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Internal Rotation and Microwave Spectroscopy*

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1. INTRODUCTION

THE study of hindered internal rotation in molecules has been a subject of interest for nearly thirty years and numerous methods have been devised for investigating this phenomenon. We discuss one of these—the method of microwave spectroscopy which has, within the last ten years, been rather extensively employed. Internal rotation interacts with the over-all rotation of a molecule and produces certain effects in its rotational spectrum which can be observed in the microwave region under high resolution. Each rotational transition exhibits a fine structure, the complexity of which depends on the height of the potential barrier hindering the internal rotation. An analysis of

this fine structure leads to an accurate evaluation of the potential barrier. Considerable work has been devoted to the studies of the microwave spectra of molecules in which one group may rotate internally with respect to another. This review gives an account of the past work in this field, including certain details of the methods employed.

Potential barriers are presumably caused by the interactions of two groups of electrons and nuclei. In principle, it should be possible to determine the barrier heights from straightforward quantum-mechanical calculations. The mathematical complexity of such a treatment, however, is so great that a rigorous computation seems highly impractical at present. An alternative approach, which is perhaps somewhat empirical, is to try to describe the origin of the barriers in terms of the forces which appear in the study of intermolecular interactions, such as Van der Waals forces and resonance forces. Although many such analyses have been published, none of these results is completely satisfying. With the new data on the barrier heights in various molecules, it may be possible ultimately to formulate a simple theory of the origin of barriers which not only accounts for all the known results but also may serve to make reliable predictions, at least in a semiquantitative way. In view of the presumed similarity in nature between the origin of the potential barriers and the general problem of intermolecular forces, a satisfactory working theory of the former may throw some light on the study of the latter. The bibliography lists a number of papers which consider the origin of potential barriers and various empirical correlations of the barrier heights with the molecular structures. A review of these papers is not covered here. A brief survey of this subject is given in two recent articles by Wilson.017,018‡

In addition to the method of microwave spectroscopy, various other procedures have been utilized in order to evaluate potential barriers. Such thermodynamic properties as entropy and vapor heat capacity are probably the most commonly used to calculate barrier heights. Generally, these thermodynamic methods complement the microwave methods and are applicable for molecules with high barriers, greater than say 3 kcal/mole (1000 cm⁻¹). Although the thermodynamic procedure does not usually give quite as accurate barrier heights as the best results from microwave work, the former is applicable to a much larger class of molecules since the latter is limited to molecules with a dipole moment. We do not, however, review the thermodynamic results or methods here. The readers are directed to the reviews by Wilson¹¹⁹ and by Pitzer.⁸³

Infrared and Raman spectra²⁹ have been used to determine the frequencies of the internal torsional oscillations. In principle, this would be the direct method for determining the torsional frequencies and

 \ddagger References will be found in the Bibliography at the end of the paper.

the potential barriers. Unfortunately, these torsional oscillations are usually inactive and lie in the very far infrared region so that their detection and assignment are usually difficult, if at all possible. Nuclear magnetic resonance^{1,17,85,96} also has been used recently to give a measure of the magnitude of barriers in liquids. Barrier heights in the range of 5 to 20 kcal/mole may be determined by measuring the widths of the resonance lines as functions of temperature. The time scale of nuclear magnetic resonance is such that if the barrier height is less than about 5 kcal/mole, the internal rotation appears to be free.

The phenomenon of internal rotation is similar to the inversion in ammonia,¹⁰⁸ a pyramidal molecule in which the nitrogen atom may be situated at either side of the plane of the hydrogen atoms. Although a small potential barrier restricts the back-and-forth motion and causes the pyramidal structure, the nitrogen atom may move from one side of the plane to the other through the quantum-mechanical tunneling effect, which splits the doubly degenerate vibrational energy levels below the barrier into pairs of levels (one symmetric and one antisymmetric state). Transitions between these states are observed in the microwave region, and the separation is very sensitive to the height of the potential barrier.

For the case of internal rotation of molecules such as ethane, $CH_3 - CH_3$, the situation is similar. In ammonia the nitrogen atom can move back and forth between the two equivalent positions, while in CH3-CH3 one methyl group can rotate into one of the three positions which are equivalent with respect to the other methyl group. If each of these configurations were considered to be independent, the torsional energy levels would all be triply degenerate. However, the tunneling effect, analogous to the case of ammonia, splits each torsional level into nondegenerate (A species of the C_3 group) and degenerate (E species) sublevels. This is shown in Fig. 1 for an assumed cosine potential function. On the left are the torsional state quantum numbers. The torsional sublevel spacing increases as the torsional energy increases.

Associated with each of the torsional sublevels, one has a set of energy levels arising from the over-all rotation of the entire molecule (referred to as over-all rotational levels). Because of the interaction between the over-all and internal rotation, the spacings of the over-all rotational levels are different in the different torsional states. A given rotational transition then appears as a number of spectral lines corresponding to the transitions in different torsional states. The separations between these lines are utilized to determine the potential barrier height.

In this review we first formulate the Hamiltonians for various molecular models. The calculations of the eigenvalues and eigenfunctions based on various approximations are given and discussed. The practical aspects of the analysis of microwave spectra are pre-



FIG. 1. Hindered rotational energy levels. A cosine potential barrier V_3 and its associated internal rotational energy levels. The torsional quantum numbers v are shown on the left ordinate. The sublevels are denoted by their symmetry under the C_3 group. The free rotational quantum numbers m are shown on the right ordinate.

sented in Sec. 5. This section is intended for those interested in evaluating potential barriers from microwave spectra. Finally, the application of group theory, vibration-torsion-rotation interaction, and experimental results are discussed in that order. The casual reader may find it convenient to omit some of the more mathematical sections in this paper. It is recommended that he first read the sections on "Symmetric Molecules" in Secs. 2 and 3 and also Sec. 4 and Sec. 8. The notation has been standardized. A glossary is given in Appendix 4 and a comparison of the notation used by other authors is given in Appendix 5.

2. HAMILTONIAN

In order to understand the problem of internal rotation and study its effects, the approximate Hamiltonian of the system must be known. The potential energy hindering a symmetric internal rotor is discussed first. Then the kinetic energy is written for rigid symmetric molecules and for rigid asymmetric molecules with an attached symmetric rotor. Methods of calculation of approximate eigenvalues and eigenfunctions are covered in succeeding sections.

I. Potential Energy

Since the origin of the potential barrier is not clearly understood, the only requirement that can be imposed on the potential function is that it be periodic in the relative angle α between the two parts of the molecule. Within the interval of $\alpha=0$ and $\alpha=2\pi$, the potential function must repeat itself N times, where N is the number of equivalent configurations in one complete internal revolution. For example, N is equal to three for acetaldehyde (CH₃CHO) and six for nitromethane (CH₃NO₂). In most cases the symmetry of the molecule is such that the potential function can be expressed as an even function of the angle α . The potential energy can then be expanded in a cosine series as

$$V(\alpha) = \sum_{k} a_k \cos k N \alpha. \tag{2-1a}$$

By a shift in the reference level of the potential energy, this may be written as

$$V(\alpha) = \frac{V_3}{2} (1 - \cos 3\alpha) + \frac{V_6}{2} (1 - \cos 6\alpha) + \cdots \quad (2-1b)$$

for the case of a threefold barrier. However, it has been customary to take the potential function as simply⁸³

$$V(\alpha) = \frac{V_3}{2} (1 - \cos 3\alpha)$$
 (2-2)§

without rigorous justification (Fig. 1).

Serious effort has been made recently^{38,39,25b} to examine the effects and magnitude of the V_6 term, and the experimental data strongly suggests that the sixfold term is indeed much smaller than the V_3 term, the ratio being the order of one-hundredth or less. If this is the case, a good approximation can then be obtained by considering only the threefold terms in the Fourier expansion of the potential energy, i.e., Eq. (2-2). The use of this simple potential function leads to solutions for the torsional wave equation in terms of Mathieu functions. In case greater accuracy is desired, the higher terms can be included and the corrections on the energy levels calculated by perturbation methods.

II. Kinetic Energy and Hamiltonian

In order to derive the kinetic energy, a model is used which consists of two rigid groups connected by a bond. At least one of these groups is a symmetric top. For convenience the symmetric group is regarded as rotating internally about the bond with respect to the other group which is taken as the framework. The entire molecule is also rotating in space. Thus there are four degrees of freedom: the three Eulerian angles θ, Φ, χ of the framework and the relative angle between the two groups, α . The method of solution is dictated by the functional form of the Hamiltonian which depends on the coordinate axes used. In the literature two methods of solution have appeared corresponding to two different frames of reference.

In that originated by Wilson¹¹⁹ and Crawford^{11a} et al., the set of principal axes of the whole molecule is used as the coordinate system (hereafter referred to as the principal axes method or PAM). Since the rotating top possesses an axis of symmetry, the principal axes of the molecule are not altered by a change of the relative orientation of the top and the frame, and the coordinate system may be regarded as rigidly attached to the frame. The Hamiltonian function consists of three groups. The first is recognized as the energy of the rigid rotating system whose moments of inertia are *different* from those of the molecule. The second corresponds to the Hamiltonian of a simple hindered rotor with one degree of freedom. The third appears as the product of the angular momentum of the over-all rotation and the angular momentum associated with the internal motion of the top. This third group represents the interaction of the two kinds of rotation. In the solution the first two groups are taken as the unperturbed system and the cross terms, i.e., the third group, are treated as a perturbation.

In an alternative method originated by Nielsen⁷⁶ and Dennison et al.,^{48,8} the axis about which the top executes internal rotation is chosen as one of the coordinate axes (hereafter referred to as the internal axis method or IAM). The other two axes are fixed with respect to the framework and their orientation is, in principle, arbitrary, but the choice is usually determined to some extent by the symmetry of the molecule. In this coordinate system the terms which describe the interaction between the over-all and internal rotation are considerably smaller than those from PAM. Thus the interaction terms in IAM lend themselves more readily to simple perturbation treatment. The chief disadvantage of this procedure is that, since the coordinate axes are, in general, not principal axes, the Hamiltonian is complicated by the presence of the terms containing the products of inertia.

A. Internal Axis Method

In the derivation of the Hamiltonian by the internal axis method (IAM), the case of a symmetric top (e.g., CH_3SiH_3) is treated first. An asymmetric molecule with a plane of symmetry is then discussed. Methyl alcohol (CH_3OH) and acetaldehyde (CH_3CHO) are examples of this class of molecules.

1. Symmetric molecules.^{76,48}—A set of coordinate axes (a,b,c) is chosen with the *c* axis along the symmetry axis of the molecule through the center of mass. One of the two symmetric groups is designated the frame (a convention set up for comparison with the asymmetric case) and the other symmetric group is designated the internal rotor or top. The *a* and *b* axes can be fixed arbitrarily with respect to the frame because of the symmetric nature of this end. The kinetic energy *T* can then be expressed in tensor notation as (see Appendix 1)

$$T = \frac{1}{2} \boldsymbol{\omega}^{+} \cdot \mathbf{I} \cdot \boldsymbol{\omega} + \frac{1}{2} (\partial \boldsymbol{\alpha} / \partial t)^{+} \cdot \mathbf{I}_{\boldsymbol{\alpha}} \cdot (\partial \boldsymbol{\alpha} / \partial t) + \frac{1}{2} [\boldsymbol{\omega}^{+} \cdot \mathbf{I}_{\boldsymbol{\alpha}} \cdot (\partial \boldsymbol{\alpha} / \partial t) + (\partial \boldsymbol{\alpha} / \partial t)^{+} \cdot \mathbf{I}_{\boldsymbol{\alpha}} \cdot \boldsymbol{\omega}], \quad (2-3)$$

or in terms of the components along the axes as

$$T = \frac{1}{2} I_{a} \omega_{a}^{2} + \frac{1}{2} I_{b} \omega_{b}^{2} + \frac{1}{2} I_{c} \omega_{c}^{2} + \frac{1}{2} I_{a} \dot{\alpha}^{2} + I_{a} \omega_{c} \dot{\alpha}$$
(2-4)
= $\frac{1}{2} I_{a} \omega_{a}^{2} + \frac{1}{2} I_{b} \omega_{b}^{2} + \frac{1}{2} (I_{c} - I_{a}) \omega_{c}^{2} + \frac{1}{2} I_{a} (\omega_{c} + \dot{\alpha})^{2},$

where **I** is the inertial tensor and I_a , I_b , $(I_a=I_b)$, and I_c are the three moments of inertia of the whole molecule about the three coordinate axes; I_{α} is the moment

[§] Some authors have used the form $1 + \cos 3\alpha'$ which merely means a shift in α , i.e., $\alpha' = \pi - \alpha$.

of inertia of the top about its symmetry axis, i.e., the c axis; ω_a, ω_b , and ω_c are the three components of angular velocity ω about the a, b, and c axes; and $\dot{\alpha}$ is the angular velocity of the top relative to the frame. Introduction of the momenta

 $P_{a} = \partial T / \partial \omega_{a} = I_{a} \omega_{a},$ $P_{b} = \partial T / \partial \omega_{b} = I_{b} \omega_{b},$ $P_{c} = \partial T / \partial \omega_{c} = I_{c} \omega_{c} + I_{a} \dot{\alpha},$ (2-5)

and

$$p = \partial T / \partial \dot{\alpha} = I_{\alpha}(\omega_c + \dot{\alpha}),$$

results in the classical Hamiltonian

$$H = \frac{P_a^2}{2I_a} + \frac{P_b^2}{2I_b} + \frac{P_c^2}{2(I_c - I_\alpha)} - \frac{pP_c}{(I_c - I_\alpha)} + \frac{I_c p^2}{2I_\alpha (I_c - I_\alpha)} + V(\alpha). \quad (2-6)$$

The physical meaning of P_a , P_b , and P_c is not immediately obvious. The results of Appendix 1 show that P_a , P_b , and P_c are the components of the total angular momentum (including the internal rotation) about the a, b, and c axes. Therefore they satisfy the usual commutation relations. The quantum-mechanical operators for P_a , P_b , and P_c in the coordinate representation depend only on the Eulerian angles θ , Φ , χ of the framework of the molecule but not on α (see Sec. IIC2). In this case p is the total angular momentum of the top including both the external and internal rotation. As a quantum-mechanical differential operator, p may be expressed as

$$p \to (\hbar/i) (\partial/\partial \alpha)_{\theta, \Phi, \chi},$$
 (2-7)

and therefore p commutes with P_a , P_b , and P_c .

