

## The RotationVibration Spectrum of C<sub>2</sub>H<sub>6</sub> and the Question of Free Internal Rotation

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Citation: *The Journal of Chemical Physics* **5**, 451 (1937); doi: 10.1063/1.1750053

View online: <http://dx.doi.org/10.1063/1.1750053>

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# The Rotation-Vibration Spectrum of $C_2H_6$ and the Question of Free Internal Rotation

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(Received December 18, 1936)

If there were *free* internal rotation in  $C_2H_6$  the rotational structure of certain perpendicular type infrared bands would be very different from that for the customary symmetrical top molecule without internal rotation. To account for the fact that this difference is not observed it is necessary to assume that there is a potential difference of *at least* 2000 cal. ( $700\text{ cm}^{-1}$ ) between the two symmetrical forms of  $C_2H_6$  differing by an internal rotation of  $2\pi/6$ . A potential of this magnitude corresponds to an internal torsion vibration of  $230\text{ cm}^{-1}$ . The above conclusion is based upon a dynamical treatment of  $C_2H_6$  in which it is assumed that vibration, over-all rotation, and internal rotation subject to a restricting potential may occur simultaneously. An approximate form of the Hamiltonian expression obtained is  $H = \frac{1}{2}\{(\mathbf{P}_x - \mathbf{p}_x)^2/A + (\mathbf{P}_y - \mathbf{p}_y)^2/A + (\mathbf{P}_z - \mathbf{p}_z)^2/C + (\mathbf{P}_\gamma - \mathbf{p}_\gamma)^2/C + \sum \mathbf{p}_k^2\} + V$ , where  $\gamma$  represents the angle of internal rotation. The rotational selection rules are determined and it is found that under ordinary circum-

stances the internal rotation when free is inactive in the infrared rotation-vibration spectrum. However, when there is *accidental* degeneracy of certain pairs of twofold degenerate vibrational levels, the internal rotation becomes active in the infrared bands for these vibrations. In such a case of accidental vibrational degeneracy, which is approximated to by at least two sets of vibrations in  $C_2H_6$ , the rotation-vibration frequency for the infrared bands involves the quantity  $(h/4\pi^2)[(K \pm K')(1 - \zeta)/C - K/A]$  if the internal rotation is free;  $K$  and  $K'$  are the quantum numbers of over-all and internal rotation about the threefold symmetry axis and  $\zeta$  is a quantity depending on the angular momentum of vibration. The observed rotational spacing, however, is well reproduced by a frequency containing instead the quantity  $(h/4\pi^2)K[(1 - \zeta)/C - 1/A]$ , which is to be expected if  $C_2H_6$  is an ordinary symmetrical top molecule without internal rotation.

## INTRODUCTION

THE study of the infrared bands of  $C_2H_6$  presented below affords strong evidence for the presence of a potential of at least 2000 cal. restricting internal rotation. Kemp and Pitzer<sup>1</sup> have also found from statistical mechanical calculations that with a potential of about 3000 cal. they can explain the results of various experiments on the entropy and specific heat of  $C_2H_6$ , and the heat of reaction and the equilibrium constant for the  $C_2H_4 + H_2 = C_2H_6$  reaction. It should be pointed out that Smith and Vaughan<sup>2</sup> in discussing the discrepancy between their statistical mechanical calculation of the equilibrium constant based on the heat of hydrogenation of  $C_2H_4$  and the assumption of almost free internal rotation of  $C_2H_6$  concluded that the principal source of uncertainty lay in the analysis of the problem of free internal rotation. In contrast to these results stands the theoretical value of about 360 cal. calculated by Eyring<sup>3</sup> for the restricting potential; the configuration of highest potential energy is that in which there is a plane of symmetry perpendicular to the C—C

axis. The contribution of the vibrational zero-point energy to such a potential is negligible according to the results of the preceding paper. The only remaining terms which may contribute to the potential are of the type suggested by Penney<sup>4</sup> in his considerations of the electronic energy of  $C_2H_6$ . In the method of molecular orbitals these terms arise from the integrals involving the overlapping of the orbitals of a C atom and the orbitals of the H atoms of one  $CH_3$  group together with the distances to the H atoms of the other group. An estimate of the effect of such terms on the restricting potential has not yet been made but their contribution to the potential must far outweigh the other contributions if the discrepancy between the theoretical value for the magnitude of the potential and the values determined from thermodynamic and spectroscopic data is to be removed.

## GENERAL CONSIDERATIONS

Before proceeding to the mathematical treatment of the rotation-vibration energy of  $C_2H_6$ , we shall present, from a slightly different viewpoint from that adopted in the main body of the paper, the essential ideas which lead one to

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<sup>1</sup> Kemp and Pitzer, *J. Chem. Phys.* **4**, 749 (1936).

<sup>2</sup> Smith and Vaughan, *J. Chem. Phys.* **3**, 341 (1935).

<sup>3</sup> Eyring, *J. Am. Chem. Soc.* **54**, 3191 (1932).

<sup>4</sup> W. G. Penney, *Proc. Roy. Soc. A* **144**, 166 (1934).

conclude that there cannot be free internal rotation in  $C_2H_6$ . There are two types of degenerate vibrations in  $C_2H_6$ , one in which the C atoms move in parallel directions while the two  $CH_3$  groups rotate relative to one another about the symmetry axis, and one in which the C atoms move in antiparallel directions. The former type is active in the infrared, the latter inactive. In both types of vibration the internal rotation is inactive since the electric moments of the  $CH_3$  groups perpendicular to the symmetry axis do not take part in the internal rotation; the relative motion of the C atoms is the same when the  $CH_3$  groups are rotating and when they are not. In a special case of accidental degeneracy of vibrations of different types, however, the electric moments can be regarded as fixed in the  $CH_3$  groups, whereupon the internal rotation becomes active in the infrared. We shall consider an ideal situation which is approximately realized separately by the  $\nu_7$  (1480) and  $\nu_{10}$  (1515) and the  $\nu_8$  (3020) and  $\nu_{11}$  (3025) sets of vibrations as the work of the preceding paper shows. Let us assume that in these degenerate vibrations, angular momentum and translational momentum are conserved in each  $CH_3$  group separately, and that the accidental degeneracy of vibrations of different types is complete (i.e.,  $\nu_7 = \nu_{10}$  and  $\nu_8 = \nu_{11}$ ). The latter signifies that the frequency of vibration is independent of whether the C atoms move in parallel or antiparallel directions. Consequently, in the resulting fourfold degenerate vibrational level it is possible to construct vibrations in which the direction of the electric moment produced in one  $CH_3$  group is independent of the relative orientation of the other  $CH_3$  group.<sup>5</sup> This situation has been discussed by Nielsen,<sup>6</sup> the selection rules for  $K$  and  $K'$ , the quantum numbers of over-all and internal rotation about the symmetry axis, respectively, are  $\Delta K = \pm 1$ ,  $\Delta K' = \pm 1$ , the changes being independent of one another. The rotation-vibration frequency corresponding to the zero branches ( $\Delta J = 0$ ) in the infrared band resulting from a transition from the ground vibrational state to the fourfold degenerate vibrational level is thus

$$\nu_{KK'} = \nu_v - (h/8\pi^2)(2/C - 1/A) \pm (h/4\pi^2)[(K \pm K')/C - K/A],$$

<sup>5</sup> See footnote 13 of the preceding paper.

