ki}l_{kj}=\begin{cases}0 \text{ if } i\neq j.\\ 1 \text{ if } i=j.\end{cases} \quad (19)$$

The inverse transformation to Eq. (3) is

$$Q_i=\sum_k l_{ki}q_k. \quad (20)$$

By using the symmetry requirements of Eq. (17) and Table I, together with the restrictions of Eq. (19), we obtain the following combinations Q_i', which are either the normal coordinates Q_i themselves (if they belong to a linear factor of the secular equation) or functions which must be combined with one or more others in order to obtain the normal coordinates (if they belong to factors of higher degree). Q_1 indicates the normal coordinate with frequency ν_1. Q_{10a}, Q_{10b} indicate two normal coordinates with the same frequency ν_{10}. Any linear combination of these two will also have the same frequency, Q_4', Q_5' connected by a parenthesis indicate that two independent combinations of these, with coefficients dependent on the force constants and determined by solving a quadratic factor of the secular equation, are the normal coordinates for ν_4 and ν_5.

$$\left.\begin{aligned}Q_X&=m^{\frac{1}{2}}[3^{\frac{1}{2}}(r_2+r_3-r_5-r_6)+2y_1+y_2-y_3-2y_4-y_5+y_6]\\&\quad+M^{\frac{1}{2}}[3^{\frac{1}{2}}(R_2+R_3-R_5-R_6)+2Y_1+Y_2-Y_3-2Y_4-Y_5+Y_6].\\Q_Y&=m^{\frac{1}{2}}[2r_1+r_2-r_3-2r_4-r_5+r_6-3^{\frac{1}{2}}(y_2+y_3-y_5-y_6)]\\&\quad+M^{\frac{1}{2}}[2R_1+R_2-R_3-2R_4-R_5+R_6-3^{\frac{1}{2}}(Y_2+Y_3-Y_5-Y_6)].\end{aligned}\right\} \quad (\Gamma_{12}(2))$$

$$Q_Z=m^{\frac{1}{2}}(z_1+z_2+z_3+z_4+z_5+z_6)+M^{\frac{1}{2}}(Z_1+Z_2+Z_3+Z_4+Z_5+Z_6). \quad (\Gamma_8)$$

$$\left.\begin{aligned}Q_{\omega_x}&=bm^{\frac{1}{2}}(2z_1+z_2-z_3-2z_4-z_5+z_6)+aM^{\frac{1}{2}}(2Z_1+Z_2-Z_3-2Z_4-Z_5+Z_6).\\Q_{\omega_y}&=bm^{\frac{1}{2}}(z_2+z_3-z_5-z_6)+aM^{\frac{1}{2}}(Z_2+Z_3-Z_5-Z_6).\end{aligned}\right] \quad (\Gamma_6(2))$$

[5a] G. Placzek, *The Structure of Molecules* (edited by P. Debye), Blackie and Son, London, 1932.

$$Q_{\omega_z}=bm^{\frac{1}{2}}(y_1+y_2+y_3+y_4+y_5+y_6)+aM^{\frac{1}{2}}(Y_1+Y_2+Y_3+Y_4+Y_5+Y_6). \qquad (\Gamma_2)$$

$$\left.\begin{aligned}Q_1'&=R_1+R_2+R_3+R_4+R_5+R_6.\\ Q_2'&=r_1+r_2+r_3+r_4+r_5+r_6.\end{aligned}\right] \qquad (2\Gamma_1)$$

$$Q_3=aM^{\frac{1}{2}}(y_1+y_2+y_3+y_4+y_5+y_6)-bm^{\frac{1}{2}}(Y_1+Y_2+Y_3+Y_4+Y_5+Y_6). \qquad (\Gamma_2)$$

$$\left.\begin{aligned}Q_4'&=Z_1-Z_2+Z_3-Z_4+Z_5-Z_6.\\ Q_5'&=z_1-z_2+z_3-z_4+z_5-z_6.\end{aligned}\right] \qquad (2\Gamma_4)$$

$$\left.\begin{aligned}Q_{6a}'&=R_1-R_3+R_4-R_6. & Q_{6b}'&=R_1-2R_2+R_3+R_4-2R_5+R_6.\\ Q_{7a}'&=r_1-r_3+r_4-r_6. & Q_{7b}'&=r_1-2r_2+r_3+r_4-2r_5+r_6.\\ Q_{8a}'&=Y_1-2Y_2+Y_3+Y_4-2Y_5+Y_6. & Q_{8b}'&=Y_1-Y_3+Y_4-Y_6.\\ Q_{9a}'&=y_1-2y_2+y_3+y_4-2y_5+y_6. & Q_{9b}'&=y_1-y_3+y_4-y_6.\end{aligned}\right] \qquad (4\Gamma_5(2))$$