At the limit of a very high potential barrier, Eq. (2-6) does not reduce readily to the case of a rigid rotor plus a simple restricted internal rotor. The reason is that the operator p defined in Eq. (2-5) contains not only the angular momentum of the internal motion of the top but also the contribution from the over-all rotation. When the internal torsion is completely frozen, the classical angular velocity $\dot{\alpha}$ becomes zero and thus p becomes $I_{\alpha}\omega_{c} = (I_{\alpha}/I_{c})P_{c}$. When this expression for p is substituted into Eq. (2-6), the usual energy equation for a rigid symmetric top is recovered.

The connection between Eq. (2-6) and the Hamiltonian for the limiting case of a rigid rotor can be brought out more explicitly through the Nielsen transformation,⁷⁶

$$p' = p - \left[(I_{\alpha}/I_{c})P_{c} \right] = \left[1 - (I_{\alpha}/I_{c}) \right] I_{\alpha} \dot{\alpha} = r I_{\alpha} \dot{\alpha}, \quad (2-8) \|$$
$$P_{c}' = P_{c},$$

which eliminates the cross product pP_c and gives

$$H = \frac{P_a^2}{2I_a} + \frac{P_b^2}{2I_b} + \frac{P_c^{\prime 2}}{2I_c} + \frac{I_c p^{\prime 2}}{2I_\alpha (I_c - I_\alpha)} + V(\alpha). \quad (2-9)$$

The quantity p' depends solely on $\dot{\alpha}$, so that it vanishes at the classical high barrier limit when α is a constant. Here p' is not to be taken as the angular momentum of the internal motion (which is $I_{\alpha}\dot{\alpha}$) but rather $rI_{\alpha}\dot{\alpha}$. Unlike Eq. (2-6), the coefficients of the P's in Eq. (2-9) are the actual rotational constants of the entire molecule. Furthermore p' does not commute with P_{α} and P_b since from Eq. (2-8),

$$p'P_a - P_a p' = i\hbar (I_a/I_c)P_b. \tag{2-10}$$

On the other hand, p' does commute with $P_a^2 + P_b^2$ and hence the Hamiltonian in Eq. (2-9) is separable into two parts corresponding to the over-all rotation and the internal rotation.

Equation (2-9) may also be derived through a transformation of the angular velocities. In terms of ω_c' and $\dot{\alpha}'$ defined as

$$\omega_{c}' = \omega_{c} + (I_{\alpha}/I_{c})\dot{\alpha}, \qquad (2-11)$$
$$\dot{\alpha}' = \dot{\alpha},$$

Eq. (2-4) has the form

$$T = \frac{1}{2} I_a(\omega_a^2 + \omega_b^2) + \frac{1}{2} I_c \omega_c'^2 + \frac{1}{2} r I_a \dot{\alpha}'^2.$$
(2-12)

With the new variable ω_c' it is natural to define

$$P_{c}' = (\partial T/\partial \omega_{c}')_{\omega_{a},\omega_{b},\dot{\alpha}'} = I_{c}\omega_{c}' = I_{c}\omega_{c} + I_{\alpha}\dot{\alpha}, \qquad (2-13)$$
$$p' = (\partial T/\partial \dot{\alpha}')_{\omega_{a},\omega_{b},\omega_{c}'} = [1 - (I_{\alpha}/I_{c})]I_{\alpha}\dot{\alpha} = rI_{\alpha}\dot{\alpha}.$$

In addition, P_a and P_b are unchanged, i.e.,

$$P_{a} = (\partial T / \partial \omega_{a})_{\omega_{b},\omega_{c}'\dot{a}'} = (\partial T / \partial \omega_{a})_{\omega_{b},\omega_{c},\dot{a},}$$

$$P_{b} = (\partial T / \partial \omega_{b})_{\omega_{a},\omega_{c}',\dot{a}'} = (\partial T / \partial \omega_{b})_{\omega_{a},\omega_{c},\dot{a}.}$$
(2-14)

Now the momenta P_c' and p' defined in Eq. (2-13) are identical to the momenta introduced in Eq. (2-8). Substitution of Eqs. (2-13) and (2-14) into Eq. (2-12) gives Eq. (2-9).

The coordinate transformation corresponding to Eq. (2-11) and also Eq. (2-8) is simply

$$\chi' = \chi + [(I_{\alpha}/I_{c})\alpha] = (1/I_{c})[I_{\alpha}\chi_{2} + (I_{c}-I_{\alpha})\chi_{1}], \P \quad (2-15)$$
$$\alpha' = \alpha.$$

Note that χ and α are related to the Eulerian angles of the two groups of the molecule χ_1 and χ_2 as $\chi = \chi_1$, $\alpha = \chi_2 - \chi_1$. One may regard θ, Φ, χ' as the Eulerian angles for a new set of axes. This coordinate system is rotating with respect to the one attached to the framework with an angular velocity of $(I_{\alpha}/I_c)\dot{\alpha}$ about the axis of symmetry of the molecule. These new coordinate

 $[\]parallel$ Here, r, the reducing factor, is an important quantity used in both the IAM and the PAM.

[¶] χ is the same as Φ used in references 8 and 48.

axes are hereafter referred to as "internal rotation axes" (called the "molecule-fixed" system by Hecht and Dennison²⁰). It should be remembered that to an observer located in this frame of reference, both the framework and the top appear to be moving. The angular momentum (z component) arising from the internal motion is

$$I_{\alpha}(\dot{\chi}_{2} - \dot{\chi}') + (I_{c} - I_{\alpha})(\dot{\chi}_{1} - \dot{\chi}') = 0. \qquad (2-16)$$

In treating the problem of vibration-rotation interaction the moving axes are usually chosen so that the angular momentum due to the internal motion vanishes to the first approximation.¹²⁰ For the present problem it would seem proper to use the internal rotation axes as the frame of reference. By letting the three components of the total angular momentum in this coordinate system be P_a' , P_b' , and P_c' , it follows that

$$P_{a}' = (\cos \rho \alpha) P_{a} + (\sin \rho \alpha) P_{b},$$

$$P_{b}' = (-\sin \rho \alpha) P_{a} + (\cos \rho \alpha) P_{b},$$

$$P_{c}' = P_{c},$$

(2-17)

where

$$\rho = I_{\alpha}/I_c. \tag{2-18}$$

For asymmetric molecules,²⁰ the quantity ρ is a more complicated function of the moments of inertia:

$$p = \frac{(I_{bb}^2 + I_{bc}^2)^{\frac{1}{2}} I_{\alpha}}{I_{bb} I_{cc} - I_{bc}^2}, \qquad (2-19)^{31,*}$$

where I_{bb} and I_{cc} are the moments of inertia about the *b* and *c* axis, respectively, and I_{bc} is the product of inertia [see Eq. (2-23)]. For symmetric molecules one has $I_{bc}=0$, so Eq. (2-19) reduces to Eq. (2-18).

Insertion of Eq. (2-17) into Eq. (2-9) gives

$$H = \frac{P_{a'^{2}}}{2I_{a}} + \frac{P_{b'^{2}}}{2I_{b}} + \frac{P_{c'^{2}}}{2I_{c}} + \frac{I_{c}p'^{2}}{2I_{\alpha}(I_{c} - I_{\alpha})} + V(\alpha). \quad (2-20)$$

Equations (2-20) and (2-9) have an identical form. This situation occurs because the two principal moments of inertia I_a and I_b of the molecule are equal. One may question the basic differences between Eqs. (2-20) and (2-9) or between P_a' , P_b' and P_a , P_b . The answer is that P_a and P_b , as pointed out previously, do not commute with p' while both P_a' and P_b' do. Therefore the matrix elements (diagonal and nondiagonal) of P_a' and P_b' do not involve the quantum number associated with the operator

$$[I_c/2I_{\alpha}(I_c-I_{\alpha})]p'^2+V(\alpha). \qquad (2-21)$$

The matrices of P_a and P_b , on the other hand, are characterized by the quantum number of the torsional operator in Eq. (2-21) as well as by the over-all rotational quantum numbers. Consequently the Heisenberg matrix elements of P_a and P_b contain both the over-all and internal rotational frequencies. The same results can be anticipated from a classical consideration. When hindered rotation is present⁶⁷ the set of the internal rotation axes of the molecule rotate in the same way as the principal axes of a rigid symmetric top, while the two groups execute rapid torsion with respect to each other. As P_a and P_b represent the components of the angular momentum along the axes fixed in one of the groups, the values of these components vary at the rate of the torsional frequency.

The cross term pP_e in Eq. (2-6) implies a coupling between the internal and over-all rotation, while according to Eq. (2-20) the internal and external motion are separable. The discrepancy arises from the different choice of the coordinate systems. When the internal rotation axes are used as the frame of reference as in Eq. (2-20), the internal torsion and over-all rotation are independent of each other and hence the Hamiltonian is separable. When the framework of the molecule is taken as the moving frame, the motion of this set of coordinate axes consists of both rotation and the rapid torsional motion. Mathematically, this is reflected by the cross term in Eq. (2-6). Because of the difference in the frames of reference in Eqs. (2-6) and (2-20), the meaning of the term "over-all rotation" is different in these two cases.

2. Asymmetric molecules with a plane of symmetry.^{8,20,31,32,84}—For an asymmetric molecule with a plane of symmetry, a set of coordinate axes is chosen similar to the symmetric top case with the *c* axis through the center of mass of the whole molecule and parallel to the top (symmetric internal rotor) axis, and the *b* axis through the center of mass and lying in the plane of symmetry. The inertial tensor assumes the form

$$\begin{bmatrix} I_{aa} & 0 & 0\\ 0 & I_{bb} & -I_{bc}\\ 0 & -I_{bc} & I_{cc} \end{bmatrix},$$
 (2-22)

where I_{aa} , I_{bb} , and I_{cc} are the moments of inertia and I_{bc} is the product of inertia. The kinetic energy, according to Eq. (2-3), can then be expressed as

$$T = \frac{1}{2} I_{aa} \omega_a^2 + \frac{1}{2} I_{bb} \omega_b^2 + \frac{1}{2} I_{cc} \omega_c^2 - I_{bc} \omega_b \omega_c + \frac{1}{2} I_a \dot{\alpha}^2 + I_a \omega_c \alpha. \quad (2-23)$$

Similarly, the momenta are defined as

$$P_{a} = \partial T / \partial \omega_{a} = I_{aa} \omega_{a},$$

$$P_{b} = \partial T / \partial \omega_{b} = I_{bb} \omega_{b} - I_{bc} \omega_{c},$$

$$P_{c} = \partial T / \partial \omega_{c} = I_{cc} \omega_{c} - I_{bc} \omega_{b} + I_{a} \dot{\alpha},$$

$$p = \partial T / \partial \alpha = I_{a} (\dot{\alpha} + \omega_{c}).$$
(2-24)

As with symmetric molecules, P_a , P_b , and P_c are again the three components of the total angular momentum.

With the substitution of Eq. (2-24) into Eq. (2-23)

^{**} The quantity ρ is the same as Itoh's³¹ λ and can be defined somewhat more simply in the principal axes coordinate system [see Eq. (2-30)].

the following quantum-mechanical Hamiltonian is obtained:

$$H = A_{a}P_{a}^{2} + B_{b}P_{b}^{2} + C_{c}P_{c}^{2} + D_{bc}(P_{b}P_{c} + P_{c}P_{b}) -2D_{bc}P_{b}p - 2C_{c}P_{c}p + Fp^{2} + V(\alpha), \quad (2-25)$$

where

$$A_{a} = \frac{h^{2}}{2I_{aa}},$$

$$B_{b} = \frac{h^{2}(I_{cc} - I_{a})}{2(I_{bb}I_{cc} - I_{a}I_{bb} - I_{bc}^{2})} = \frac{(I_{cc} - I_{a})h^{2}}{2r(I_{bb}I_{cc} - I_{bc}^{2})}$$

$$= \frac{(I_{cc} - I_{a})h^{2}}{2d}$$

$$C_{c} = \frac{h^{2}I_{bb}}{2(I_{bb}I_{cc} - I_{a}I_{bb} - I_{bc}^{2})} = \frac{h^{2}I_{bb}}{2r(I_{bb}I_{cc} - I_{bc}^{2})} = \frac{I_{bb}h^{2}}{2d},$$

$$D_{bc} = \frac{h^{2}I_{bc}}{2(I_{bb}I_{cc} - I_{a}I_{bb} - I_{bc}^{2})} = \frac{h^{2}I_{bc}}{2r(I_{bb}I_{cc} - I_{bc}^{2})} = \frac{I_{bc}h^{2}}{2d},$$

$$F = \frac{h^{2}(I_{bb}I_{cc} - I_{a}I_{bb} - I_{bc}^{2})}{2I_{a}(I_{bb}I_{cc} - I_{bc}^{2})} = \frac{h^{2}}{2rI_{a}},$$

$$r = \frac{I_{bb}I_{cc} - I_{bb}I_{a} - I_{bc}^{2}}{I_{bb}I_{cc} - I_{bc}^{2}} = 1 - \frac{\lambda y^{2}I_{a}}{I_{y}} - \frac{\lambda z^{2}I_{a}}{I_{z}}, \text{ and }$$

$$d = I_{bb}I_{cc} - I_{bb}I_{a} - I_{bc}^{2} = r(I_{bb}I_{cc} - I_{bc}^{2}) = rI_{y}I_{z}.$$

Here I_x , I_y , and I_z are the principal moments of inertia of the whole molecule, and λ_x , λ_y , and λ_z are the direction cosines of the internal axis with respect to the principal axes.