<sup>6</sup> Nielsen, Phys. Rev. **40**, 445 (1932).

where  $\nu_v$  is the vibrational frequency and the sign combinations are four in number. When the coupling of rotation and vibration is taken into consideration the fourfold vibrational degeneracy is lifted and the expression for the frequency becomes

$$\nu_{KK'} = \nu_v - (h/8\pi^2)(2/C - 1/A) \pm (h/4\pi^2)[(K \pm K')(1 - \zeta)/C - K/A],$$

where  $\zeta$  is a quantity which is determined by vibrational angular momentum directed along the symmetry axis of the molecule. The rotational structure of the infrared band corresponding to this expression consists of a series of lines of spacing  $(h/4\pi^2)[2(1 - \zeta)/C - 1/A]$  about each of which appears a second series of spacing  $(h/4\pi^2)1/A$ . The rotational structure actually observed in the  $C_2H_6$  spectrum is that of a single series of lines with a spacing corresponding to  $\Delta\nu = (h/4\pi^2)[(1 - \zeta)/C - 1/A]$ , which is the spacing to be expected if  $C_2H_6$  is an ordinary symmetrical top without internal rotation. The magnitude of the restricting potential which is necessary in order that a distortion of the rotational structure of the  $\nu_7$  and  $\nu_8$  bands by internal rotation would probably just escape observation is about 2000 cal. (700  $cm^{-1}$ ).

#### APPROXIMATE HAMILTONIAN EXPRESSION<sup>7</sup>

In the appendix of this paper it is shown that the approximate form of the Hamiltonian of  $C_2H_6$  corresponding to the form used by Johnston and Dennison<sup>8</sup> for symmetrical and spherical top molecules is

$$H = \frac{1}{2} \{ (\mathbf{P}_x - \mathbf{p}_x)^2/A + (\mathbf{P}_y - \mathbf{p}_y)^2/A + (\mathbf{P}_z - \mathbf{p}_z)^2/C + (\mathbf{P}_\gamma - \mathbf{p}_\gamma)^2/C + \sum \mathbf{p}_k^2 \} + V. \quad (1)$$

The notation and coordinate system used is fully explained in the appendix and in the preceding paper,<sup>9</sup> and the following explanations will suffice here.  $A$  and  $C$  are equilibrium moments of inertia of  $C_2H_6$  about axes perpendicular to and

<sup>7</sup> The present study is related to that of Nielsen (reference 6) in the following way. Nielsen developed the dynamical theory of a rigid symmetrical top the two halves of which may undergo a constrained relative rotation about the axis of symmetry. The model of  $C_2H_6$  studied here is one in which vibration may occur as the molecule undergoes internal and over-all rotation.

<sup>8</sup> Johnston and Dennison, Phys. Rev. **48**, 868 (1935).

<sup>9</sup> The preceding paper will henceforth be referred to as I.

collinear with the symmetry axis, respectively;  $\mathbf{P}_x, \mathbf{P}_y, \mathbf{P}_z$  are the components of the total overall angular momentum (see Eqs. (30) in appendix) and  $\mathbf{p}_x, \mathbf{p}_y, \mathbf{p}_z$  are the corresponding components of the vibrational angular momentum (Eqs. (34));  $\mathbf{p}_k$  is the momentum conjugate to the  $k$ th normal coordinate,  $Q_k$  (Eq. (32)).  $V$  is the potential energy.

Special notice should be taken of the fact that  $\mathbf{P}_\gamma$  and  $\mathbf{p}_\gamma$  do not correspond to the total internal angular momentum and the vibrational internal angular momentum. Their expressions, to the approximation with which we are dealing, are (see Eqs. (31), (34))

$$P_\gamma = C\dot{\gamma} + \sum_k (\beta'_k + \beta''_k) \dot{Q}_k + \sum_k \Delta_k \dot{Q}_k, \quad (2)$$

$$p_\gamma = \sum_k (\beta'_k + \beta''_k) \dot{Q}_k + \sum_k \Delta_k \dot{Q}_k, \quad (3)$$

where  $\beta'_k, \beta''_k$  and  $\Delta_k$  are given in Eqs. (25), (27), (28). The last term  $\sum \Delta_k \dot{Q}_k$  which is common to both expressions distinguishes  $P_\gamma$  and  $p_\gamma$  from the total and vibrational internal angular momenta, respectively. It has its origin in the fact that when a degenerate vibration is excited the kinetic energy relative to the rotating axis systems of the individual CH<sub>3</sub> groups depends upon the velocity of internal rotation, in other words, the normal coordinates for the degenerate vibrations contain the internal angle implicitly. The additional term arises only through the interaction of two degenerate vibrations of different symmetry types (i.e.,  $E$  and  $\bar{E}$  vibrations).

## ENERGY MATRIX

### Case of free internal rotation

In setting up the energy matrix for the Hamiltonian operator (1), it is convenient to use a set of wave functions  $\psi^\circ$  which diagonalize the Hamiltonian

$$\begin{aligned} \mathbf{H}^\circ = \frac{1}{2} \{ & \mathbf{P}_x^2/A + \mathbf{P}_y^2/A + \mathbf{P}_z^2/C + \mathbf{P}_\gamma^2/C \\ & + \sum \mathbf{p}_k^2 + \sum \lambda_k Q_k^2 \}. \end{aligned} \quad (4)$$

The remaining terms

$$\begin{aligned} \mathbf{H}' = - \{ & \mathbf{P}_x \mathbf{p}_x/A + \mathbf{P}_y \mathbf{p}_y/A \\ & + \mathbf{P}_z \mathbf{p}_z/C + \mathbf{P}_\gamma \mathbf{p}_\gamma/C \} \end{aligned} \quad (5)$$

may be considered as a perturbation. We have

neglected squares of the vibrational angular momentum since their contribution to the vibrational energy is negligible. It is evident from the expressions for  $\mathbf{P}_x, \mathbf{P}_y, \mathbf{P}_z$  in Eq. (30) that the first three terms of Eq. (4) are identical with the Hamiltonian of a rigid symmetrical top. We may therefore, for the case of free internal rotation, write the wave functions<sup>6</sup> which diagonalize  $\mathbf{H}^\circ$  (except for a normalization factor) as

$$\begin{aligned} \psi^\circ &= \Theta_{JKM}(\vartheta) e^{iM\varphi} e^{iK\chi} e^{iK'\gamma} \psi_v(Q) \\ M, K &= -J, -J+1, \dots, J, \end{aligned} \quad (6)$$

where  $\Theta_{JKM} e^{iM\varphi} e^{iK\chi}$  is the wave function for a symmetrical top and  $J$  is the total quantum number.  $\psi_v$  is the vibrational wave function involving Hermitean polynomials.