$$\left.\begin{aligned}Q_{10a}&=aM^{\frac{1}{2}}(z_1+z_2-z_4-z_5)-bm^{\frac{1}{2}}(Z_1+Z_2-Z_4-Z_5).\\ Q_{10b}&=aM^{\frac{1}{2}}(z_1-z_2-2z_3-z_4+z_5+2z_6)-bm^{\frac{1}{2}}(Z_1-Z_2-2Z_3-Z_4+Z_5+2Z_6).\end{aligned}\right] \qquad (\Gamma_6(2))$$

$$Q_{11}=M^{\frac{1}{2}}(z_1+z_2+z_3+z_4+z_5+z_6)-m^{\frac{1}{2}}(Z_1+Z_2+Z_3+Z_4+Z_5+Z_6). \qquad (\Gamma_8)$$

$$\left.\begin{aligned}Q_{12}'&=R_1-R_2+R_3-R_4+R_5-R_6.\\ Q_{13}'&=r_1-r_2+r_3-r_4+r_5-r_6.\end{aligned}\right](2\Gamma_9) \qquad \left.\begin{aligned}Q_{14}'&=Y_1-Y_2+Y_3-Y_4+Y_5-Y_6.\\ Q_{15}'&=y_1-y_2+y_3-y_4+y_5-y_6.\end{aligned}\right] \qquad (2\Gamma_{10})$$

$$\begin{aligned}Q'_{16a}&=Z_2-Z_3+Z_5-Z_6.\\ Q'_{17a}&=z_2-z_3+z_5-z_6.\end{aligned} \qquad \left[\begin{aligned}Q'_{16b}&=2Z_1-Z_2-Z_3+2Z_4-Z_5-Z_6.\\ Q'_{17b}&=2z_1-z_2-z_3+2z_4-z_5-z_6.\end{aligned}\right] \qquad (2\Gamma_{11}(2))$$

$$\left.\begin{aligned}Q'_{18a}&=2r_1+r_2-r_3-2r_4-r_5+r_6+3^{\frac{1}{2}}(y_2+y_3-y_5-y_6).\\ Q'_{19a}&=2R_1+R_2-R_3-2R_4-R_5+R_6+3^{\frac{1}{2}}(Y_2+Y_3-Y_5-Y_6).\\ Q'_{20a}&=M^{\frac{1}{2}}[2r_1+r_2-r_3-2r_4-r_5+r_6-3^{\frac{1}{2}}(y_2+y_3-y_5-y_6)]\\ &\qquad -m^{\frac{1}{2}}[2R_1+R_2-R_3-2R_4-R_5+R_6-3^{\frac{1}{2}}(Y_2+Y_3-Y_5-Y_6)].\\ Q'_{18b}&=3^{\frac{1}{2}}(r_2+r_3-r_5-r_6)-(2y_1+y_2-y_3-2y_4-y_5+y_6).\\ Q'_{19b}&=3^{\frac{1}{2}}(R_2+R_3-R_5-R_6)-(2Y_1+Y_2-Y_3-2Y_4-Y_5+Y_6).\\ Q'_{20b}&=M^{\frac{1}{2}}[3^{\frac{1}{2}}(r_2+r_3-r_5-r_6)+(2y_1+y_2-y_3-2y_4-y_5+y_6)]\\ &\qquad -m^{\frac{1}{2}}[3^{\frac{1}{2}}(R_2+R_3-R_5-R_6)+(2Y_1+Y_2-Y_3-2Y_4-Y_5+Y_6)].\end{aligned}\right] \qquad (3\Gamma_{12}(2))$$

The above equations should be multiplied by appropriate factors in order that they may be normalized in the sense of Eq. (19). a and b are the radii of the carbon and hydrogen rings, respectively; while M and m are the masses of the carbon and hydrogen atoms.

Fig. 3 shows these modes diagrammatically. The component along any coordinate direction of the arrow attached to a given atom gives the coefficient of that coordinate in the above expressions. Since these numbers are also the coefficients in the reverse transformation of Eq. (3), they represent the amplitudes of the motions of the atoms in the corresponding modes of vibration. Plus and minus signs refer to motions perpendicular to the plane of the paper.

POTENTIAL ENERGY FUNCTION

When the modes of vibration are known and the potential energy as a quadratic function of the coordinates is given, it is possible to calculate the corresponding frequencies. In this treatment a much simplified potential function was used, involving only six force constants: K, q, κ, h, H, k. Fig. 4 shows some of the coordinates of the distorted molecule in terms of which the potential energy is expressed.