By following the method used for the symmetric case, we can apply the transformation in Eq. (2-8) to eliminate the coupling between over-all rotation and internal rotation. Unfortunately, this transformation does not completely remove the coupling for asymmetric molecules. The results of the transformation on Hare given in Eq. (2-26),

$$H = A_{a}P_{a}^{2} + B_{b}P_{b}^{2} + C_{c}'P_{c}'^{2} + \frac{I_{cc} - I_{\alpha}}{I_{cc}}D_{bc}(P_{b}P_{c}' + P_{c}'P_{b}) - D_{bc}(P_{b}p' + p'P_{b}) - 2\frac{I_{bc}}{I_{cc}}D_{bc}P_{c}'p' + F'p'^{2} + V(\alpha), \quad (2-26)$$

where

$$C_{c}' = \frac{\hbar^{2}}{2I_{cc}} \left[1 + \frac{2I_{bc}^{2}B_{b}}{\hbar^{2}I_{cc}} \right],$$
$$F' = \frac{\hbar^{2}I_{cc}}{2I_{\alpha}(I_{cc} - I_{\alpha})} + \frac{I_{bc}D_{bc}\hbar^{2}}{I_{cc} - I_{\alpha}}$$

Equation (2-26) is essentially the same Hamiltonian employed by Burkhard and Dennison⁸ to obtain the Schroedinger equation. The equivalence between Eq. (2-26) and Burkhard and Dennison's wave equation is discussed later in this section. Again p' in Eq. (2-26) does not commute with P_a and P_b .

Although the coupling between p and P_e can be eliminated for the symmetric case by the transformation (2-8), it is not removed completely for the asymmetric case but is reduced by the factor $I_{bc}^2/I_{bb}I_{cc}$. In order to minimize the coupling term the internal angular momentum must be made to vanish. This is brought about by a slightly different transformation given by Hecht and Dennison²⁰ or by a modification in the formulation given by Itoh.³¹

Hecht and Dennison apply three transformations to the Hamiltonian given in Eq. (2-25). First, a rotation is performed in order to eliminate the P_bp coupling. Secondly, a modified Nielsen transformation is applied to remove the P_cp coupling. These two transformations are given in Eqs. (2-27) and (2-28),

$$P_{a}^{\prime\prime} = P_{a},$$

$$P_{b}^{\prime\prime} = (I_{bb}P_{b} - I_{bc}P_{c})(I_{bb}^{2} + I_{bc}^{2})^{-\frac{1}{2}},$$

$$P_{c}^{\prime\prime} = (I_{bc}P_{b} + I_{bb}P_{c})(I_{bb}^{2} + I_{bc}^{2})^{-\frac{1}{2}},$$
(2-27)

and

$$p' = p - \rho P_c''$$

= $p - I_a (I_{bb}^2 + I_{bc}^2)^{\frac{1}{2}} P_c'' (I_{bb} I_{cc} - I_{bc}^2)^{-1}.$ (2-28)

The transformed Hamiltonian which results from these two operations is

$$H'' = A_a P_a''^2 + B_b'' P_b''^2 + C_c'' P_c''^2 + D_{bc}'' (P_b'' P_c'' + P_c'' P_b'') + F p'^2 + V(\alpha), \quad (2-29)$$

where

$$B_{b}^{\prime\prime} = \frac{\hbar^{2}}{2} I_{bb} (I_{bb}^{2} + I_{bc}^{2})^{-1} = rI_{a}h^{2}(1-r)/2\rho^{2}d,$$

$$C_{c}^{\prime\prime} = \frac{\hbar^{2}}{2} \left[\frac{I_{bb} + I_{cc}}{I_{bb}I_{cc} - I_{bc}^{2}} - \frac{I_{bb}}{I_{bb}^{2} + I_{bc}^{2}} \right] = \frac{\hbar^{2}}{2} \left(\frac{1}{I_{y}} + \frac{1}{I_{z}} \right) - B_{b}^{\prime\prime},$$

$$D_{bc}^{\prime\prime} = \frac{\hbar^{2}}{2} I_{bc} (I_{bb}^{2} + I_{bc}^{2})^{-1} = (rI_{a})^{2} D_{bc}/\rho^{2}d$$

$$= \frac{\hbar^{2}}{2} \frac{\rho_{y}\rho_{z}}{\rho} \left(\frac{1}{I_{y}} - \frac{1}{I_{z}} \right),$$

$$\rho = \frac{(I_{bb}^{2} + I_{bc}^{2})^{\frac{1}{2}}I_{a}}{(I_{bb}I_{cc} - I_{bc}^{2})} = \left[\Sigma_{g} \left(\frac{\lambda_{g}I_{a}}{I_{g}} \right)^{2} \right]^{\frac{1}{2}}, \quad (g = x, y, z),$$

$$\rho_{g} = \lambda_{g}I_{a}/I_{g}. \quad (2-30)$$

Finally, the transformation described in Eq. (2-17), with ρ given by the more complicated expression Eq. (2-30), is applied to Eq. (2-29). This transformation defines the "internal rotational axes system." Referred to these axes the internal angular momentum vanishes. The resulting Hamiltonian²⁰ is

$$H' = \frac{1}{2} (A_a + B_b'') (P_a'^2 + P_b'^2) + C_c'' P_c'^2 + F p'^2 + V(\alpha) + \frac{1}{2} (A_a - B_b'') [(P_a'^2 - P_b'^2) \cos 2\rho\alpha - (P_a' P_b' + P_b' P_a') \sin 2\rho\alpha] + D_{bc}'' [(P_b' P_c' + P_c' P_b') \cos \rho\alpha + (P_a' P_c' + P_c' P_a') \sin \rho\alpha].$$
(2-31)

It can be easily shown that P_a' , P_b' , and P_c' satisfy

the usual commutation rules and they all commute with p'.

Itoh³¹ has derived the Hamiltonian (2-29) in an interesting and useful way. He also expressed the Hamiltonian in a form convenient for comparison with the PAM formulation. The over-all angular velocity is divided into two parts ω_1 and ω_2 , such that the angular momentum of the whole molecule associated with ω_1 balances the internal angular momentum. This is equivalent to choosing a set of axes in which the internal angular momentum vanishes. Thus one has

$$\mathbf{I} \cdot \boldsymbol{\omega}_1 + I_{\alpha} (\partial \alpha / \partial t) = 0, \qquad (2-32a)$$

or where

$$\omega_1 = -\mathbf{I}^{-1} \cdot \hat{k} (I_{\alpha} \dot{\alpha}) = - \varrho \dot{\alpha}, \qquad (2-32b)$$

$$\boldsymbol{\rho} = I_{\boldsymbol{\alpha}}(\mathbf{I}^{-1} \cdot \hat{k}). \tag{2-32c}$$

Here I is the inertia tensor and \hat{k} is a unit vector in the direction of $(\partial \alpha / \partial t)$. The components of the vector $\boldsymbol{\varrho}$ can be found from Eqs. (2-22) and (2-32c). Referred to the *a*, *b*, and *c* axes, one obtains

 $\rho_a = 0$, $\rho_b = I_{\alpha} I_{bc} (I_{bb} I_{cc} - I_{bc}^2)^{-1}$,

and

$$\rho_c = I_{\alpha} I_{bb} (I_{bb} I_{cc} - I_{bc}^2)^{-1}. \qquad (2-33)$$

The three components of ϱ along the principal axes and the magnitude of the vector are given by Eq. (2-30). By expressing Eq. (2-3) in terms of ω , ω_1 , and α , one obtains

$$T = \frac{1}{2} (\omega - \omega_1)^+ \cdot \mathbf{I} \cdot (\omega - \omega_1) - \frac{1}{2} \omega_1^+ \cdot \mathbf{I} \cdot \omega_1 + \frac{1}{2} (\partial \alpha / \partial t)^+ \cdot \mathbf{I}_{\alpha} \cdot (\partial \alpha / \partial t).$$
(2-34)

The substitution of Eq. (2-32b) into Eq. (2-34) yields

$$T = \frac{1}{2} (\boldsymbol{\omega} + \boldsymbol{\varrho} \dot{\boldsymbol{\alpha}})^+ \cdot \mathbf{I} \cdot (\boldsymbol{\omega} + \boldsymbol{\varrho} \dot{\boldsymbol{\alpha}}) + \frac{1}{2} (\mathbf{I}_{\boldsymbol{\alpha}} - \boldsymbol{\varrho}^+ \cdot \mathbf{I} \cdot \boldsymbol{\varrho}) \dot{\boldsymbol{\alpha}}^2$$

= $\frac{1}{2} \sum_{jk} I_{jk} (\omega_j + \rho_j \dot{\boldsymbol{\alpha}}) (\omega_k + \rho_k \dot{\boldsymbol{\alpha}}) + \frac{1}{2} r I_{\boldsymbol{\alpha}} \dot{\boldsymbol{\alpha}}^2.$

The resulting Hamiltonian is

$$H = \frac{\hbar^2}{2} \sum_{jk} I_{jk}^{-1} P_j P_k + \frac{\hbar^2}{2} \left(\frac{1}{r I_{\alpha}} \right) (p - \Pi)^2 + V(\alpha), \quad (2-35)$$

where

$$\Pi = \rho_b P_b + \rho_c P_c = \varrho \cdot \mathbf{P}$$

This Hamiltonian is the same as Eq. (2-25). A rotation of the *c* axis to the ϱ direction (*c'* direction) brings the Hamiltonian to the form given in Eq. (2-29) which then can be transformed to Eq. (2-31). This transformation is not strictly necessary since the quantum-mechanical matrix elements can be determined from Eq. (2-29) as well as Eq. (2-31) with only a different torisonal wave function. This point is discussed in Sec. 3.

Finally, two other types of molecular symmetry have been considered in the literature. Molecules with two perpendicular planes of symmetry, e.g., nitromethane, have been considered by Wilson *et al.*¹²¹ and by Tannenbaum, Johnson, Meyers, and Gwinn.^{106,107} Here all the previous formulas apply with $I_{bc}=0$.

Molecules with no planes of symmetry have been treated by Hecht and Dennison²⁰ and by Burkhard,⁷ and the method is similar to that outlined in this section.

B. Principal Axes Method (PAM)^{11a,23,101,119,121}

In the PAM the symmetric top Hamiltonian is given by Eq. (2-6) with the principal axes x, y, and z coincident with the a, b, and c axes. The transformation (2-8) is not applied. In this method (for an asymmetric molecule) a coordinate system x, y, and z, rigidly attached to the framework of the molecule, is used. Furthermore, this set of axes is chosen to be the principal axes of the entire molecule with the origin at the center of mass so that the principal moments of inertia I_x , I_y , and I_z ^{††} of the molecule are used. The orientation of the principal axes relative to the framework is not altered by the rotation of the top because of its cylindrical symmetry. Therefore from Eq. (2-3), the kinetic energy for an asymmetric molecule has the form

$$T = \frac{1}{2}I_x\omega_x^2 + \frac{1}{2}I_y\omega_y^2 + \frac{1}{2}I_z\omega_z^2 + I_a\lambda_x\omega_x\dot{\alpha} + I_a\lambda_y\omega_y\dot{\alpha} + I_a\lambda_z\omega_z\dot{\alpha} + \frac{1}{2}I_a\dot{\alpha}^2, \quad (2-36)$$

where ω_x , ω_y , and ω_z are the components of the angular velocity along the principal axes, and λ_x , λ_y , and λ_z are the direction cosines of the symmetry axis of the top to the principal axes. In terms of the momenta defined as

$$P_i = \frac{\partial T}{\partial \omega_i} \quad (i = x, y, z),$$

$$p = \frac{\partial T}{\partial \dot{\alpha}},$$

the Hamiltonian can be written in the form¹⁰¹

$$=A_{x}P_{x}^{2}+B_{y}P_{y}^{2}+C_{z}P_{z}^{2}+\frac{1}{2}\sum_{x,y,z,i\neq j}D_{ij}(P_{i}P_{j}+P_{j}P_{i})$$
$$-2\sum_{x,y,z}Q_{i}P_{i}p+Fp^{2}+V(\alpha), \quad (2-37)$$

where

H

$$A_x = \frac{\hbar^2}{2I_x} \left[1 + \frac{\lambda_x^2 I_\alpha}{rI_x} \right] = \frac{\hbar^2}{2I_x} + F \rho_x^2,$$

and similarly for B_y and C_z by the permutation (x, y, z),

$$D_{ij} = \frac{\hbar^2 \lambda_i \lambda_j I_\alpha}{2 r I_i I_j} = F \rho_i \rho_j \quad (i, j = x, y, z \text{ and } i \neq j),$$

$$Q_i = \frac{\hbar^2 \lambda_i}{2 r I_i} = F \rho_i \quad (i = x, y, z),$$

$$F = \hbar^2 / 2 r I_\alpha,$$

$$\rho = (\rho_x^2 + \rho_y^2 + \rho_z^2)^{\frac{1}{2}} = \left[\sum_{g = x, y, z} \left(\frac{\lambda_g I_\alpha}{I_g} \right)^2 \right]^{\frac{1}{2}}, \quad \rho_g = \lambda_g I_\alpha / I_g,$$

$$r = 1 - \frac{\lambda_y^2 I_\alpha}{I_y} - \frac{\lambda_z^2 I_\alpha}{I_z}.$$

^{††} Note that the notation I_x , I_y , and I_z is used instead of I_{xz} , I_{yy} , and I_{zz} because of the absence of the product of inertia terms.

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Alternatively one may express the Hamiltonian^{25a} as

$$H = (\hbar^2 / 2r I_{\alpha}) (p - \Pi)^2 + (\hbar^2 / 2) \sum_{g} P_{g^2} / I_{g} + V(\alpha), \quad (2-38)$$

where

where

$$\Pi = \boldsymbol{\varrho} \cdot \mathbf{P} = \sum_{g} \rho_{g} P_{g} = (\lambda_{x} I_{\alpha} / I_{x}) P_{x} + (\lambda_{y} I_{\alpha} / I_{y}) P_{y} + (\lambda_{z} I_{\alpha} / I_{z}) P_{z}$$

The similarity between Eqs. (2-38) and (2-35) should be noted.

From Eq. (A1-7) it is clear that P_x , P_y , and P_z represent the three components of the total angular momentum defined in the usual way. The commutation relations between the various momenta can be summarized as

$$(P_i, P_j) = -i\hbar P_k$$
 $(i, j, k = x, y, z \text{ in cyclic order}),$
 $(p, P_i) = 0.$

Furthermore, the coupling between over-all rotation and internal rotation is apparent in the Hamiltonian by the cross terms pP_i , etc.