In order that  $\psi^\circ$  be single valued it must remain unchanged under the transformation  $\chi' \rightarrow \chi' + 2\pi$  or  $\chi'' \rightarrow \chi'' + 2\pi$ , each of which restores the molecule to its initial configuration if the displacements of the atoms relative to the equilibrium framework are held fixed. The transformations of the angles are equivalent to  $\chi \rightarrow \chi + \pi$ ,  $\gamma \rightarrow \gamma \pm \pi$ . The interesting feature in this connection is that the normal coordinates transform differently under the operation in question. From Eqs. (5) of I it is seen that when  $\gamma \rightarrow \gamma \pm \pi$  and the displacements of the atoms are held fixed  $Q \rightarrow Q$  if the normal coordinate is non-degenerate and  $Q \rightarrow -Q$  if the normal coordinate is degenerate. Consequently, under the operation,  $\psi_{ve} \rightarrow \psi_{ve}$  if the number of quanta in excited degenerate vibrations is even and  $\psi_{vo} \rightarrow -\psi_{vo}$  if this number is odd. These cases will be designated as  $V_e$  and  $V_o$ , respectively. Furthermore,  $e^{iK\chi} \rightarrow (-1)^K e^{iK\chi}$  and  $e^{iK'\gamma} \rightarrow (-1)^{K'} e^{iK'\gamma}$  under the transformation. Consequently, given a value of  $K$  it is evident that the choice of  $K'$  is limited by the fact that the following equations must be satisfied:  $(-1)^{K+K'} = 1$  in the  $V_e$  case and  $(-1)^{K+K'+1} = 1$  in the  $V_o$  case. It is evident that the following wave functions meet these requirements of single valuedness

$$\begin{aligned} \psi_e^\circ &= \Theta_{JKM}(\vartheta) e^{iM\varphi} e^{iK\chi} e^{i(2S+K)\gamma} \psi_{ve} \\ \psi_o^\circ &= \Theta_{JKM}(\vartheta) e^{iM\varphi} e^{iK\chi} e^{i(2S+K+1)\gamma} \psi_{vo} \end{aligned} \quad \left. \vphantom{\begin{aligned} \psi_e^\circ \\ \psi_o^\circ \end{aligned}} \right\} \quad S=0, \pm 1, \pm 2, \dots \quad (7)$$

With these wave functions it is possible to

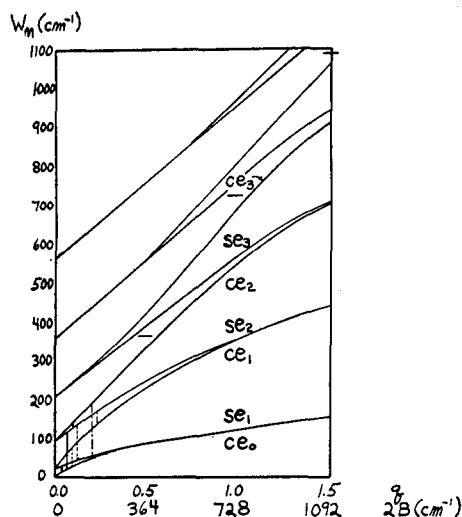


FIG. 1. Diagram of certain energy levels as functions of  $q$  and  $2B$  for internal rotation in  $C_2H_6$ , and related eigenfunctions  $ce_0(x)$ ,  $se_1(x)$ , etc., where  $x=3\gamma$ .

write down the energy matrix corresponding to the operator  $\mathbf{H}^0 + \mathbf{H}'$ . The eigenvalues of  $\mathbf{H}^0$  are evidently

$$W = (\hbar^2/8\pi^2) \{ J(J+1)/A + K^2(1/C - 1/A) + K'^2/C \} + W_v, \quad (8)$$

where  $K'$  is given by  $2S+K$  and  $2S+K+1$  in the  $V_e$  and  $V_o$  cases, respectively, and  $W_v$  is the vibrational energy. If we let  $R, R'$  and  $V, V'$  denote two sets of rotational quantum numbers and two sets of vibrational quantum numbers, respectively, a typical element of the perturbation matrix  $\mathbf{H}'$  may be written

$$(H')_{RV; R'V'} = -\sum_{\alpha} \alpha (P_{\alpha})_{R; R'} (p_{\alpha})_{V; V'} / I_{\alpha}, \quad (9)$$

where  $\alpha = x, y, z, \gamma$  and  $I_x = I_y = A$ ,  $I_z = I_{\gamma} = C$ .

### Case of restricted internal rotation

The portion of the Schrödinger wave equation of the molecule which depends on the internal angle may be written

$$[(\mathbf{P}_{\gamma} - \mathbf{p}_{\gamma})^2/2C + B \cos 6\gamma] \psi(\gamma) = W_{\gamma} \psi(\gamma). \quad (10)$$

In this expression it is assumed that the potential energy between  $CH_3$  groups may be expressed in the form  $B \cos 6\gamma$ . In I it was shown that this form of the potential is not changed even if we include the dependence of the normal vibrations on the internal angle.

Let us break the expanded Hamiltonian of

(10) into

$$\mathbf{H}_{\gamma}^0 = \mathbf{P}_{\gamma}^2/2C + B \cos 6\gamma \quad (11)$$

and a perturbation Hamiltonian

$$\mathbf{H}'_{\gamma} = -\mathbf{P}_{\gamma} \mathbf{p}_{\gamma} / C + \mathbf{p}_{\gamma}^2/2C. \quad (12)$$

The wave functions and energy levels as functions of  $B$  for the equation  $\mathbf{H}_{\gamma}^0 \psi(\gamma) = W_{\gamma}^0 \psi(\gamma)$  have been discussed by Nielsen, who considered the equation as a special form of the Mathieu equation

$$y''(x) + (a - 16q \cos 2x)y(x) = 0, \quad (13)$$

where

$$x = 3\gamma, a = (8\pi^2 C/9\hbar^2) W_{\gamma}^0 \text{ and } 16q = (8\pi^2 C/9\hbar^2) B.$$

The latter equation has been studied extensively by Goldstein,<sup>10</sup> among others.

In Fig. 1 is reproduced a diagram of the energy levels corresponding to Eq. (13) for different values of  $q$ . We have omitted for the sake of simplicity the energy levels for values of  $K'$  which are not multiples of 3. The omitted levels, doubly degenerate when  $q=0$ , retain their degeneracy when  $q$  becomes finite and do not cross the other levels. When  $q=0$  the eigenfunctions  $ce_n(x)$  and  $se_n(x)$  (in the notation of Goldstein) reduce, except for a constant factor, to  $\cos 3n\gamma$  and  $\sin 3n\gamma$ , respectively. The correlation of wave functions and energy levels given in the diagram is for  $q>0$ , which corresponds to a molecule in which the configuration of lowest potential energy has a center of symmetry. When  $q<0$  and the configuration of lowest potential energy has a plane of symmetry perpendicular to the C-C axis, the same diagram obtains but the proper wave functions are obtained by making the substitution  $\gamma = \gamma + \pi/6$ , i.e.,  $x = x + \pi/2$ .