K is the constant for the stretching of the carbon-carbon bond and q is the corresponding constant for the carbon-hydrogen bond.

$$\therefore \quad 2V_1 = K\{(\Delta R_{12})^2 + (\Delta R_{23})^2 + (\Delta R_{34})^2 + (\Delta R_{45})^2 + (\Delta R_{56})^2 + (\Delta R_{61})^2\}. \quad (21)$$

$$2V_2 = q\{(\Delta S_1)^2 + (\Delta S_2)^2 + (\Delta S_3)^2 + (\Delta S_4)^2 + (\Delta S_5)^2 + (\Delta S_6)^2\}. \quad (22)$$

According to the quantum-mechanical view of the structure of benzene,[6] each of the carbon-carbon bonds is of partially double bond character, which would give the bond a resistance to twisting such as is found in ethylene. κ is the force constant for this twisting and enters into the equations whenever the carbon atoms move out of a plane. This is seen if any four adjacent carbon atoms are considered and the effect on the central bond of motion out of the plane is calculated.

$$\therefore \quad 2V_3 = \kappa c^2(\varphi_{12}^2 + \varphi_{23}^2 + \varphi_{34}^2 + \varphi_{45}^2 + \varphi_{56}^2 + \varphi_{61}^2). \quad (23)$$

φ_{12} is the angle of twist of the bond between the first and second carbon atoms, while c is the length indicated in Fig. 1. h is the force constant for the bending of the carbon-hydrogen bond out of the plane of the three adjacent carbon atoms. μ_i is the angle of this bending.

$$\therefore \quad 2V_4 = h(b-a)^2(\mu_1^2 + \mu_2^2 + \mu_3^2 + \mu_4^2 + \mu_5^2 + \mu_6^2). \quad (24)$$

b and a are given in Fig. 1.

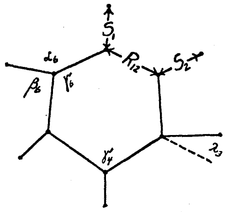

FIG. 4. Distorted molecule and coordinates used in potential energy function.

There are several methods of representing the other angular distortions of the bonds, one being given by

$$2V_5 = ka^2\{(\Delta\gamma_1)^2 + (\Delta\gamma_2)^2 + (\Delta\gamma_3)^2 + (\Delta\gamma_4)^2 + (\Delta\gamma_5)^2 + (\Delta\gamma_6)^2\}. \quad (25)$$

$$2V_6 = H(b-a)^2(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 + \lambda_4^2 + \lambda_5^2 + \lambda_6^2), \quad (26)$$

in which $\Delta\gamma_i$ is the change in the carbon-carbon bond angle at the ith carbon and λ_i is the angle of deviation of the carbon-hydrogen bond from the bisector of the carbon-carbon bond angle (all lying in the same plane). This is equivalent to

$$2V_6 = H'(b-a)^2 \sum_i \{(\Delta\alpha_i)^2 + (\Delta\beta_i)^2\} \quad (27)$$

with α and β given by Fig. 4, with the restriction that $\Delta\alpha_i + \Delta\beta_i + \Delta\gamma_i = 0$.

The methods used to obtain the frequencies are not restricted to the above choice of potential function but could be applied to any homogeneous quadratic function of the coordinates.

CALCULATION OF THE FREQUENCIES

The procedure used to calculate the frequencies from a knowledge of the modes of vibration and the potential function is best illustrated by an example. From Fig. 3 or the analytical equations for the normal coordinates, Q_3 is seen to come from a linear factor of the secular equation, which means that the positions of the atoms during this motion can be completely described by giving the value of one coordinate, say y_1. In an infinitesimal vibration of this type the only force constant which enters is H, since the carbon and hydrogen rings merely rotate with respect to each other and are not deformed. If we call the amplitude of the vibration at any instant

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[6] Linus Pauling and G. W. Wheland, J. Chem. Phys. **1**, 362 (1933).

δ, then the hydrogen atoms have each undergone a displacement $y_i' = a(M/m)^{\frac{1}{2}}\delta$, the carbon atoms a displacement $Y_i' = -b(m/M)^{\frac{1}{2}}\delta$, in ordinary units. From this it can be calculated that the potential energy of the distortion, using Eq. (26) and the geometry of the distorted molecule, is

$$2V = 6H\delta^2(a^2M + b^2m)^2/(a^2mM), \tag{28}$$

while the kinetic energy of the motion is

$$2T = 6(a^2M + b^2m)(d\delta/dt)^2. \tag{29}$$

Substitution of these in the equation of motion in terms of δ and solution of this equation gives for the frequency:

$$\nu_3 = (1/2\pi)[H(a^2M + b^2m)/(a^2mM)]^{\frac{1}{2}}. \tag{30}$$

In case the frequencies come from a quadratic equation the method is similar, except that two amplitudes δ and ϵ must be used. Thus ν_1 and ν_2 come from a quadratic factor involving Q_1' and Q_2'. If the amplitude of Q_1' is δ, every carbon atom is displaced a distance δ outward; if ϵ refers to Q_2', every hydrogen atom is moved radially outward a distance ϵ. None of the angles is altered by these displacements, the only effects being to stretch the carbon-carbon bond an amount δ and the hydrogen-carbon bond an amount $(\epsilon - \delta)$. The potential energy for this motion is therefore, from Eqs. (21) and (22),

$$\begin{aligned} 2V &= 6K\delta^2 + 6q(\epsilon - \delta)^2 \\ &= 6(K+q)\delta^2 - 12q\epsilon\delta + 6q\epsilon^2. \end{aligned} \tag{31}$$

The kinetic energy is:

$$2T = 6M(d\delta/dt)^2 + 6m(d\epsilon/dt)^2. \tag{32}$$

The equations of motion become

$$\left.\begin{aligned} 6M(d^2\delta/dt^2) + 6(K+q)\delta - 6q\epsilon = 0 \\ 6m(d^2\epsilon/dt^2) + 6q\epsilon - 6q\delta = 0 \end{aligned}\right\}. \tag{33}$$

These have a solution of the form

$$\delta = A \sin \lambda^{\frac{1}{2}}t; \quad \epsilon = B \sin \lambda^{\frac{1}{2}}t \tag{34}$$

if the secular determinant vanishes.

$$\therefore \quad \begin{vmatrix} K+q-M\lambda & -q \\ -q & q-m\lambda \end{vmatrix} = 0. \tag{35}$$

This is satisfied for

$$\lambda_{1,\,2} = (1/2mM)\{mK + q(m+M) \pm [\{mK + q(m+M)\}^2 - 4mMqK]^{\frac{1}{2}}\}. \tag{36}$$

$$\nu^2 = \lambda/4\pi^2. \tag{37}$$

The other frequencies were obtained in an exactly similar manner and are listed below, with the exception of those which come from the cubic and quartic factors of the secular equation. These higher degree equations are also given and may be solved numerically for any given values of the force constants.

ν_{18}, ν_{19} and ν_{20} are the roots of the equation.

$$\begin{vmatrix} 3(K+k)+q+H\zeta^2-2M\lambda & -q-H\zeta & ql-H\zeta l \\ -q-H\zeta & q+H-2m\lambda & -ql+Hl \\ ql-H\zeta l & -ql+Hl & ql^2+Hl^2-2Ml\lambda \end{vmatrix} = 0, \tag{38}$$

in which $\zeta = (3b-a)/2a$, $l = (M+m)/m$.

ν_6, ν_7, ν_8 and ν_9 are the roots of the equation.

$$\begin{vmatrix} q-m\lambda & 0 & -q & 0 \\ 0 & 4H-4m\lambda & 3^{\frac{1}{2}}H\eta & -H\xi \\ -16q & 12(3^{\frac{1}{2}})H\eta & 4K+108k+16q+9\eta^2H-16M\lambda & -3^{\frac{3}{2}}\{4K+12k+H\xi\eta\} \\ 0 & -4H\xi & -3^{\frac{1}{2}}\{4K+12k+H\xi\eta\} & 36K+12k+H\xi^2-16M\lambda \end{vmatrix} = 0, \tag{39}$$

in which $\eta = (b-a)/a$, $\xi = (b+3a)/a$.

$$\lambda_{4,\,5}=(1/2mM)\{36\kappa m+(3-4b/a)^2hm+Mh\pm[\{36\kappa m+(3-4b/a)^2hm+Mh\}^2-144mM\kappa h]^{\frac{1}{2}}\}. \quad (40)$$

$$\lambda_{10}=h(b^2m+a^2M)/a^2mM. \quad (41)$$

$$\lambda_{11}=h(m+M)/mM. \quad (42)$$

$$\lambda_{12,\,13}=(1/2mM)\{12km+q(m+M)\pm[\{12km+q(m+M)\}^2-48mMkq]^{\frac{1}{2}}\}. \quad (43)$$

$$\lambda_{14,\,15}=(1/2mM)\{3Km+H(m+M)\pm[\{3Km+H(m+M)\}^2-12mMKH]^{\frac{1}{2}}\}. \quad (44)$$

$$\lambda_{16,\,17}=(1/2mM)\{12\kappa m+mhf+Mh\pm[(12\kappa m+mhf+Mh)^2-48mM\kappa h]^{\frac{1}{2}}\}. \quad (45)$$

where $f=(3b-2a)^2/a^2$.

It is planned to apply the above results to the analysis of the experimental data for benzene.

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