For the molecules with a plane of symmetry in their framework all the above formulation applies with $\lambda_x = 0$ (or $\lambda_y = 0$).^{68,38} With two planes of symmetry both of the direction cosines are set to zero.¹²¹

C. Comparison of the Two Methods

The chief difference between the two methods lies in the different choice of coordinate axes. Hence, the Hamiltonian functions can be transformed to each other simply through a coordinate transformation which is given in the first part of this section. In the second part the Schroedinger equations in terms of the Eulerian angles are given for each method. While it is not necessary to express the Hamiltonian and the wave function in the coordinate representation in order to find the energy levels, a comparison of the momentum operators in terms of the Eulerian angles does show more clearly the difference between the two formulations.

1. Connecting relations .- For the purpose of demonstrating the connection between the two procedures a molecule with a plane of symmetry is taken. The relation between the components of a vector \mathbf{r} in the principal axes x, y, z and the set of axes a, b, c, defined in the internal axis method is

$$\begin{pmatrix} r_a \\ r_b \\ r_c \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \lambda_z & -\lambda_y \\ 0 & \lambda_y & \lambda_z \end{pmatrix} \begin{pmatrix} r_x \\ r_y \\ r_z \end{pmatrix}.$$
(2-39)

The various terms in these two systems are then related by the equations

$$I_{bb} = \lambda_z^2 I_y + \lambda_y^2 I_z,$$

$$I_{cc} = \lambda_z^2 I_z + \lambda_y^2 I_y,$$

$$I_{bc} = \lambda_y \lambda_z (I_z - I_y),$$

$$I_{aa} = I_x,$$

$$r = \frac{I_{bb}I_{cc} - I_{bb}I_{a} - I_{bc}^{2}}{I_{bb}I_{cc} - I_{bc}^{2}} = 1 - \frac{\lambda_{y}^{2}I_{\alpha}}{I_{y}} - \frac{\lambda_{z}^{2}I_{\alpha}}{I_{z}}, \quad (2-40)$$

$$\rho = \frac{(I_{bb}^{2} + I_{bc}^{2})^{\frac{1}{2}}I_{\alpha}}{(I_{bb}I_{cc} - I_{bc}^{2})} = \left(\frac{\lambda_{y}^{2}I_{\alpha}^{2}}{I_{y}^{2}} + \frac{\lambda_{z}^{2}I_{\alpha}^{2}}{I_{z}^{2}}\right)^{\frac{1}{2}}.$$

From these formulas one can prove the equivalence of Eq. (2-25) or Eq. (2-35) and Eq. (2-37) or Eq. (2-38).

2. Comparison by Eulerian angles.—(a) Principal axes method: To express the angular momentum operators in coordinate representation use is made of the relation

$$P_{x} = \frac{\partial T}{\partial \omega_{x}} = \frac{\partial \dot{\theta}}{\partial \omega_{x}} \frac{\partial T}{\partial \dot{\theta}} + \frac{\partial \dot{\Phi}}{\partial \omega_{x}} \frac{\partial T}{\partial \dot{\Phi}} + \frac{\partial \dot{\chi}}{\partial \omega_{x}} \frac{\partial T}{\partial \dot{\chi}}$$
$$= \frac{\partial \dot{\theta}}{\partial \omega_{x}} P_{\theta} + \frac{\partial \dot{\Phi}}{\partial \omega_{x}} P_{\Phi} + \frac{\partial \dot{\chi}}{\partial \omega_{x}} P_{\chi}. \tag{2-41}$$

Since ω_x , ω_y , and ω_z constitute the angular velocity of the framework of the molecule, they are related to the Eulerian angles describing the orientation of the framework through the equations

$$\omega_{x} = \dot{\theta} \sin\chi - \dot{\Phi} \sin\theta \cos\chi,$$

$$\omega_{y} = \dot{\theta} \cos\chi + \dot{\Phi} \sin\theta \sin\chi,$$
 (2-42)

$$\omega_{z} = \dot{\chi} + \dot{\Phi} \cos\theta.$$

The quantum-mechanical operators for P_x , P_y , and P_z are readily obtained if one replaces p_{θ} by $(\hbar/i)(\partial/\partial\theta)_{\Phi_{\chi\alpha}}$ etc. It follows that

$$\frac{iP_{x}}{h} = \sin\chi \left(\frac{\partial}{\partial\theta}\right)_{\Phi_{\chi\alpha}} - \cos\chi \csc\theta \left(\frac{\partial}{\partial\Phi}\right)_{\theta_{\chi\alpha}} + \cos\chi \cot\theta \left(\frac{\partial}{\partial\chi}\right)_{\theta\Phi\alpha}$$
$$\frac{iP_{y}}{h} = \cos\chi \left(\frac{\partial}{\partial\theta}\right)_{\Phi_{\chi\alpha}} + \sin\chi \csc\theta \left(\frac{\partial}{\partial\Phi}\right)_{\theta_{\chi\alpha}} - \sin\chi \cot\theta \left(\frac{\partial}{\partial\chi}\right)_{\theta\Phi\alpha}$$
$$\frac{iP_{z}}{h} = \left(\frac{\partial}{\partial\chi}\right)_{\theta\Phi\alpha}. \tag{2-43}$$

These expressions for the angular momentum are identical to those for a rigid rotor, and the customary commutation rules can thereby be established. Since $\omega_x, \omega_y, \omega_z$ have no dependence on $\dot{\alpha}$ and α , one can see that

$$p = (\partial T / \partial \dot{\alpha})_{\omega_x, \omega_y, \omega_z} = (\partial T / \partial \dot{\alpha})_{\theta \Phi_{\chi}}, \qquad (2-44)$$

and the quantum-mechanical for p is, accordingly,

$$p = -\frac{h}{i} \left(\frac{\partial}{\partial \alpha} \right)_{\theta \Phi_{\chi}}.$$
 (2-45)

Inspection of Eqs. (2-43) and (2-45) confirms the commutation relation

$$pP_i - P_i p = 0, \quad i = x, y, z.$$

Equations (2-43) and (2-45) may now be substituted in the Hamiltonian in order to derive the desired wave equation.

(b) Internal axis method: The coordinate transformation from θ , Φ , χ , α to θ , Φ , χ' , α' , as described in Eq. (2-15), can be used to express P_a , P_b , P_c' , and p'in terms of the new set of variables

$$(\partial/\partial\chi)_{\alpha} = (\partial/\partial\chi')_{\alpha'}$$

$$(\partial/\partial\alpha)_{\chi} = \rho(\partial/\partial\chi')_{\alpha'} + (\partial/\partial\alpha')_{\chi'}.$$

$$(2-46)$$

Equation (2-46) is valid so long as the *c* axis is parallel to the bond connecting the framework and the top. However, after the transformation Eq. (2-27), this is no longer true and the Eulerian angles χ , α , χ' , and α' are related by more complicated expressions [see Eq. (8) of reference (20)]. In order to simplify the mathematical details, only Eq. (2-46) is used.

It is now possible to write with the aid of Eqs. (2-15) and $(2-46),\ddagger\ddagger$ the following angular momenta,

$$P_{a} = \cos \rho \alpha' P_{a} \chi' \alpha' - \sin \rho \alpha' P_{b} \chi' \alpha',$$

$$P_{b} = \sin \rho \alpha' P_{a} \chi' \alpha' + \cos \rho \alpha' P_{b} \chi' \alpha',$$

$$P_{c} = \frac{h}{i} \left(\frac{\partial}{\partial \chi'}\right)_{\theta \Phi \alpha'},$$
(2-47)

where

$$P_{a}^{\chi'\alpha'} = \frac{\hbar}{i} \left[\sin\chi' \left(\frac{\partial}{\partial \theta} \right)_{\Phi\chi'\alpha'} - \cos\chi' \csc\theta \left(\frac{\partial}{\partial \Phi} \right)_{\theta\chi'\alpha'} + \cos\chi' \cot\theta \left(\frac{\partial}{\partial\chi'} \right)_{\theta\Phi\alpha'} \right], \quad (2-48)$$
$$P_{b}^{\chi'\alpha'} = \frac{\hbar}{i} \left[\cos\chi' \left(\frac{\partial}{\partial \theta} \right)_{\Phi\chi'\alpha'} + \sin\chi' \csc\theta \left(\frac{\partial}{\partial\Phi} \right)_{\theta\chi'\alpha'} - \sin\chi' \cot\theta \left(\frac{\partial}{\partial\chi'} \right)_{\theta\Phi\alpha} \right].$$

The two superscripts on P_a and P_b denote two of the four "independent variables" (the other two being always θ and Φ) one chooses in taking the partial derivatives. One might well recognize that $P_a^{\chi'\alpha'}$ and $P_b^{\chi'\alpha'}$ have almost the same form as P_x and P_y in Eq. (2-43) (which in our present notation, would be written as $P_x^{\chi\alpha}$ and $P_y^{\chi\alpha}$) aside from the fact that χ' and α' are used as variables for one case while χ and α are

$$P_{a} = \frac{\partial \theta}{\partial \omega_{a}} P_{\theta} + \frac{\partial \Phi}{\partial \omega_{a}} P_{\Phi} + \frac{\partial \chi'}{\partial \omega_{a}} P_{\chi'} + \frac{\partial \alpha'}{\partial \omega_{a}} p, \text{ etc.}$$

used for the other. It is important to specify the independent variables in the partial derivatives because Eq. (2-46) shows that $(\partial/\partial\alpha)_{\chi}$ is different from $(\partial/\partial\alpha)_{\chi'}$ and also from $(\partial/\partial\alpha')_{\chi'}$. Since P_a and P_b involve all four angular variables, the eigenfunctions of the operator

$$P_a^2/2I_a + P_b^2/2I_b + P_c^2/2I_b$$

depend on the internal coordinate α' , in addition to the three Eulerian angles, in a rather complex manner. For example, these functions are not identical to the asymmetric top wave function. It is apparent that the absence of the cross product between the two kinds of momentum operators in Eq. (2-29) does not signify a complete separation between the external and internal coordinates inasmuch as the *P*'s are actually functions of α . When the momentum operators in Eq. (2-26) are written in their differential form given in Eqs. (2-47) and (2-48) [where ρ is I_{α}/I_{cc} from Eq. (2-8)], the Schroedinger equation is obtained. This equation was given by Burkhard and Dennison.§§

The rather unsatisfactory feature of having α' mixed in the *P*'s can be removed by a transformation which is the inverse of Eq. (2-47), i.e., introducing P_a' and P_b' so that

$$\binom{P_{a}}{P_{b}'} = \binom{\cos\rho\alpha & \sin\rho\alpha}{-\sin\rho\alpha & \cos\rho\alpha} \binom{P_{a}}{P_{b}} = \binom{P_{a}x'\alpha'}{P_{b}x'\alpha'}.$$
 (2-49)

This transformation is similar to the one employed previously in Eq. (2-17) in connection with the internal rotation axes. Equation (2-49) shows that $P_{a'}$ and $P_{b'}$ do not contain α explicitly and thus commute with p'.

The Hamiltonian may then be written in the Schroedinger representation with the aid of Eqs. (2-48) and (2-49).

3. HIGH BARRIER APPROXIMATIONS

In Sec. 2 the Hamiltonians were derived for various coordinate systems and for molecules of various kinds of symmetry. These Hamiltonians can generally be divided into three parts: the over-all rotational part, the internal rotation torsional part, and a coupling between over-all rotation and internal rotation. Since the separation is not complete, except in the case of a symmetric type molecule, the Schroedinger equation cannot be solved exactly; perturbation theory is usually applied. For ease in computation we use a matrix formulation, and two approximate methods for diagonalizing the matrix are commonly used. The high barrier approximation is applicable to the cases where the separations of the torsional energy levels are large compared with the rotational energy separations. The other is the low barrier approximation where the problem of the free internal rotor is first solved and the barrier treated as a perturbation. Section 4 deals with this low barrier approximation.

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^{‡‡} These may be obtained by a procedure similar to that employed in Eq. (2-41), i.e., from the relations

^{§§} See p. 411 of reference 8.

The Schroedinger equation for a high barrier can be solved by using either the PAM or IAM.

In the PAM the energy matrix is constructed in a representation in which the over-all rotation part and the internal torsion part of the Hamiltonian are separately diagonal. The cross terms (coupling terms) between the total angular momentum and the internal angular momentum are chosen as the perturbation. The basis functions are then the product of the rigid symmetric rotor wave functions and the functions of the internal angle α , known as the torsional functions which are related to the tabulated Mathieu functions. The perturbation terms are treated by the Van Vleck transformation³⁴ so that after this transformation the secular equation can be approximately factored into blocks corresponding to the different torsional states. Associated with each torsional state there are two different submatrices in the energy matrix and thus two sets of rotational levels. From the separation of the pair of spectral lines arising from a given rotational transition in the two sets of rotational levels, the barrier hindering internal rotation is determined.

In the IAM the Nielsen transformation (or the modified form given by Hecht and Dennison²⁰ or Itoh³¹) is applied to the Hamiltonian so that the coupling terms between the internal and external coordinates in the transformed Hamiltonian are completely removed or become much smaller than those which occur in the PAM, and hence can be treated by perturbation method more readily. The basis functions of the energy matrix are again taken as the product of the rigid symmetric rotor functions and the torsional functions which are the solution of a differential equation similar to the Mathieu equation. The torsional functions here are different from those in PAM because of the different boundary conditions as explained in Sec. I. B. Because of the interaction of the external and internal rotation, the torsional functions depend on the quantum number K and, in principle, the differential equation for the torsional functions should be solved for each value of K. Since it is necessary to have the torsional functions in order to evaluate the elements of the energy matrix, the determination of the torsional functions becomes one of the major difficulties of this method. Approximate formulas²⁰ have been derived for the matrix elements involving the torsional functions. At the high barrier approximation the infinite energy matrix can be reduced to a series of $(2J+1) \times (2J+1)$ blocks, corresponding to the case of limiting rigid rotor. Since the coordinate axes used in setting up the Hamiltonian in Eq. (2-25) are not the principal axes for the asymmetric rotor, a coordinate transformation to the principal axes should be made so as to simplify the solution of the secular equation. When this is done, each of the submatrices becomes very similar to that of a rigid rotor with some additional elements which represent the effect of the internal torsion on the over-all rotation. From the structure of the energy levels it was found that each of

the rigid-rotor spectral lines is split into a doublet as also predicted by the PAM. The relations between the separations of the doublets to the barrier height have been given by Hecht and Dennison²⁰ and also by Lide and Mann.⁶² These approximate equations are equivalent to those derived by PAM so that one has in many cases an equal choice as to which method to use: PAM or IAM. In the discussion to follow the symmetric molecule is covered first by the PAM and the IAM. With these principles in mind the effect of asymmetry in the molecular frame is introduced into both the PAM and the IAM.