### SELECTION RULES

It was explained in I that if the components of the electric moment  $\mu$  and the polarizability tensor  $\alpha$  are referred to the  $x, y, z$  axes carried by the molecule (see Fig. 1b of I) the components then involve only the normal coordinates, with two exceptions in which the internal angle

<sup>10</sup> S. Goldstein, Trans. Camb. Phil. Soc. **23**, 303 (1927).

appears as follows:

$$\begin{aligned} -\alpha_{xx} + \alpha_{yy} &= \cos 3\gamma \sum \tau_k Q_{k\alpha} + \sin 3\gamma \sum \bar{\tau}_k \bar{Q}_{k\alpha}, \\ 2\alpha_{xy} &= \cos 3\gamma \sum \tau_k Q_{k\beta} + \sin 3\gamma \sum \bar{\tau}_k \bar{Q}_{k\beta}. \end{aligned} \quad (14)$$

Inasmuch as the part of the nuclear wave functions depending on  $\theta$ ,  $\varphi$ ,  $\chi$  and determining the motion of the  $x$ ,  $y$ ,  $z$  system of axes are identical with rigid symmetrical top wave functions, and since electric moment and polarizability can be referred to the  $x$ ,  $y$ ,  $z$  axes without employing  $\theta$ ,  $\varphi$ ,  $\chi$ , the selection rules for  $J$ ,  $K$ ,  $M$  will be identical with those for a rigid symmetrical top. The internal rotation will be inactive in the infrared spectrum except in the case of accidental degeneracy of an  $E$  and an  $\bar{E}$  vibration as discussed below. It will also be inactive in the Raman spectrum with the exceptional case arising because of the appearance of  $\gamma$  in the expressions (14); the selection rules corresponding to these components of the polarizability, which involve  $E$  and  $\bar{E}$  normal vibrations, are  $\Delta K = \pm 3$ . It is to be noted that the selection rules for  $K$  and  $K'$  are compatible with the values of the quantum number  $K'$  allowed by boundary conditions, Eq. (7).

When a potential restricting the internal rotation is applied, only those vibrational transitions, with one exception, are permitted in which the state of the internal motion is the same in the initial and final states of the transition, since the internal angle does not enter in the electric moment and polarizability. The exception once again concerns the polarizability components (14). In these components the  $E$  vibrations have as coefficient  $\cos 3\gamma$ , typical matrix elements of which occur between states connected by the dotted vertical lines of Fig. 1. The  $\bar{E}$  vibrations have as coefficient  $\sin 3\gamma$ , typical matrix elements of which are represented by the dot-dash vertical lines of Fig. 1. Thus, in the limit  $q = \infty$ ,  $-\alpha_{xx} + \alpha_{yy}$  and  $2\alpha_{xy}$  may be expanded in terms of states involving  $E$  vibrations plus odd multiples of the normal coordinate of internal torsion vibration  $Q_{M\gamma}$  and in terms of  $\bar{E}$  vibrations plus even multiples of  $Q_{M\gamma}$ . The limit  $q = \infty$  in the case represented by Fig. 1 corresponds to a molecule with a center of symmetry. When  $q < 0$ , the situation is reversed. The dotted lines represent matrix elements of  $\sin 3\gamma$  and the dot-dash lines ele-

ments of  $\cos 3\gamma$ , so that in the limit  $q = -\infty$ , the  $E$  vibrations are associated with even multiples of  $Q_{M\gamma}$  and the  $\bar{E}$  vibrations with odd multiples in the expansion of  $-\alpha_{xx} + \alpha_{yy}$  and  $2\alpha_{xy}$ . This case corresponds to a molecule with a plane of symmetry. These selection rules for the internal motion when  $|q| = \infty$  are identical, as they should be, with the selection rules derived for a molecule in which the internal motion is regarded as a normal coordinate vibration.

## ROTATIONAL STRUCTURE OF INFRARED BANDS

### $P_z p_z$ coupling

The effect of introducing the  $z$  coupling term in  $\mathbf{H}'$ , Eqs. (5), (9), will be the same as in the case of a symmetrical top without internal rotation. This coupling is of greatest importance in the case of a pair of degenerate vibrations. The rotational spacing in the infrared perpendicular type band arising from degenerate vibrations has been fully discussed by Johnston and Dennison.<sup>8</sup> We shall give only the expression for the rotational spacing:  $\Delta\nu = (h/4\pi^2)[(1-\xi)/C - 1/A]$ . The  $z$  component of the angular momentum of vibration in the pair of vibrational states resulting from the rotation-vibration coupling is given by  $p_z = \pm \xi h/2\pi$ ;  $\xi$  is a positive or negative quantity according as the sense of rotation of the electric moment and the direction of the angular momentum of vibration are parallel or antiparallel. Transitions from the ground state to a degenerate-type vibration occur with  $\Delta K = +1$  or  $-1$  according as the vibration is such that the  $+$  or  $-$  sign appears before  $\xi$  in the expression for  $p_z$ . With the use of the normal coordinates obtained in I the quantity  $\xi$  has been computed for the three perpendicular-type bands from the expression for  $p_z$  given in Eqs. (34), (24), (25) of the appendix. The comparison of the observed and calculated<sup>11</sup> rotational spacings is shown in

TABLE I. Rotational spacing in  $\text{cm}^{-1}$  of perpendicular type infrared bands of C<sub>2</sub>H<sub>6</sub>.

$\nu$	$\xi$	$\Delta\nu_{\text{obs}}$	$\Delta\nu_{\text{calc}}$
$\nu_6$ (827)	0.218	2.6	2.63
$\nu_7$ (1480)	-0.368	4.9	5.60
$\nu_8$ (3000)	0.150	3.3	2.98

<sup>11</sup> The values used for the moments of inertia were  $C = 10.94 \times 10^{-40}$  g cm<sup>2</sup> and  $A = 41.88 \times 10^{-40}$  g cm<sup>2</sup>. All

Table I. The agreement is surprisingly good in view of the simplicity of the normal coordinate treatment given. In the absence of rotation-vibration coupling we would expect a rotational spacing  $\Delta\nu = 3.74 \text{ cm}^{-1}$ . It can be shown that the sum of the  $\zeta$ 's for the three  $E$  vibrations is  $\sum \zeta_k = 0$ , so that the sum of the calculated rotational spacings for the corresponding infrared bands should be three times the normal spacing, i.e.,  $3 \times 3.74 = 11.22 \text{ cm}^{-1}$ .

### $\mathbf{P}_\gamma \mathbf{p}_\gamma$ coupling

If the matter of rotation-vibration coupling ended at this point the agreement between the observed and calculated rotational spacing would be gratifying. The matrix elements of  $\mathbf{p}_\gamma$  connecting  $E$  and  $\bar{E}$  vibrations, however, may be quite appreciable and in view of the approximate degeneracy<sup>12</sup> of  $\nu_7$  (1480) and  $\nu_{10}$  (1515) and of  $\nu_8$  (3020) and  $\nu_{11}$  (3025), the coupling terms in Eq. (12) must be considered. It is not difficult to obtain the effect of the coupling on the appearance of an infrared band in the case discussed at the beginning of the paper, namely where there is complete degeneracy of an  $E$  and an  $\bar{E}$  vibration and where there is complete freedom of internal rotation. As a result of the rotation-vibration coupling, Eq. (12), the fourfold degenerate vibrational state, for a given value of  $K$  and  $K'$ , is split into four components which are characterized by the four possible different combinations of signs in the expressions  $\mathbf{p}_z = \pm \zeta h/2\pi$  and  $\mathbf{p}_\gamma = \pm \rho h/2\pi$ . In such a case the expression for the rotation-vibration frequency, corresponding to the zero branches ( $J \rightarrow J$ ) of the perpendicular type band, assumes a par-

ticularly simple form, namely,

$$\nu_{KK'} = \nu_V - (h/8\pi^2) \{ (1 - \rho^2)/C - 1/A \} \\ \pm (h/4\pi^2) \{ K[(1 - \zeta)/C - 1/A] \mp K'\rho/C \}, \quad (15)$$

where the quantum numbers  $K$  and  $K'$  refer to the final state in the transition. Since the electric moment does not involve the internal angle, as it does  $\chi$ , the duplicity in signs in  $\mathbf{p}_\gamma$  appears in the frequency. In the special case of vibrational degeneracy which we are discussing,  $\rho = \zeta - 1$ , so that the expression for the rotational frequency in the perpendicular type band assumes the form<sup>13</sup>

$$\nu_{KK'} = \nu_V - (h/8\pi^2) (2\zeta/C - 1/A) \\ \pm (h/4\pi^2) \{ (K \pm K')(1 - \zeta)/C - K/A \} \quad (16)$$

if we neglect squares of  $\zeta$ .

Whereas the  $E$  and  $\bar{E}$  vibrations are not actually degenerate, the proximity of  $\nu_7$  and  $\nu_{10}$  and of  $\nu_8$  and  $\nu_{11}$  is enough to produce a marked effect of the  $\mathbf{P}_\gamma \mathbf{p}_\gamma$  coupling on the rotational structure. The infrared band structures for  $\text{C}_2\text{H}_6$  are not, however, discernibly different from those of such molecules as the methyl halides, which have no internal rotation. The fact that the secondary structure depending upon different values of  $K'$  is not observed can only mean that there is present a potential restricting internal rotation to such an extent that the internal angular momentum of rotation is quenched in all those levels of the internal motion which have an appreciable relative Boltzmann factor. By quenching of the internal angular momentum is meant that the matrix for  $\mathbf{P}_\gamma$  is altered to such a degree that the perturbation  $\mathbf{P}_\gamma \mathbf{p}_\gamma/C$  has an imperceptible effect on the energy.

In the following paragraphs we give the method used for making a quantitative estimate of a lower limit to the magnitude of the restricting potential  $B \cos 6\gamma$  below which the structure

bond angles were assumed to have the tetrahedral value and  $C$  was chosen as twice the moment of inertia of  $\text{CH}_4$  as given by Johnston and Dennison (reference 8). To calculate  $A$  the following distances were assumed:  $\text{C}-\text{C} = 1.54\text{\AA}$  and  $\text{C}-\text{H} = 1.11\text{\AA}$ . The former value was taken from Pauling and Huggins, *Zeits. f. Krist.* **A87**, 205 (1934), and the latter from Johnston and Dennison.

<sup>12</sup> The values given for the frequencies are those calculated in the preceding paper. Since the magnitudes of the  $\nu_7$ ,  $\nu_{10}$  and  $\nu_8$ ,  $\nu_{11}$  separations are important for what follows, a word may be said concerning them. If the forces between distant H atoms are neglected,  $\nu_7$  and  $\nu_8$  should be less than  $\nu_{10}$  and  $\nu_{11}$ , respectively, since in the former, the motion of the C atoms in parallel directions produces less change in potential energy than the antiparallel motion of the C atoms in the latter. A change of only a few  $\text{cm}^{-1}$  in the separations is produced by introducing a repulsion between distant H atoms which is represented by a fraction of a Morse potential and which gives 350 cal. for the potential restricting internal rotation.

<sup>13</sup> From the derivation of this expression it appears as if the term  $K'(1 - \zeta)/C$  arose purely out of the coupling of internal angular momentum and the vibrational angular momentum. However, even if the vibrational angular momentum is absent, i.e.,  $\zeta = 0$ , the contribution of the term  $\mathbf{P}_\gamma \mathbf{p}_\gamma$  in the Hamiltonian does not vanish. This illustrates the fact mentioned above that  $\mathbf{P}_\gamma$  and  $\mathbf{p}_\gamma$  do not correspond simply to the total internal angular momentum and the internal vibrational angular momentum. The difference between expression (16) and that obtained for  $\nu_{KK'}$  earlier is that in the present instance  $K' = 2S + K + 1$  whereas in the earlier expression  $K' = 2S + K$ .

TABLE II. Relative displacements  $\Delta\nu_n$  of frequencies in  $\text{cm}^{-1}$  due to the perturbation  $\mathbf{P}_\gamma \mathbf{p}_\gamma / C$ , relative energies  $W_n$  in  $\text{cm}^{-1}$  and relative Boltzmann factors at  $T=300^\circ\text{K}$  for the three lowest levels of the internal motion with  $B=364 \text{ cm}^{-1}$ .

$\nu_l - \bar{\nu}_l$	0	-20	-40	$W_n$	$e^{-W_n/kT}$
$\Delta\nu_0$	0	0	0	0	1.00
$\Delta\nu_1$	$-0.25\rho^2$	$0.24\rho^2$	$0.76\rho^2$	230	0.33
$\Delta\nu_2$	$3.68\rho^2$	$4.40\rho^2$	$5.25\rho^2$	430	0.13

$$\rho_{7,10} = -1.37;$$

$$\rho_{8,11} = -0.85$$

of the perpendicular type bands of C<sub>2</sub>H<sub>6</sub> cease to resemble those of a molecule with completely restricted internal rotation.

For this purpose it is necessary to evaluate the matrix elements  $-(P_\gamma)_{RR'}(p_\gamma)_{VV'}/C$  of the perturbation Hamiltonian (12). We shall confine our attention to the elements of  $\mathbf{p}_\gamma$  connecting the almost degenerate vibrational states corresponding to  $\nu_7$  and  $\nu_{10}$  and to  $\nu_8$  and  $\nu_{11}$ . From the normal coordinates obtained for these vibrations in I and the expression (3) for  $\mathbf{p}_\gamma$  we find that  $\rho_{7,10} = -1.37h/2\pi$  and  $\rho_{8,11} = -0.85h/2\pi$ . Certain of the matrix elements of  $\mathbf{P}_\gamma$  can be calculated using the solutions  $ce_0(x)$ ,  $se_2(x)$  and  $ce_2(x)$  of the Mathieu equation (13) as obtained by Goldstein. Another pair of solutions  $se_4(x)$  and  $ce_4(x)$ , which reduce to  $\sin 12\gamma$  and  $\cos 12\gamma$  (except for a constant factor) when  $B=0$ , have been obtained from the orthogonality relations with the above solutions. Solutions of higher energy,  $se_6(x)$ ,  $ce_6(x)$ , etc., have been assumed to be well represented, within the range of values of  $B$  in which we are interested, by their values when  $B=0$ , namely  $\sin 18\gamma$ ,  $\cos 18\gamma$ , etc. In Fig. 1 typical matrix elements of  $\mathbf{P}_\gamma$  (for either of the cases  $q>0$  and  $q<0$ ) are represented by the solid vertical lines. Having obtained the matrix elements of  $\mathbf{P}_\gamma$  connecting the states in question it is possible by a second-order perturbation treatment to evaluate the perturbation energy corresponding to  $\mathbf{P}_\gamma \mathbf{p}_\gamma / C$  for the states  $ce_0(x)$ ,  $se_2(x)$  and  $ce_2(x)$ . When  $B$  is reasonably large these states become components of the three lowest levels of the internal torsion oscillation (see Fig. 1).