I. Symmetric Molecules

A. Principal Axes Method (PAM)

As derived in the previous section [see Eq. (2-6)], the Hamiltonian for this class of molecules can be written as

$$H = H_R + H_T + H_{IR}, \tag{3-1}$$

where

$$H_{R} = A_{x}(P_{x}^{2} + P_{y}^{2}) + C_{z}P_{z}^{2},$$

$$H_{T} = Fp^{2} + V(\alpha),$$

$$H_{IR} = -2C_{z}P_{z}p,$$

$$A_{x} = \frac{\hbar^{2}}{2I_{x}} = \frac{\hbar^{2}}{2I_{y}},$$

$$C_{z} = \frac{\hbar^{2}}{2(I_{z} - I_{\alpha})} = \frac{\hbar^{2}}{2I_{z}} + F\rho^{2},$$

$$F = \frac{\hbar^{2}}{2rI_{\alpha}} = \frac{\hbar^{2}I_{z}}{2I_{\alpha}(I_{z} - I_{\alpha})}.$$
(3-2)

Here, H_R and H_T comprise, respectively, the terms describing the over-all rotation and internal rotation, and H_{IR} represents the interaction term. []] In the calculation of the energy levels of H, we take $H_R + H_T$ as the unperturbed Hamiltonian and treat H_{IR} as the perturbation. Since H_{IR} does not vanish at the limit of infinite barrier, the effect of the perturbation is not *small*. Consequently, for molecules with an intermediate barrier, fourth-order perturbation procedure must be applied in order to obtain accurate results for the barrier heights. Nevertheless, the advantages of this approach will be seen.

1. Rotational equation H_R .—The eigenfunctions of H_R are the symmetric rotor functions and they are usually expressed as

$$S_{JKM}(\theta,\varphi)e^{iK\chi}$$

where J is the total angular momentum and K and M are the projection of J on the body-fixed and spacefixed axes, respectively. The energy and the matrix

 $^{\|\|}$ For a discussion of the "interaction" between over-all and internal rotation see the last paragraph of Sec. 2 II. A1.

elements of P are

$$E = A_{x}J(J+1) + (C_{z} - A_{z})K^{2},$$

$$(JK | P^{2} | JK) = J(J+1)\hbar^{2},$$

$$(JK | P_{z} | JK) = K\hbar.$$

The rotational constant, C_z , associated with P_z^2 is not that of the limiting rigid rotor and hence H_R does not represent the entire Hamiltonian for the case of infinite barrier height. The reduction of H into the rigid-rotor Hamiltonian for the limiting high barrier is discussed in Sec. I. A5.

2. Torsional equation H_T .—(a) Eigenfunctions and eigenvalues: The eigenfunction $U(\alpha)$ and the eigenvalues E of H_T are to be determined from the differential equation

$$\left[-Fd^2/d\alpha^2 + V(\alpha)\right]U(\alpha) = EU(\alpha). \tag{3-3}$$

Physically we know that $U(\alpha)$ must be periodic in 2π . When $V(\alpha)$ is taken as a simple sinusoidal function such as $\frac{1}{2}V_3(1-\cos 3\alpha)$, the above equation can readily be transformed through the substitutions

$$3\alpha + \pi = 2x, \quad s = 4V_3/9F,$$

 $U[(3\alpha + \pi)/2] = M(x), \quad b = 4E/9F,$ (3-4)

to the Mathieu equation

$$\frac{d^2M(x)}{dx^2} + \left[(b - \frac{1}{2}s) - \frac{1}{2}s \cos 2x \right] M(x) = 0. \quad (3-5)$$

The solutions of Eq. (3-5) may be expanded by Fourier series

$$M(x) = \sum_{k} c_k \cos kx + d_k \sin kx$$

Since Eq. (3-5) is invariant under the operation $x \to -x, x \to x + \pi$, the eigenfunctions of Eq. (3-5) have one of the following forms¹⁰⁴:

$$Se_{2r}(s,x) = \sum_{k} De_{2k}^{(2r)} \cos 2kx \qquad (\text{period } \pi) \qquad (3-6a)$$

$$Se_{2r+1}(s,x) = \sum_{k} De_{2k+1}^{(2r+1)} \cos(2k+1)x$$
(period 2π) (3-6b)

 $So_{2r}(s,x) = \sum_{k} Do_{2k}^{(2r)} \sin 2kx \qquad (\text{period } \pi) \qquad (3-6c)$

$$So_{2r+1}(s,x) = \sum_{k} Do_{2k+1}^{(2r+1)} \sin(2k+1)x$$
(period 2 π). (3-6d)

Here s is a parameter associated with the differential equation (3-5). For each type of the functions, Se(s,x) and So(s,x), one finds a series of eigenfunctions and they are labeled by the superscript r. The values of b corresponding to these functions are denoted by be_{2r} , be_{2r+1} , bo_{2r} , bo_{2r+1} . When Eqs. (3-6) are substituted in Eq. (3-5), four different infinite secular equations are obtained from which the eigenvalues can be determined. This procedure can be carried out in a systematic fashion which is described in Appendix 2. The Fourier coefficients of the eigenfunctions are then obtained from the recursion relations. The eigenvalues and the

Fourier coefficients of the associated eigenfunctions can be found in the *Tables Relating to Mathieu Functions*.¹⁰⁴

From the torsional equation one may readily see that since the C_3 group operations leave Eq. (3-3) invariant \P ; the solution of this equation can be expanded in the form

$$\sum_{k} A_{3k} e^{i3k\alpha} \qquad (A) \qquad (3-7a)$$

$$\sum_{k} A_{3k+1} e^{i(3k+1)\alpha} \quad (E_1) \tag{3-7b}$$

$$\sum_{k} A_{3k-1} e^{i(3k-1)\alpha} \quad (E_2) \tag{3-7c}$$

corresponding to the symmetry species A and E of the C_3 group. The first form of the expansion in Eq. (3-7) gives rise to nondegenerate eigenfunctions while the last two constitute the doubly degenerate pairs. The series of eigenvalues and eigenfunctions of the non-degenerate solutions can be obtained from the tabulated Mathieu functions with period π , Eqs. (3-6a) and (3-6c), after the slight modification as set down in Eq. (3-4). The degenerate solutions have been tabulated recently by Kilb.³⁶ The relations between the notations adopted here and those used in the various tabulations may be summarized as follows:

Each member of the series of the degenerate and nondegenerate solutions is labeled by the index v with v=0 for the lowest eigenvalue. At very high barriers the spacings between the nondegenerate and degenerate energy levels of the torsional equation associated with a given v are much smaller than those between levels with different v (see Fig. 1). For this reason, the index vis called the torsional quantum number and the different energy levels associated with a given v are thought of as the torsional sublevels belonging to the same torsional state. The sublevels are distinguished by the index σ with $\sigma = 0$ for the nondegenerate level (species A) and $\sigma = \pm 1$ for the levels of species E $(E_1: \sigma = +1, E_2: \sigma = -1)$. In Fig. 2 the energy levels are plotted as a function of the barrier height from free internal rotation to a relatively high barrier. The solution of the free rotational energy levels and the meaning of the "m" quantum number are discussed in Sec. 4.

A solution of the torsional equation can then be written as

$$U_{v\sigma}(\alpha) = \sum_{k} A_{3k+\sigma} e^{i(3k+\sigma)\alpha}, \qquad (3-9)$$

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^{¶¶} Strictly speaking, Eq. (3-3) belongs to the C_{3v} group. However, in the present discussion, it is more convenient to consider only the subgroup C_3 .

and the eigenvalues associated with these functions are correspondingly denoted by E_{vo} .

(b) Harmonic oscillator approximation: With a very high barrier the internal motion degenerates into small oscillations, and the potential energy $\frac{1}{2}V_3(1-\cos 3\alpha)$ may be expanded about the equilibrium point yielding $(9/4)V_3\alpha^2$. The torsional wave function in the vicinity of the equilibrium configuration can be approximated by the harmonic oscillator functions which are denoted as $H_v(\alpha)$. The corresponding eigenvalues are

$$E_{v} = 3(V_{3}F)^{\frac{1}{2}}(v + \frac{1}{2}). \tag{3-10}$$

There are three functions of $H_{\nu}(\alpha)$; one situated at each of three potential minima. These functions are denoted by $H_{\nu}^{(1)}$, $H_{\nu}^{(2)}$, and $H_{\nu}^{(3)}$. When the tunneling effect is considered, the correct zeroth-order torsional functions are^{20,99}

$$U_{v,0}(\alpha) = \frac{1}{\sqrt{3}} [H_{v}^{(1)} + H_{v}^{(2)} + H_{v}^{(3)}],$$

$$U_{v,1}(\alpha) = \frac{1}{\sqrt{3}} [H_{v}^{(1)} + \omega H_{v}^{(2)} + \omega^{2} H_{v}^{(3)}], \quad (3-11)$$

$$U_{v,-1}(\alpha) = \frac{1}{\sqrt{3}} [H_{v}^{(1)} + \omega^{2} H_{v}^{(2)} + \omega H_{v}^{(3)}],$$

where $\omega = \exp(2\pi i/3)$ and v, as before, denotes the torsional quantum number. The first function in Eq.



FIG. 2. The hindered internal rotational energy levels as a function of the barrier height. The free rotation quantum numbers m are at the left ordinate, i.e., a zero barrier, and the torsional quantum numbers v are on the right ordinate, i.e., a relatively high barrier. The diagonal line V_3 shows the actual height of the barrier in relation to the energy levels. Those energy levels below the top of the barrier are clearly discernible.



FIG. 3. The torsional matrix. Each block on the diagonal contains the over-all rotation and internal rotational matrix elements associated with that torsional level. The shaded area represents the coupling between the rotational levels of the various torsional states. With the Van Vleck transformation the matrix elements in these shaded areas are folded into the blocks on the diagonal.

(3-11) is nondegenerate (A levels) and the last two are degenerate (E levels).

3. Perturbation treatment.—The energy matrix for H as given in Eqs. (3-1) and (3-2) is now constructed in a representation in which H_R and H_T are diagonal. From Eq. (3-9) it is obvious that p is diagonal in the quantum number σ but not in v. Consequently, the secular equation can be grouped into blocks corresponding to different v and σ . Within each block the Hamiltonian is given by $H_R + H_T$, and blocks of different v are connected by the matrix elements of H_{IR} . If the energy separations between different torsional states are large compared to those between rotational levels of the same v, a VanVleck transformation³⁴ may be applied to the energy matrix to reduce the matrix elements nondiagonal in v to the second order; such matrix elements can then contribute only fourth-order terms to the energy and can usually be neglected. The elements diagonal in v are, of course, modified by this transformation and the effect of this transformation is to fold the elements not diagonal in v onto the vblocks.*** The matrix is illustrated in Fig. 3 where the shaded areas contain those matrix elements off diagonal in v which are transformed into the v blocks shown on the diagonal. Therefore, the infinite secular equation is effectively factored into separate blocks corresponding to various combinations of v and σ , and only one such

^{***} For this particular class of molecules, both H_R and H_{IR} are diagonal in K and v is the only nondiagonal index; consequently the Van Vleck transformation is identical to the ordinary perturbation treatment. However, the difference between these two methods becomes apparent for the asymmetric molecules.

block need be considered at a time. To the second-order approximation the matrix elements of a v, σ block are given by the Hamiltonian operator¹²¹

$$H_{v\sigma} = A_{x}(P_{x}^{2} + P_{y}^{2}) + C_{v\sigma}P_{z}^{2} - 2C_{z}P_{z}p_{v\sigma,v\sigma} + E_{v\sigma}, \quad (3-12)$$

where

$$p_{v\sigma,v'\sigma} = \int_{0}^{2\pi} U_{v\sigma}^{*}(\alpha) \frac{1}{i} \frac{d}{d\alpha} U_{v'\sigma}(\alpha) d\alpha,$$

$$C_{v\sigma} = C_{z} \left(1 + 4C_{z} \sum_{v'} \frac{|\dot{p}_{v\sigma,v'\sigma}|^{2}}{E_{v\sigma} - E_{v'\sigma}} \right)$$

$$= C + F\rho^{2} \left(1 + 4F \sum_{v'} \frac{|\dot{p}_{v\sigma,v'\sigma}|^{2}}{E_{v\sigma} - E_{v'\sigma}} \right),$$

$$c = \hbar^{2}/2I_{z},$$

Here $H_{v\sigma}$ can be regarded as the effective rotational Hamiltonian for a given torsional state. The energy is then

$$E(JKMv\sigma) = A_x J(J+1) + (C_{v\sigma} - A_x)K^2 -2C_z K \not p_{v\sigma, v\sigma} + E_{v\sigma}. \quad (3-13a)$$

The perturbation treatment can also be carried to higher order. The energy obtained from the *n*th order perturbation calculation can be expressed simply as^{25a}

$$E_{v\sigma} = AJ(J+1) + (C-A)K^{2} + F \sum_{n} w_{v\sigma}^{(n)}(\rho K)^{n}, \quad (3-13b)$$

where

$$\rho = I_{\alpha}/I_{z},$$

$$w_{v\sigma}^{(0)} = 9b_{v\sigma}/4,$$

$$w_{v\sigma}^{(1)} = -2p_{v\sigma,v\sigma},$$

$$w_{v\sigma}^{(2)} = 1 + (16/9)\sum_{v} \frac{|p_{v\sigma,v'\sigma}|^{2}}{b_{v\sigma}-b_{v'\sigma}},$$
 etc.

The first two terms of Eq. (3-13b) are the energy of a rigid symmetric rotor while the last term, which is a power series in ρK , represents the effect of the internal torsion on the rotational energy levels.

The convergence of the power series depends mainly on the magnitude of ρK . Although the coefficients $w_{\tau\sigma}^{(n)}$ are strongly dependent on the barrier height (more precisely s) of the approximate form⁹⁹ $As^B \exp(-C\sqrt{s})$, they do not converge very rapidly with increasing *n* (see Fig. 8). Consequently the magnitude of the factor $(\rho K)^n$ must be examined and the perturbation calculation should then be carried out to the desired accuracy.