The perturbation treatment has been made for two magnitudes of the restricting potential,  $B=182 \text{ cm}^{-1}$  and  $B=364 \text{ cm}^{-1}$ . Table II gives the results of the calculation for the latter case. With such a value of  $B$  the three lowest energy levels closely correspond to an internal torsion vibration. In Table II  $\Delta\nu_n$  represents the perturbation energy of the  $n$ th level minus that of the ground level,  $n=0$ . Consequently,  $\Delta\nu_n$  gives the spacing of the secondary structure about each zero branch of the perpendicular type bands where  $n$  denotes the particular level of the internal motion which is involved in both the initial and final states of the transition. The energy of the  $n$ th level relative to the level  $n=0$  is given under  $W_n$  in the table. In the last column of the table are given the relative Boltzmann factors of these levels at  $T=300^\circ\text{K}$ . Below the table are given the values of  $\rho$  connecting the  $\nu_7$  and  $\nu_{10}$  and the  $\nu_8$

and  $\nu_{11}$  vibrations. To make the perturbation calculation it is necessary to know the separations  $\nu_7 - \nu_{10}$  and  $\nu_8 - \nu_{11}$ . The values obtained in the preceding paper for these separations are  $-35 \text{ cm}^{-1}$  and  $-5 \text{ cm}^{-1}$ , respectively. Although the sign of these values is probably correct the magnitudes may be in error. Hence the calculation has been carried out for three values of the separation of the  $E$  and  $\bar{E}$  frequencies,  $\nu_l - \bar{\nu}_l = 0, -20$  and  $-40 \text{ cm}^{-1}$ .

From Table II we may conclude in the case of the perpendicular type bands corresponding to  $\nu_7$  ( $1480 \text{ cm}^{-1}$ ) and  $\nu_8$  ( $3020 \text{ cm}^{-1}$ ) that the effects of the coupling term  $-\mathbf{P}_\gamma \mathbf{p}_\gamma / C$  are, respectively, as follows (we assume for explicitness that  $\nu_{10}=1520 \text{ cm}^{-1}$  and  $\nu_{11}=3020 \text{ cm}^{-1}$ ): of the molecules in the three lowest levels of the internal torsion oscillation 9 percent give rise to lines displaced by  $10 \text{ cm}^{-1}$  and  $2.7 \text{ cm}^{-1}$  from the zero branches of the two bands and 23 percent give rise to lines which are displaced by  $1.4 \text{ cm}^{-1}$  and  $0.2 \text{ cm}^{-1}$ . This is the situation with  $B=364 \text{ cm}^{-1}$ . With the lower value  $B=182 \text{ cm}^{-1}$  the displacements are far greater. We would probably be justified in stating that the internal potential must be at least as high as  $546 \text{ cm}^{-1}$  since the C<sub>2</sub>H<sub>6</sub> perpendicular type bands closely resemble those of an ordinary symmetrical top molecule but it was not thought worthwhile to repeat the perturbation calculations with this higher value of  $B$ . The value  $2B=728 \text{ cm}^{-1}$  ( $2070 \text{ cal.}$ ) may be taken as a reasonable lower limit for the magnitude of the restricting potential. This value of the potential corresponds to an internal torsion frequency of  $230 \text{ cm}^{-1}$ ; when  $B=546 \text{ cm}^{-1}$  the torsion frequency is  $300 \text{ cm}^{-1}$ .

The above considerations concerning the coupling of  $E$  and  $\bar{E}$  vibrations are complicated by the fact that there exists a second type of coupling between such vibrations (see Eq. (9) of I) which may arise when there are forces restricting internal rotation. The effect of this second type of coupling on the selection rules for the  $\bar{E}$  vibrations is similar to that produced by the presence in the electric moment of such a term as  $\sin 6\gamma \sum \bar{\tau}_k \bar{Q}_k$  where  $\bar{Q}_k$  is an  $\bar{E}$  vibration. Typical nonvanishing matrix elements of  $\sin 6\gamma$  are represented by the solid vertical lines in Fig. 1. The frequency in the infrared spectrum associated with an  $\bar{E}$  normal vibration will be the  $\bar{E}$  fundamental frequency augmented or diminished by the energy difference of states of the internal motion connected by the solid



vertical lines. The resulting band would be very complex in the limit of small  $q$  whereas in the limit  $q = \infty$  the active frequency would be  $\bar{\nu}_k \pm \nu_\gamma$ , where  $\bar{\nu}_k$  is the  $\bar{E}$  fundamental frequency and  $\nu_\gamma$  is the frequency of the internal torsion oscillation. The two infrared bands found by Bartholomé and Sachsse<sup>14</sup> at 1465 and 1495  $\text{cm}^{-1}$  cannot, however, be explained with any value of  $q$ . If  $q$  is large, then, since the  $E$  and  $\bar{E}$  fundamental frequencies in this region,  $\nu_7$  and  $\nu_{10}$ , are almost degenerate, the two bands should be separated by the frequency of the internal torsion oscillation, instead of by the small difference of 30  $\text{cm}^{-1}$  calculated for the separation in the preceding paper. If  $q$  is small, say of such a magnitude that  $2B = 350$  cal., then instead of a single  $\bar{E}$  frequency there should appear several frequencies separated from this by about 25  $\text{cm}^{-1}$ , 50  $\text{cm}^{-1}$ , 100  $\text{cm}^{-1}$ , etc.

The presence of the second type of coupling between  $E$  and  $\bar{E}$  vibrations represented by Eq. (9) of I does not seriously alter the conclusions reached concerning the  $\mathbf{P}_\gamma \mathbf{p}_\gamma$  coupling of such states. The former coupling should be of the same order of magnitude as the similar coupling terms in Eq. (8) of I. The latter have been calculated and for a potential which gives a difference of 125  $\text{cm}^{-1}$  (350 cal.) between the  $D_{3h}$  and  $D_{3d}$  configurations of  $\text{C}_2\text{H}_6$  this type of coupling is less important than the rotation-vibration coupling. When the potential difference reaches 2000  $\text{cm}^{-1}$  the former coupling may be of the same order of magnitude as the rotation-vibration coupling for the  $\nu_7, \nu_{10}$  pair but is still much less than the rotation-vibration coupling for the  $\nu_8, \nu_{11}$  pair.

### $\mathbf{p}_x, \mathbf{p}_y$ coupling

Because of the symmetry relations involved,  $\mathbf{p}_x$  and  $\mathbf{p}_y$  may have matrix elements connecting only  $E$  with  $\bar{E}$  or  $A_1$  with  $\bar{E}$  or  $\bar{A}_2$  with  $E$  vibrations. In order for coupling to occur the vibrations so connected must be approximately degenerate. Fortunately, because of the similarity of those  $E$  and  $\bar{E}$  vibrations which are quasidegenerate, the elements of  $\mathbf{p}_x$  and  $\mathbf{p}_y$  connecting them should be vanishingly small. The  $\bar{A}_2$  vibrations are separated from the  $E$  vibrations by about 100

$\text{cm}^{-1}$  and we should not expect coupling here, at least for the lower values of  $K'$ , since it is found that  $(p_x)_{lk} \hbar^2 / 4\pi^2 A$  is only equal to 0.066  $\text{cm}^{-1}$  and 0.80  $\text{cm}^{-1}$  for the  $\nu_4, \nu_7$  and  $\nu_5, \nu_8$  combinations, respectively, when internal rotation is free. Similarly  $\nu_8$  is separated by about 100  $\text{cm}^{-1}$  from the combination bands of  $\nu_2, \nu_4$  and of  $\nu_7, \nu_{10}$ . Consequently, we should not expect the structures of the infrared bands of the  $E$  vibrations to be seriously perturbed by coupling through  $\mathbf{p}_x, \mathbf{p}_y$  with other vibrations.

In conclusion I would like to thank Professor E. Bright Wilson, Jr., for suggesting the problem of the ethane type molecule to me and for his invaluable advice during the course of this study.

### APPENDIX: THE KINETIC ENERGY OF $\text{C}_2\text{H}_6$

#### Classical kinetic energy

The method used to obtain the Hamiltonian form of the kinetic energy is very similar to that used by Wilson and Howard,<sup>15</sup> and we shall present here only the more important equations and expressions which appear in the derivation. Whereas the complete Hamiltonian expression has been derived, only the equations leading to the simplified form used in the present paper will be given. To obtain the simplified Hamiltonian from the complete expression one neglects linear and quadratic terms in the normal coordinates  $Q_k$  except for the terms in  $Q_k \dot{Q}_k$  which appear in the vibrational angular momenta.

The kinetic energy  $T$  prior to the introduction of the normal coordinates is, to the approximation with which we are dealing,

$$2T = A\omega_x^2 + A\omega_y^2 + C\omega_z^2 + C\dot{\gamma}^2 + 2(\omega_x M_x + \omega_y M_y + \omega_z M_z + \dot{\gamma} M_\gamma) + \sum_i (\dot{\xi}^2_i + \dot{\eta}^2_i + \dot{\zeta}^2_i) + \sum_i (\dot{\xi}^{\prime 2}_i + \dot{\eta}^{\prime 2}_i + \dot{\zeta}^{\prime 2}_i), \quad (17)$$

where  $A$  and  $C$  are the equilibrium moments of inertia of  $\text{C}_2\text{H}_6$  about axes perpendicular to and collinear with the symmetry axis, respectively;  $\omega_x, \omega_y, \omega_z$  are the components relative to the  $x, y, z$  axes (see Fig. 1 of I) of the angular velocity of these axes;  $\dot{\gamma}$  is the time derivative of the internal angle. The expressions for the latter quantities in terms of the  $x', y', z'$  and  $x'', y'', z''$  components of the vector angular velocities  $\omega'$  and  $\omega''$ , respectively, of the primed sets of axes are

$$\begin{aligned} \omega_x &= (1/2)[(\omega'_x + \omega''_x) \cos \gamma - (\omega'_y + \omega''_y) \sin \gamma]; \\ \omega_y &= (1/2)[(\omega'_x - \omega''_x) \sin \gamma + (\omega'_y - \omega''_y) \cos \gamma]; \\ \omega_z &= (1/2)(\omega'_z - \omega''_z); \quad \dot{\gamma} = (1/2)(\omega'_z + \omega''_z). \end{aligned} \quad (18)$$

$M_x, M_y, M_z$  are the  $x, y, z$  components of the vibrational angular momentum and  $M_\gamma$  is the internal angular momentum; they are given by the following expressions in

<sup>14</sup> Bartholomé and Sachsse, *Zeits. f. physik. Chemie* **B30**, 40 (1935).

<sup>15</sup> Wilson and Howard, *J. Chem. Phys.* **4**, 260 (1936).

terms of the displacement coordinates (see Fig. 2 of I)

$$\begin{aligned} M_x &= (M'_x + M''_x) \cos \gamma - (M'_y + M''_y) \sin \gamma; \\ M_y &= (M'_x - M''_x) \sin \gamma + (M'_y - M''_y) \cos \gamma; \\ M_z &= (M'_z - M''_z); \quad M_\gamma = (M'_z + M''_z). \end{aligned} \quad (19)$$

where

$$\begin{aligned} M'_x &= \sum (\eta'_i \xi'_i - \dot{\eta}'_i \xi'_i); \quad M'_y = \sum (\xi'_i \xi'_i - \dot{\xi}'_i \xi'_i); \\ M'_z &= \sum (\xi'_i \dot{\eta}'_i - \xi'_i \eta'_i) \end{aligned} \quad (20)$$

and  $M''_x, M''_y, M''_z$  are given by similar expressions in  $\xi''_i, \eta''_i, \zeta''_i$ .

The transformation (2) of I to the normal coordinates is next made. The displacement coordinates  $\xi'_i, \eta'_i$ , etc., are completely defined by the following seven conditions on the normal coordinates

$$\begin{aligned} Q_x &= (Q'_x + Q''_x) \cos \gamma - (Q'_y + Q''_y) \sin \gamma = 0; \\ Q_y &= (Q'_x - Q''_x) \sin \gamma + (Q'_y - Q''_y) \cos \gamma = 0; \\ Q_z &= Q'_z - Q''_z = 0; \\ Q_{Mx} &= (Q'_{Mx} + Q''_{Mx}) \cos \gamma - (Q'_{My} + Q''_{My}) \sin \gamma = 0; \\ Q_{My} &= (Q'_{Mx} - Q''_{Mx}) \sin \gamma + (Q'_{My} - Q''_{My}) \cos \gamma = 0; \\ Q_{Mz} &= Q'_{Mz} - Q''_{Mz}; \quad Q_{M\gamma} = Q'_{Mz} + Q''_{Mz}; \end{aligned} \quad (21)$$

where

$$\begin{aligned} Q'_x &= N_T \sum \sqrt{m_i} \xi'_i; \quad Q'_y = N_T \sum \sqrt{m_i} \eta'_i; \\ Q'_z &= N_T \sum \sqrt{m_i} \zeta'_i; \quad Q'_{Mx} = N_R \sum \sqrt{m_i} (b_i \xi'_i - c_i \eta'_i); \\ Q'_{My} &= N_R \sum \sqrt{m_i} (c_i \xi'_i - a_i \zeta'_i); \\ Q'_{Mz} &= N_R \sum \sqrt{m_i} (a_i \eta'_i - b_i \zeta'_i), \end{aligned} \quad (22)$$

with similar expressions in  $\xi''_i, \eta''_i, \zeta''_i$  for  $Q''_x, Q''_y, Q''_z, Q''_{Mx}, Q''_{My}, Q''_{Mz}$ .  $N_T$  and  $N_R$  are normalization constants,  $a_i, b_i, c_i$  are the equilibrium values of  $x'_i, y'_i, z'_i$  ( $x''_i, y''_i, z''_i$ ) for the  $i$ th atom, and  $m_i$  is the mass of the  $i$ th atom. To evaluate the terms which appear in the kinetic energy (17) we note that from Eq. (2) of I,  $\xi'_i = \sum l'_{ik} \dot{Q}_k + \sum l'_{il} \dot{Q}_l$ , etc., and that from Eq. (6) of I,  $\dot{s}'_{ika} = -s'_{ik\beta} \dot{\gamma}$ ,  $\dot{s}'_{ika} = s'_{ik\beta} \dot{\gamma}$ ,  $\dot{s}'_{ik\beta} = s'_{ika} \dot{\gamma}$ ,  $\dot{s}'_{ik\beta} = -s'_{ika} \dot{\gamma}$ , where  $s'_{ika}, s'_{ik\beta}$ , etc., represent the coefficients of the transformation (2) of I to the degenerate type normal coordinates. Using this information we have, from Eqs. (19), (20),