4. Energy levels and spectra.—For a given torsional state v there are two torsional sublevels characterized by the symmetry properties A and E (or $\sigma = 0$ and ± 1). Associated with each such torsional sublevel is a set of rotational energy levels, the structure of which is governed by the effective rotational Hamiltonian $H_{v\sigma}$.

For the nondegenerate Λ level the torsional functions are real and hence the diagonal elements of odd order in p vanish, i.e., $w_{v\sigma}^{(1)} = 0$. The rotational Hamiltonian is given to the second order by the first two terms of Eq. (3-12). This is formally identical to the Hamiltonian of a rigid symmetric rotor with a modified rotational constant $C_{v\sigma}$. Consequently, the rotational levels associated with a nondegenerate A type torsional level (hereafter referred to as A rotational level or simply Alevels) have the same structure as the levels of a rigid rotor (referred to also as the pseudo-rigid rotor levels). For the case of the degenerate torsional levels, $p_{v1,v1}$ is different from zero, so that the structure of the rotational levels here (called E rotational levels or E levels) differs from that of a rigid rotor. The linear term in P_z in the Hamiltonian has the effect of removing the Kdegeneracy characteristic of the rigid symmetric rotors. Furthermore, since the second-order perturbation term $w_{v\sigma}^{(2)}$ in Eq. (3-13b) is different for the A and E levels, each torsional sublevel will have a different effective rotational constant, $C_{v\sigma}$. The rotational levels with $\sigma = \pm 1$ are doubly degenerate with respect to σ but nondegenerate with respect to K, and vice versa for the levels with $\sigma = 0$. Hence, all the energy levels are doubly degenerate with the exception of the ones for which $\sigma = K = 0$. Here the spatial M degeneracy has been disregarded. The three pairs of doubly degenerate levels $\sigma = 0, \pm K; \sigma = +1, +K; \sigma = -1, -K;$ and $\sigma = -1, +K; \sigma = +1, -K$ are shown in Fig. 4.

Physically, the presence of two sets of rotational levels with $\sigma=0$ and ± 1 may be understood from a semiclassical point of view. For a high barrier the in-



FIG. 4. Correlation of rotational energy levels. The rotational energy levels and rotational parallel $(\Delta K=0)$ transitions for various conditions of asymmetry and barrier height. At either end the symmetric rotor energy levels and transition are shown. Introduction of hindered internal rotation splits each energy level in three levels for a threefold potential barrier. The three transitions however are coincident, giving only one line. Asymmetry splits the *A* level (*K* doubling), but only shifts the *E* levels. Two weaker lines on each side of the pattern are possible transitions between the *E* levels, but these are not shown in the figure. If the barrier height is raised, the energy levels tend toward the asymmetry doublets, and two doublets are observed in the spectrum. Finally, if the asymmetry is removed we are back to the symmetric rotor. The thickness of the lines for each energy level is approximately in agreement with the degeneracy of that level.

ternal motion can be pictured as a back-and-forth oscillation about the equilibrium configuration of the molecule. The over-all rotation of the molecule along with this mode of internal torsion gives rise to the set of the A levels. The E levels can be associated with a different mode of internal motion in which the molecule passes from one equilibrium configuration to another in a circulatory manner through the tunneling effect. The double degeneracy of the E torsional levels is related to the two senses (counterclockwise and clockwise) of tunneling internal rotation. One may then expect the E levels and wave functions to have some free rotational character.

As the dipole moment of the molecule is independent of α , the selection rules for the rotational transitions are $\Delta J = \pm 1, \Delta K = 0$, and $\Delta \sigma = 0$ (see Sec. 6). Equation (3-13) shows that the frequencies of the rotational lines are not changed by the internal rotation. Both the Aand E levels give rise to the same spectral lines and the three transitions shown in Fig. 4 are all coincident. Thus the effects of the internal rotation in the symmetric molecules are not detectable in the rotational spectra associated with the ground torsional state. This result can also be understood from the classical description by noticing that the rotation of a symmetric top about its figure axis causes no change in the orientation of the dipole moment and thus no dipole interaction with the radiation. When internal rotation is present in a symmetric top molecule, only the angular velocities of the two groups along the figure axis are affected.⁶⁷ In the excited torsional states, however, the frequencies of rotational transitions are appreciably altered by the internal rotation through the interaction with the other molecular vibrations.42 The shifts of the frequencies of these lines then serve as a means of determining the barrier heights for the symmetric top molecules. This method is more fully discussed in Sec. 7.

5. Reduction to a rigid rotor at a very high barrier.— At the limit of a very high barrier, the torsional functions can be taken as Eq. (3-11). Furthermore, the overlapping between $H_v^{(1)}$, $H_v^{(2)}$, and $H_v^{(3)}$ can be neglected, i.e., the diagonal elements of p (i.e., $w_{v\sigma}^{(1)}$) approach zero. At first sight one might conclude that the effect of H_{IR} vanishes for infinitely high barriers and the Hamiltonian is then given by H_R . This, however, is not correct because the rotational constant of P_z^2 in H_R is not the rotational constant of the rigid molecule. The reason for this is that the off-diagonal elements of p increase with the barrier height so that the secondorder term

$$\sum_{v'} (b_{v\sigma} - b_{v'\sigma})^{-1} |p_{v\sigma,v'\sigma}|^2$$

remains finite in such a way that $w_{\nu}^{(2)}$ tends to zero. This latter fact would be expected since Eq. (3-13b) is in the form of a rigid molecule with the actual rotation constant. With Eq. (3-11) it can be shown that the only nonvanishing matrix elements are

$$p_{v,\sigma;v+1,\sigma} = \frac{1}{\sqrt{2}i} \left(\frac{9V_3}{4F}\right)^{\frac{1}{2}} (v+\frac{1}{2})^{\frac{1}{2}}$$

$$p_{v,\sigma;v-1,\sigma} = -\frac{1}{\sqrt{2}i} \left(\frac{9V_3}{4F}\right)^{\frac{1}{2}} v^{\frac{1}{2}}.$$
(3-14)

Furthermore, the energy of a torsional harmonic oscillator was given by Eqs. (3-4) and (3-10) as

$$E_v = 3(v + \frac{1}{2})(V_3F)^{\frac{1}{2}} = (9/4)Fb_v.$$

When this equation and Eq. (3-14) are substituted into Eq. (3-13) the second-order term $w_{v\sigma}^{(2)}$ becomes zero. Therefore, the effective rotational constant $C_{v\sigma}$ becomes the rigid rotational constant C.

B. Internal Axis Method (IAM)

The essential feature of the IAM is the application of the Nielsen transformation to remove the coupling term between the angular momentum for over-all rotation and that associated with the internal rotation. Therefore, external and internal rotation become separable for the case of symmetric molecules. The IAM, however, has the disadvantage that the torsional functions are difficult to determine and are not conveniently tabulated.

For the PAM the coupling term H_{IR} (which is not small) is reduced by the Van Vleck transformation to a power series in K whose coefficients vanish at the limit of an infinite barrier. On the other hand, the coupling term H_{IR} is removed in the IAM by the Nielsen transformation, Eq. (2-8). The difference between these two transformations is that the Van Vleck is barrier dependent while the Nielsen is barrier independent.

The Hamiltonian was given in Eq. (2-20) as

$$H = A_a (P_a'^2 + P_b'^2) + C_c P_c'^2 + F p'^2 + V(\alpha),$$

where
$$A_c = A_c = \hbar^2/2I_c,$$

$$C_c = C = \hbar^2 / 2I_z (\neq C_z).$$

The *a*, *b*, *c* axes are the same as the principal axes for symmetric molecules, and the differential operators for P_a', P_b', P_c' , and p' are given in Sec. 2 II. C2(b). Since the *P*''s do not contain α , the wave function can be written as a product of the symmetric rotor wave functions and the torsional wave function:

$$\psi = S_{JKM}(\theta, \varphi) e^{iK\chi'} M_{Kv\sigma}(\alpha'). \qquad (3-15)$$

The symmetric rotor functions are the eigenfunctions of the first three terms of the Hamiltonian Eq. (2-20) and $M_{Kv\sigma}(\alpha')$ represent the eigenfunctions of the equation

$$\left[-F\frac{d^2}{d\alpha'^2} + V(\alpha')\right]M(\alpha') = EM(\alpha'), \qquad (3-16)$$

with the appropriate boundary conditions. The symmetric top wave function of Eq. (3-15) contains χ' instead of χ as a variable. The angle χ' was defined in Eq. (2-15).

The boundary condition for Eq. (3-16) must now be considered. Obviously, the wave function must be periodic in 2π with respect to χ_1 and χ_2 (the Eulerian angles of the two parts), i.e.,

$$\psi(\theta,\varphi,\chi_1,\chi_2) = \psi(\theta,\varphi,\chi_1+2\pi n_1,\chi_2+2\pi n_2), \quad (3-17)$$

where n_1 and n_2 are integers. In terms of χ' and α' , the wave function ψ becomes

$$\psi(\theta,\varphi,\chi',\alpha') = \psi\{\theta,\varphi,\chi' + (2\pi/I_c)[I_{\alpha}n_2 + (I_c - I_{\alpha})n_1], \alpha' + 2\pi(n_2 - n_1)\}. \quad (3-18)$$

In order to satisfy this condition use is made of the fact that according to Floquet's theorem, a particular (nonperiodic) solution of the Mathieu equation can be written as

$$M(\alpha) = e^{i\alpha f} P(\alpha), \qquad (3-19)$$

where $P(\alpha)$ is periodic in 2π and f is a real constant which is chosen so that Eq. (3-19) has the periodicity as demanded by the physical situation. For the present case one has

$$(K/I_c)[I_{\alpha}n_2+(I_c-I_{\alpha})n_1]+f(n_2-n_1)=n$$
(an integer). (3-20)

This can be satisfied by setting f equal to either $-\rho K$ [i.e., $-(I_{\alpha}K/I_c)$] or $(1-\rho)K$ [i.e., $+(I_c-I_{\alpha}/I_c)K$]. In the first of the series of papers on the internal rotation in methyl alcohol, Koehler and Dennison chose $(1-\rho)K$. [Also their internal angle χ is equal to $-\alpha$ which is used here (see Appendix 4).] However, it turns out, for most cases, to be convenient to take $f = -\rho K$. The resulting wave equation is then

$$\psi = S_{JKM}(\theta, \varphi) e^{iK\chi'} e^{-i\rho K\alpha'} P(\alpha'). \qquad (3-21)$$

Equation (3-21) shows that the internal and external motion are separable inasmuch as the wave function can be expressed as a product of a function of the three external Eulerian angles and a function of α ($\alpha' = \alpha$) alone. The fact that the quantum number K appears in the torsional part of the wave function does not signify a physical coupling between the over-all rotation and the internal motion in the sense that the torsion of one group of the molecule about the other does not affect the motion of the "internal rotation axes" (see Sec. 2 II. A1). On the other hand, the reader may recall that in the treatment of the symmetric molecules by PAM there is a coupling term H_{IR} between the external and internal motion. In the PAM the set of moving axes is rigidly attached to one group of the molecule; while in the IAM the internal rotation axes, which are used as the coordinate system, are moving with respect to both of the groups. Since only

the rotation of the internal rotation axes is unaltered by the internal motion, the coordinate frame used in PAM also oscillates at the frequency of the internal torsion.

1. Rotational equation.—The first three terms of the Hamiltonian Eq. (2-20) are the same as a rigid symmetric rotor molecule with energies as

$$H_{R} = A \left(P_{a}^{2} + P_{b}^{2} \right) + C P_{c}^{2}$$

$$E_{JKM} = A J (J+1) + (C-A) K^{2},$$
(3-22)

where

$$A = \hbar^2/2I_a$$
 and $C = \hbar^2/2I_c$.

2. Torsional function.—Although the torsional equations for the PAM and the IAM are identical, the torsional functions for these two cases are not the same because of the different boundary conditions. As explained above, the torsional function of IAM may be written as

$$M(\alpha) = e^{-i\rho K\alpha} P(\alpha). \tag{3-23}$$

The differential equation for $P(\alpha)$ is obtained by substituting Eq. (3-23) into Eq. (3-16) with the result

$$-F(d^{2}P/d\alpha^{2})+2iF\rho K(dP/d\alpha) +\frac{1}{2}V_{3}(1-\cos 3\alpha)P=(E-F\rho^{2}K^{2})P, \quad (3-24)$$

where

or

$$F
ho = rac{\hbar^2}{2(I_c - I_{lpha})}$$
 and $F
ho^2 = rac{\hbar^2}{2} rac{I_{lpha}}{I_c(I_c - I_{lpha})}$.

This equation [or Eq. (3-16)] can be solved in the most general way by the method of continued fraction which is discussed in Appendix 2.