$$\begin{aligned} M_x &= \sum \mathfrak{X}_k \dot{Q}_k; \quad M_y = \sum \mathfrak{Y}_k \dot{Q}_k; \\ M_z &= \sum \mathfrak{Z}_k \dot{Q}_k; \quad M_\gamma = \sum \Gamma_k \dot{Q}_k; \end{aligned} \quad (23)$$

where

$$\begin{aligned} \mathfrak{X}_k &= (\mathfrak{X}'_k + \mathfrak{X}''_k) \cos \gamma - (\mathfrak{Y}'_k + \mathfrak{Y}''_k) \sin \gamma; \\ \mathfrak{Y}_k &= (\mathfrak{X}'_k - \mathfrak{X}''_k) \sin \gamma + (\mathfrak{Y}'_k - \mathfrak{Y}''_k) \cos \gamma; \\ \mathfrak{Z}_k &= (\mathfrak{Z}'_k - \mathfrak{Z}''_k); \quad \Gamma_k = (\mathfrak{Z}'_k + \mathfrak{Z}''_k), \end{aligned} \quad (24)$$

and

$$\begin{aligned} \mathfrak{X}'_k &= \sum_{il} (m'_{il} n'_{ik} - m'_{ik} n'_{il}) Q_l; \\ \mathfrak{Y}'_k &= \sum_{il} (n'_{il} l'_{ik} - n'_{ik} l'_{il}) Q_l; \\ \mathfrak{Z}'_k &= \sum_{il} (l'_{il} m'_{ik} - l'_{ik} m'_{il}) Q_l. \end{aligned} \quad (25)$$

Similarly,

$$\begin{aligned} \sum_i (\dot{\xi}'^2_i + \dot{\eta}'^2_i + \dot{\zeta}'^2_i) + \sum_i (\dot{\xi}''^2_i + \dot{\eta}''^2_i + \dot{\zeta}''^2_i) \\ = \sum_k \dot{Q}_k^2 + 2\dot{\gamma} \sum_k \dot{Q}_k \Delta_k, \end{aligned} \quad (26)$$

where

$$\begin{aligned} \Delta_k &= \Delta'_k + \Delta''_k; \\ \dot{\gamma} \Delta'_k &= \sum_{il} (l'_{il} l'_{ik} + m'_{il} m'_{ik} + n'_{il} n'_{ik}) Q_l. \end{aligned} \quad (27)$$

$\Delta_k$  is different from zero only between normal coordinates of different degenerate types ( $E$  and  $\bar{E}$ ). Its nature is more completely revealed by the expression

$$\sum_k \Delta_k \dot{Q}_k = \sum_{kl} \Delta_{kala} \{ \dot{Q}_{ka} Q_{l\alpha} + \dot{Q}_{k\beta} Q_{l\beta} - Q_{ka} \dot{Q}_{l\alpha} - Q_{k\beta} \dot{Q}_{l\beta} \}, \quad (27a)$$

where  $k$  refers to an  $E$  coordinate and  $l$  to an  $\bar{E}$  coordinate, and

$$\Delta_{kala} = \sum_i (l_{ika} l_{ila} + m_{ika} m_{ila} + n_{ika} n_{ila}). \quad (28)$$

The coefficients  $l_{ika}, l_{ila}$ , etc., correspond to the constant coefficients  $s_{ika}, s_{ila}$ , etc., of Eq. (6) of I and the summation is over all the atoms of the molecule.

Substituting the Eqs. (23), (26) into the kinetic energy (17) we obtain

$$\begin{aligned} 2T &= A \omega_x^2 + A \omega_y^2 + C \omega_z^2 + C \dot{\gamma}^2 + \sum_k \dot{Q}_k^2 \\ &\quad + 2\omega_x \sum_k \mathfrak{X}_k \dot{Q}_k + 2\omega_y \sum_k \mathfrak{Y}_k \dot{Q}_k + 2\omega_z \sum_k \mathfrak{Z}_k \dot{Q}_k \\ &\quad + 2\dot{\gamma} \sum_k (\Gamma_k + \Delta_k) \dot{Q}_k. \end{aligned} \quad (29)$$

### Hamiltonian form

The next step is to obtain the Hamiltonian form of the kinetic energy. The components of the total angular momentum are given by

$$\begin{aligned} P_x &= \partial T / \partial \omega_x = A \omega_x + \sum \mathfrak{X}_k \dot{Q}_k; \\ P_y &= A \omega_y + \sum \mathfrak{Y}_k \dot{Q}_k; \quad P_z = C \omega_z + \sum \mathfrak{Z}_k \dot{Q}_k. \end{aligned} \quad (30)$$

The momenta  $P_\gamma$  and  $p_k$  conjugate to  $\gamma$  and  $Q_k$  are

$$P_\gamma = \partial T / \partial \dot{\gamma} = C \dot{\gamma} + \sum (\Gamma_k + \Delta_k) \dot{Q}_k \quad (31)$$

and

$$p_k = \partial T / \partial \dot{Q}_k = \mathfrak{X}_k \omega_x + \mathfrak{Y}_k \omega_y + \mathfrak{Z}_k \omega_z + (\Gamma_k + \Delta_k) \dot{\gamma} + \dot{Q}_k. \quad (32)$$

$P_\gamma$  is not identical with the total internal angular momentum given by  $C \dot{\gamma} + \sum \Gamma_k \dot{Q}_k$ . By means of Eqs. (30), (31), (32) the kinetic energy (29) may be rewritten

$$\begin{aligned} 2T &= (P_x - p_x)^2 / A + (P_y - p_y)^2 / A + (P_z - p_z)^2 / C \\ &\quad + (P_\gamma - p_\gamma)^2 / C + \sum_k p_k^2, \end{aligned} \quad (33)$$

where

$$\begin{aligned} p_x &= \sum \mathfrak{X}_k p_k, \quad p_y = \sum \mathfrak{Y}_k p_k, \\ p_z &= \sum \mathfrak{Z}_k p_k, \quad p_\gamma = \sum (\Gamma_k + \Delta_k) p_k. \end{aligned} \quad (34)$$

The transformation of the classical Hamiltonian expression into the corresponding Schrödinger equation in operator form has been discussed in reference 15. The momenta  $P_x, P_y, P_z$  are given by Eq. (30) of reference 15 in terms of the momenta conjugate to the Eulerian angles  $\theta, \varphi, \chi$ . The operators  $\mathfrak{p}_\theta, \mathfrak{p}_\varphi, \mathfrak{p}_\chi, \mathfrak{p}_\gamma, \mathfrak{p}_k$  are obtained by replacing  $p_\theta, p_\varphi, p_\chi, p_\gamma, p_k$  by  $\hbar/2\pi i$  times  $\partial/\partial\theta, \partial/\partial\varphi, \partial/\partial\chi, \partial/\partial\gamma, \partial/\partial Q_k$ , respectively, in the classical expressions for the momenta. The quantum-mechanical analog of (33) is thus found to be identical in form with it but  $P_x, P_y, P_z, P_\gamma, p_x, p_y, p_z, p_\gamma, p_k$  are to be construed as operators.