(a) Properties of the torsional levels: Since the solutions of Eq. (3-23) are different for different K, the value of K should be included as a labeling index for $P(\alpha)$ and E. Furthermore, as α appears explicitly in Eq. (3-16) only as $\cos 3\alpha$, an eigenfunction $M(\alpha)$ can be classified into one of the three general types corresponding to $\sigma = 0, \pm 1^{\dagger\dagger\dagger}$ in the expression

$$P_{Kv\sigma} = \sum_{k} A_{3k+\sigma}^{Kv} e^{i(3k+\sigma)\alpha},$$

$$M_{Kv\sigma} = e^{-i\rho K\alpha} \sum_{k} A_{3k+\sigma}^{Kv} e^{i(3k+\sigma)\alpha}.$$
(3-25)

Analogous to the solution of the torsional equation in the PAM, for each given σ one has a family of the functions $P_{Kv\sigma}(\alpha)$ and these functions are again labeled by the index v. Unlike the $U(\alpha)$'s given in Eq. (3-9), the eigenfunctions $P_{K,v,1}(\alpha)$ here are not degenerate with $P_{K,v,-1}(\alpha)$ because the differential Eq. (3-24) for $P(\alpha)$ contains imaginary coefficients. On the other hand, since $P^*(\alpha)$ is a solution of the equation obtained by taking the complex conjugate of Eq. (3-24) (the same

^{†††} The quantity σ is the same as Itoh's $-\mu$ and is related to τ used by Dennison *et al.*^{8,20,32,48} by the expression $K+\tau=\sigma+1 \pmod{3}$.

as the differential equation for $P(\alpha)$ with -K), we have

$$P_{K,v,1}(\alpha) = P_{-K,v,-1}^{*}(\alpha),$$

$$P_{K,v,0}(\alpha) = P_{-K,v,0}^{*}(\alpha),$$

$$M_{K,v,\sigma}(\alpha) = M_{-K,v,-\sigma}^{*}(\alpha),$$

$$P_{0,v,\sigma} = U_{v,\sigma},$$

$$E_{K,v,1} = E_{-K,v,-1},$$

and

$$E_{K,v,1} = E_{-K,v,-1},$$

$$E_{K,v,0} = E_{-K,v,0}.$$

At high barriers the arrangement of the eigenvalues $(E_{Kv\sigma})$ in the IAM is similar to that in the PAM, i.e., the levels are grouped in a number of clusters corresponding to different values of the torsional quantum number v. Within each torsional state there are three distinct levels (rather than two in contrast with the results of the PAM) characterized by $\sigma = 0, 1, -1$, for $K \neq 0$. The three levels are shown in Fig. 4. When K is equal to zero, the levels with $\sigma = 1$ and $\sigma = -1$ are degenerate. The result that the eigenvalues are different for the PAM and the IAM comes as no surprise for the torsional equation is actually defined differently in these two methods. Physically, this discrepancy arises from the fact that the external rotation in the IAM is not the same as that in the PAM. However, the composite energy levels for the combination of the external and internal rotation calculated by both methods are identical as one would expect. This is illustrated in Sec. I. B3.

(b) Eigenvalues of the torsional equation: The tabulated solutions of the Mathieu equation are not directly applicable to the torsional function in the IAM since these functions do not have the periodicity of 2π . The general method for obtaining the solution by the use of continued fraction is described in Appendix 2. The procedure for determining the eigenfunctions is in general complicated but at the very high barrier these functions can be approximated by the harmonic oscillator functions. In addition, the eigenvalues can be simply obtained by the following approximate method: when $\rho K - \sigma$ is replaced by $\rho K - \sigma + 3$, the form of Eq. (3-25) is not altered, and therefore the eigenvalues remain unchanged. One may then regard the eigenvalues as periodic functions of $(2\pi/3)(\rho K - \sigma)$ and expand them in a Fourier series as

$$E_{Kv\sigma} = F \sum_{n} a_n^{(v)} \cos(2\pi n/3) \left(\rho K - \sigma\right). \quad (3-27)$$

If $\rho K - \sigma$ is equal to zero or a whole multiple of three, then Eq. (3-25) reduces to the solution of the Mathieu equation (with a periodicity of π) when the substitutions given in Eq. (3-4) are made, i.e.,

$$E(\rho K - \sigma = 0) \rightarrow b(\pi).$$

Here b and E differ by the scale factor given by Eq. (3-4). Similarly, one can show that

$$E(\rho K - \sigma = \frac{3}{2}) \longrightarrow b(2\pi),$$

$$E(\rho K - \sigma = 1) \longrightarrow b(3\pi),$$

and more generally

$$E(\rho K - \sigma = x) \rightarrow b(3\pi/x).$$

Up to this time only the low integral values of 3/x have been tabulated (see Appendix 3).

If the series in Eq. (3-27) converges so rapidly that E may be approximated by the first two terms in the Fourier expansion, i.e.,

$$E = F \lceil a_0 + a_1 \cos(2\pi/3)(\rho K - \sigma) \rceil, \qquad (3-28)$$

then the coefficients a_0 and a_1 may be determined from the tabulated values¹⁰⁴ of $b(\pi)$ and $b(2\pi)$. When this is done, Eq. (3-28) can be used to calculate the approximate values of $b(N\pi)$. To this approximation the equation for $b(N\pi)$ is

$$b(N\pi) = \frac{1}{2} \left(1 + \cos \frac{2\pi}{N} \right) b(\pi) + \frac{1}{2} \left(1 - \cos \frac{2\pi}{N} \right) b(2\pi), \quad (3-29)$$

such that any Mathieu eigenvalue can be approximated²³ from $b(\pi)$ and $b(2\pi)$ provided that the Fourier coefficient a_1 is small. If the coefficient a_1 is not small then $b(3\pi)$, $b(4\pi)$, etc., can be used to obtain the coefficients a_2 and a_3 and a better value of $b(N\pi)$ (see Table III). Therefore, the Mathieu eigenvalues can be readily approximated for any periodicity.

(c) Harmonic oscillator approximation: As in the case of the PAM, the torsional function can be approximated by harmonic oscillator wave functions at very high barriers. Since the classical amplitude of the internal torsion approaches zero at the limit of very high barriers, the factor $e^{-i\rho K\alpha}$ in the torsional function $M(\alpha)$ may be replaced by unity and $M_{Kv\sigma}(\alpha) \rightarrow$ $P_{Kv\sigma}(\alpha)$. Under such circumstances $M(\alpha)$ can be approximated by Eq. (3-11). The energy levels of Eq. (3-16) are then given by Eq. (3-10).

3. Energy levels and spectra.—The total energy of a symmetric top exhibiting internal rotation is equal to the sum of the energy associated with the over-all rotation E_{JKM} and the torsional energy $E_{Kv\sigma}$, or

$$E(JKMv\sigma) = E_{JKM} + E_{Kv\sigma}.$$
 (3-30)

Since the K degeneracy remains in the rigid symmetric rotor energy, from Eq. (3-26) it may be seen that

$$E(J,K,M,v,\sigma) = E(J, -K, M, v, -\sigma).$$

Therefore, all the energy levels are doubly degenerate except the $K=0, \sigma=0$ levels—a result which was also found by the PAM. Now substituting Eqs. (3-22) and (3-27) into Eq. (3-30), we obtain

$$E(JKMv\sigma) = AJ(J+1) + (C-A)K^{2}$$
$$+F\sum_{n} a_{n}^{(v)} \cos\frac{2\pi n}{3}(\rho K - \sigma). \quad (3-31a)$$

The last term in this equation represents the effect of the internal torsion on the rotational energy levels. If ρK is reasonably small and the Fourier series converges rapidly, the cosine terms in the last member of Eq. (3-31) can be expanded in the following manner:

$$\sum a_{n}^{(v)} \cos \frac{2\pi n}{3} (\rho K - \sigma)$$

= $\sum_{n} a_{n}^{(v)} \cos \frac{2\pi \sigma}{3} \left[1 - \frac{1}{2} \left(\frac{2\pi n}{3} \rho K \right)^{2} + \cdots \right]$
+ $\sum a_{n}^{(v)} \sin \frac{2\pi \sigma}{3} \left[\frac{2\pi n}{3} \rho K + \cdots \right].$ (3-31b)

For $\sigma = 0$ the K^2 term from Eq. (3-31b) can be incorporated into the term $(C-A)K^2$ in Eq. (3-31a), and therefore it has the effect of modifying the rotational constant. The rotational levels for this case have the same pattern as a rigid symmetric rotor-pseudo-rigid rotor level. In the case of the degenerate torsional levels ($\sigma = \pm 1$), the expansion in Eq. (3-31b) introduces a term linear in K, into the energy equation. This causes a splitting of the K degeneracy of the rigid symmetric rotors. The conclusions obtained here are therefore in complete agreement with those derived from the PAM. When ρK becomes larger, the $(\rho K)^3$ and $(\rho K)^4$ terms should be included in the expansion of $\cos(2\pi/3)(\rho K - \sigma)$. In terms of the PAM the higherorder Van Vleck perturbation treatment must be applied to the Hamiltonian in order to obtain accurate results.

By following the selection rules $\Delta J = \pm 1$, $\Delta K = 0$, and $\Delta \sigma = 0$ one finds again that the rotational frequencies depend only on the rotational constant A and the quantum number J, and are not affected by the internal torsion. Therefore, only one line is observed as shown in Fig. 4 for this model.

C. Comparison of the Two Methods

The main difference between the two methods is that the IAM gives a relatively simple Hamiltonian but more complicated torsional functions, whereas the PAM gives a more complex Hamiltonian but simpler torsional functions. The chief difficulty in the IAM is associated with the determination of the torsional eigenfunctions and eigenvalues. On the other hand, the coupling term pP_z in the PAM is not a small perturbation, so fourthorder perturbation calculation is sometimes necessary to obtain accurate results for the energy levels.

A comparison of Eqs. (3-13b) and (3-31a) shows that the effects of the internal torsion on the rotational energy levels are expressed by a power series in the PAM and a Fourier series in the IAM. Generally, calculation of the first- and second-order terms in the power series $(w_{v,\sigma}^{(1)})$ and $w_{v,\sigma}^{(2)}$ is comparatively simple, but the higher-order terms are more difficult to evaluate. Herschbach²³ has suggested that the tabulated eigenvalues of the Mathieu equation and the first two perturbation terms in PAM be used to determine the Fourier coefficients in the IAM which are otherwise tedious to calculate by the method of continuous fraction. Since the Fourier series in IAM converges much faster than the power series in Eq. (3-13b), the former may be used to obtain the rotational energy levels and also the higher-order perturbation terms of the PAM. This technique is really very interesting for we have solved the problem approximately by the PAM where the boundary conditions are simple and have then converted this to the more exact solution of the IAM.

II. Asymmetric Molecules

A. Principal Axis Method (PAM)

The Hamiltonian given in Eq. (2-37) can be grouped in the following manner:

$$H_{0} = \frac{1}{2} (A_{x} + B_{x}) (P_{x}^{2} + P_{y}^{2}) + C_{z} P_{z}^{2} + F p^{2} + V(\alpha), \quad (3-32a)$$

$$H_{1} = -2 \sum Q_{i} P_{i} p, \quad (3-32b)$$

and

$$H_{2} = \frac{1}{2} (A_{x} - B_{x}) (P_{x}^{2} - P_{y}^{2}) + \frac{1}{2} \sum_{i \neq j} D_{ij} (P_{i}P_{j} + P_{j}P_{i}). \quad (3-32c)$$

The energy matrix is now constructed with the basis functions

$$S_{JKM}(\theta,\varphi)e_i{}^{K\chi}U_{v\sigma}(\alpha).$$

$$H_{v\sigma} = A_{v\sigma} P_{x}^{2} + B_{v\sigma} P_{y}^{2} + C_{v\sigma} P_{z}^{2} + E_{v\sigma} + \frac{1}{2} \sum_{i \neq j} D_{ij} w_{v\sigma}^{(2)} (P_{i} P_{j} + P_{j} P_{i}) + \sum_{i} Q_{i} P_{i} w_{v\sigma}^{(1)}, \quad (3-33)$$

where

$$A_{v\sigma} = \frac{\hbar^2}{2I_x} \left[1 + \frac{\lambda_x^2 I_\alpha}{r I_x} w_{v\sigma}^{(2)} \right],$$

$$w_{v\sigma}^{(1)} = -2 p_{v\sigma,v\sigma},$$

$$w_{v\sigma}^{(2)} = 1 + \frac{16}{9} \sum_{v'} \frac{|p_{v\sigma,v'\sigma}|^2}{b_{v\sigma} - b_{v'\sigma}},$$

^{‡‡‡} Here we have assumed that the torsional levels of different v are much more widely spaced compared to the rotational levels. When this is not the case, the (K|K') elements, introduced by H_1 to the diagonal v blocks through the Van Vleck transformation, have a very complicated form.^{26b}

and similarly for B_v and C_v with the appropriate permutations of x, y, and z.

Alternatively the Hamiltonian given in Eq. (2-38) could be used for the perturbation treatment. The Van Vleck transformation now gives the following²³:

$$H_{v\sigma} = \frac{\hbar^2}{2} \sum_{g} \frac{P_g^2}{I_g} + F \sum_{n} w_{v\sigma}^{(n)} \Pi^n, \qquad (3-34)$$

where

$$\mathbf{II} = \boldsymbol{\varrho} \cdot \mathbf{P},$$

and the $w_{v\sigma}^{(n)}$'s are the same perturbation terms given in Eq. (3-13b). Naturally, Eqs. (3-33) and (3-34) are identical. Equation (3-33) shows the perturbation calculation more clearly and shows that the rotational constants are modified by the internal rotation. Equation (3-34) shows the similarity to the symmetric molecule formulas and leads more naturally, as we will see later, to higher-order perturbation corrections.

1. Energy levels and spectra.—From Eq. (3-33) the rotational constants for the over-all rotation of the molecule are modified by the internal rotation. Also the orientation of the "effective" principal axes is changed by the cross terms $D_{ij}w_{v\sigma}^{(2)}(P_iP_j+P_jP_i)$. Both of these changes depend on the torsional state v and σ . As in the case of the symmetric molecules, there exist two sets of rotational levels for each torsional state. The Hamiltonian for the pseudo-rigid rotor levels ($\sigma=0$) to second order is given by Eq. (3-35),

$$H_{v0} = A_{v0}P_{x}^{2} + B_{v0}P_{y}^{2} + C_{v0}P_{z}^{2} + \sum_{i \neq j} \frac{1}{2} D_{ij} w_{v0}^{(2)} (P_{i}P_{j} + P_{j}P_{i}), \quad (3-35)$$

where the rotational constants A_{v0} , etc., differ from the respective constants of a rigid molecule by terms proportional to $w_{v0}^{(2)}$. Also the cross terms between the P's contain $w_{v0}^{(2)}$. As mentioned before, the quantity $w_{v0}^{(2)}$ decreases rapidly with increasing value of the reduced barrier height s [defined in Eq. (3-4)] and approaches zero for very high barrier.

For the *E* levels the Hamiltonian is also given by Eq. (3-33). Because of the linear terms in P_x , P_y , and P_z the spacings of the *E* levels are different even qualitatively from those of a pseudo-rigid rotor. However, in some cases, especially for high barriers and low *K* energy levels, when the asymmetry splitting of the *K* doublet is not too small, the effect of the terms containing $p_{v\sigma,v\sigma}$ is negligible §§§ The effective rotational constants $A_{v,\pm 1}$, etc., are, however, appreciably different from those for the *A* states as well as those for the rigid molecule. Under such circumstances both sets of the *A* and *E* levels are similar in structure but have different effective rotational constants.

The selection rules are identical to those for a rigid asymmetric top with the additional restriction of $\Delta \sigma = 0$ since the dipole moment is independent of the angle α . The most intense spectrum arises from the molecules in the lowest torsional state, i.e., v=0. For each rotational transition one finds two lines; one originates from the rotational levels associated with the nondegenerate torsional levels and the other one from the degenerate E levels. The essential feature of the spectrum is that doublets occur instead of a single line as in the case of a rigid molecule. This is illustrated in Fig. 4. The lines belonging to the A species follow a pseudo-rigid spectrum to the second order and the *E* lines may or may not be fitted to a pseudo-rigid Hamiltonian depending on the height of the barrier and the asymmetry of the molecule. The two members of the doublet are of more or less the same intensity; the ratio of the intensity is governed by the relative nuclear statistical weight assigned to the A and E levels (see Sec. 6). The separation of the two lines of a doublet depends very critically on the height of the barrier. It is from these splittings that we determine the barrier height. In the next section we discuss the calculation of the doublet splittings. The methods of evaluation of the barrier height from the measured values of the splittings are presented in Sec. 5.

2. Calculation of energy and doublet splittings.—The matrix elements of $H_{v\sigma}$ in Eq. (3-33)¹⁰¹ are

$$(K | H_{v\sigma} | K) = \frac{1}{2} (A_{v\sigma} + B_{v\sigma}) J (J+1) + [C_{v\sigma} - \frac{1}{2} (A_{v\sigma} + B_{v\sigma})] K^{2} + Q_{z} w_{v\sigma}^{(1)} K, (K | H_{v\sigma} | K\pm 1) = \frac{1}{2} [(D_{yz} \pm i D_{xz}) w_{v\sigma}^{(2)} (2K\pm 1) + (Q_{y} \pm i Q_{x}) w_{v\sigma}^{(1)}] [J (J+1) - K (K\pm 1)]^{\frac{1}{2}}, (K | H_{v\sigma} | K\pm 2) = -\frac{1}{4} [A_{v\sigma} - B_{v\sigma} \pm 2i D_{xy} w_{v\sigma}^{(2)}] \times [J (J+1) - K (K\pm 1)]^{\frac{1}{2}} \times [J (J+1) - (K\pm 1) (K\pm 2)]^{\frac{1}{2}}.$$
(3-36)

The indices J, M have been deleted since $H_{v\sigma}$ is diagonal in these quantum numbers, and the constant term $E_{v\sigma}$ has been dropped. Here, in addition to the $(K|K\pm 2)$ contribution from the usual asymmetry of H_2 , there are off-diagonal elements from the cross terms in $D_{ij}w_{v\sigma}^{(2)}$. Also H_1 has contributed both a diagonal term in $Q_z w_{v\sigma}^{(1)}$ and off-diagonal terms in $Q_x w_{v\sigma}^{(1)}$ and $Q_y w_{v\sigma}^{(1)}$.

The Hamiltonian $H_{v\sigma}$ in Eq. (3-33) may be simplified by performing a rotation of coordinate axes to eliminate the cross terms between the components of the total angular momentum *P*. Referred to this new coordinate axes system which is the "effective principal axes" system for a torsional level, the effective Hamiltonian becomes

$$H_{v\sigma}' = A_{v\sigma}' P_{x'}^{2} + B_{v\sigma}' P_{y'}^{2} + C_{v\sigma}' P_{z'}^{2} + \sum_{i} Q_{i}' P' w_{v\sigma}^{(1)}.$$
 (3-37)

The orientation between the two sets of axes can be determined either by diagonalizing the 3×3 matrix in

^{§§§} It should be noted that the effect of the linear terms is negligible only when it connects no near degenerate levels. Also if the quantity ρK becomes large, higher-order perturbation terms are needed [see Eq. (3-34) and Sec. 3].

TABLE I. Low J energy levels.^a

$$\begin{split} E_{JK} \\ E_{00} = 0 \\ E_{10} = A_{v\sigma}' + B_{v\sigma}' - (g^+ + g^-) \\ & \pm [(Q_z'w_v^{(1)})^2 + \frac{1}{4}(A_{v\sigma}' - B_{v\sigma}')^2 - (A_{v\sigma}' - B_{v\sigma}')(g_y - g_x)]^{\frac{1}{2}} \\ E_{20} = W_r(A_{v\sigma}'B_{v\sigma}'C_{v\sigma}'J = 2, K = 0) - 3(g^+ + g^-) \\ & + 0[(A - B)(2C - A - B)^{-1}g] \\ E_{21} = (5/2)(A_{v\sigma}' + B_{v\sigma}') + C_{v\sigma}' + 3(g^+ + g^-)/2 - (k^+ + k^-) \\ & \pm [(Q_z'w_v^{(1)})^2 + (9/4)(A_{v\sigma}' - B_{v\sigma}')^2 - 9(A_{v\sigma}' - B_{v\sigma}')(g_y - g_x)]^{\frac{1}{2}} \\ \end{split}$$
where $g^{\pm} = (Q_{z}'^2 + Q_{y}'^2)[w_{v\sigma}^{(1)}]^2[2C_{v\sigma}' - A_{v\sigma}' - B_{v\sigma}' \pm 2Q_{z}'w_{v\sigma}^{(1)}]^{-1} \\ g_i = Q_i'^2[w_{v\sigma}^{(1)}]^2[2C_{v\sigma}' - A_{v\sigma}' - B_{v\sigma}']^{-1}(i = x, y) \\ g_{z} + g_{y} \approx \frac{1}{2}(g^+ + g^-) \\ k^{\pm} = 2(Q_{z}'^2 + Q_{y}'^2)[w_{v\sigma}^{(1)}]^2[6C_{v\sigma}' - 3A_{v\sigma}' - 3B_{v\sigma}' \pm 2Q_{z}'w_{v\sigma}^{(1)}]^{-1} \end{split}$

• The $A_{rq'}$, $B_{rq'}$, and $C_{rq'}$ are not necessarily identical with the A, B, and C of King *et al.*,⁴¹ and the quantum number K is no longer a good quantum number, but it is still used for labeling. In the expression for the E_{20} energy W_r is the rigid rotor energy with the rotational constants $A_{x'}$, $B_{r'}$, and C'.

the usual manner or by applying successive 2×2 rotations. The relations between the new coefficients $A_{v\sigma}'$, etc., in Eq. (3-37) and the old ones in Eq. (3-33) can be set down by noting that A, B, C, D_{xy} , etc., transform like the six components of a symmetric secondrank tensor and Q_x, Q_y, Q_z , transform like the components of a vector. Very often the change in the effective rotational constants introduced by such a rotation is negligible. For instance, in the case of acetaldehyde (CH₃CHO) the cross term P_iP_j is removed by rotating the body axes through an angle of approximately one degree.

For the nondegenerate A levels the last term of Eq. (3-37) vanishes. The rotational energies are just those for a pseudo-rigid rotor with slightly corrected rotational constants and can be calculated by well-known methods or obtained from published tables.41,97,108 In the case of the E levels the energy matrices for both Eq. (3-33) and Eq. (3-37) contain a term linear in Kon the diagonal and also $(K|K\pm 1)$ elements. The two kinds of factoring available for rigid asymmetric tops are spoiled, and for a given J, a (2J+1)(2J+1) determinantal equation must be solved. Except for low J, the straightforward diagonalization of this matrix is very difficult. The procedure of diagonalization may be somewhat simplified by applying a Van Vleck transformation to reduce the $(K|K \pm 1)$ elements. Except for the energy levels with small asymmetry splitting, after a second-order Van Vleck transformation the new $(K|K\pm 1)$ elements are usually such that their contributions to the diagonal terms are negligible for low J levels. The approximate formulas for some of the energy levels are given in Table I. Also approximate formulas for the splitting of the A and E levels (not the lines) can be derived; these are given in Table II.

When the barrier is very high the value of $w_{v\sigma}^{(1)}$

becomes so small that the E levels for low K also conform to the pattern of a rigid rotor with effective rotational constants different from those belonging to the A levels. The energy splitting between the A and Elevels, ΔW , is simply equal to the difference between the "rigid rotor energy" of the two types of levels, W_A , and W_E , as

$$\Delta W = W_A - W_E = (\partial W/\partial A)\Delta A + (\partial W/\partial B)\Delta B + (\partial W/\partial C)\Delta C. \quad (3-38)$$

If the rigid rotor energy is written in the usual form⁴¹

$$W = \frac{1}{2}(A+C)J(J+1) + \frac{1}{2}(A-C)E(\kappa), \|\|\|\|$$
(3-39)

then it follows that

$$\frac{\partial W}{\partial A} = \frac{1}{2}J(J+1) + \frac{1}{2}E(\kappa) - \frac{1}{2}(\kappa+1)\left[\frac{\partial E(\kappa)}{\partial \kappa}\right],$$

$$\frac{\partial W}{\partial B} = \frac{\partial E(\kappa)}{\partial \kappa},$$

$$\frac{\partial W}{\partial C} = \frac{1}{2}J(J+1) - \frac{1}{2}E(\kappa) + \frac{1}{2}(\kappa-1)\left[\frac{\partial E(\kappa)}{\partial \kappa}\right].$$

(3-40)

The values of $[\partial E(\kappa)/\partial \kappa]$ can be estimated from the tabulated eigenvalues of rigid rotors.^{41,108} By substituting the results of Eq. (3-40) into Eq. (3-38) the energy separation between the *A* and *E* levels is obtained.

3. Higher-order effects.—(a) Third- and fourth-order perturbation terms^{23,25b}: Up to this point the discussion of the PAM represents the second-order theory in the Van Vleck perturbation treatment. When the barrier is not sufficiently high and/or the quantity ρK is large (as in the case of CH₃COOH),¹⁰⁵ the third- and fourthorder perturbation terms should be taken into consideration. The form of the effective Hamiltonian given in Eq. (3-34) is very convenient for the calculation of the higher-order terms. Also, the perturbation coefficients are the same as those given in Eq. (3-13b)for a symmetric molecule. The higher-order perturbation corrections can be calculated directly from the matrix elements of p or by the labor-saving method given in Sec. I. C. Herschbach^{23,25b} has tabulated a number of these terms. The readers are directed to Sec. 5 for more detail of this method. With the higher-order terms,

TABLE II. Low J energy splitting (A - E).

$\Delta E_{00} = 0$
$\Delta E_{10} = \Delta A + \Delta B + g^+ + g^-$
$\Delta E_{11} = \Delta C + \frac{1}{2} (\Delta A + \Delta B) - \frac{1}{2} (g^+ + g^-)$
$\pm \left[\frac{1}{2} (\Delta A - \Delta B) + (g_y - g_x) - \frac{Q_z^2 [w_{v\sigma}^{(1)}]^2}{A - B} \right]$
$\Delta E_{21} = \Delta C + (5/2) \left(\Delta A + \Delta B \right) - (3/2) \left(g^+ + g^- \right) + (k^+ + k^-)$
$\pm \left[(3/2) (\Delta A - \Delta B) + 3(g_y - g_z) - \frac{Q_z^2 [w_{v\sigma}^{(1)}]^2}{3(A - B)} \right]$
where $ Q_{z}w_{vs}^{(1)} < (A-B) $

 $^{\| \| \|}$ In this equation the rotation constants A, B, C, are such that $A \ge B \ge C$ and they are not necessarily identical to $A_{v\sigma}$, $B_{v\sigma}$, and $C_{v\sigma}$.

or

matrix elements of the form $(K|K\pm 3)$ and $(K|K\pm 4)$ are introduced and these can be treated in a manner similar to Kivelson and Wilson's treatment⁴⁷ of the centrifugal distortion problem.

(b) Sixfold potential energy term, $V_6^{25b,38}$: So far we have assumed that the potential function is sinusoidal in α without rigorous justification. If the expansion of the potential function in Eq. (2-1b) converges rapidly, the V_6 term can be treated as a perturbation. When this is done, the V_6 contribution merely changes the values of all the perturbation coefficients $w_{v\sigma}^{(n)}$ in such a way that its contribution cannot be separated from that of V_3 without data from more than one torsional state. In order to evaluate the V_6 coefficient, it is necessary then to study the internal rotational effects in more than one torsional state. $\P\P$ This V_6 term should be generally smaller than the threefold potential by a factor ranging from ten to a thousand.

B. Internal Axis Method (IAM)

Since the treatment by the IAM for the most general type of molecule (no symmetry aside from that of the CH₃ group) is algebraically very complicated, the discussion here is confined to those molecules which have a planar framework. Papers by Pitzer and Gwinn,⁸⁴ Hecht and Dennison,²⁰ and Burkhard⁷ discuss the general type of asymmetric molecule by the IAM.

1. Hamiltonian and matrix elements.—In Sec. 2 three different forms of the Hamiltonian were derived. They were given in Eqs. (2-26), (2-29), and (2-31). We are now at liberty to use any one of these Hamiltonians to solve for the energy levels. Let us first consider the Hamiltonian $(2-29)^{.20.31}$ This Hamiltonian can be divided as follows:

$$H_0 = \frac{1}{2} (A_a + B_b'') (P_a''^2 + P_b''^2) + C_c'' P_c''^2 + F p'^2 + V(\alpha),$$

$$H_1 = \frac{1}{2} (A_a - B_b'') (P_a''^2 - P_b''^2) + D_{bc}'' (P_b'' P_c'' + P_c'' P_b'').$$

 $P_{a''}$, $P_{b''}$, and $P_{c''}$ are the components of the total angular momentum along the axes fixed in the framework of the molecule (rather than the internal axes which rotate with respect to both the framework and the top), i.e., the orientation of this axes system is described by the Eulerian angles θ , Φ , and χ (but not χ'). Consequently, we choose the eigenfunctions of H_0 as the basis functions for constructing the energy matrix. These functions are

$$\psi = S_{JKM}(\theta, \Phi) e^{iK\chi} Q(\alpha), \qquad (3-41)$$

where $Q(\alpha)$ is the solution of the torsional equation

$$[Fp'^{2}+V(\alpha)]Q(\alpha) = EQ(\alpha). \qquad (3-42)$$

Since
$$P_c''$$
 is diagonal in H_0 , using Eq. (2-28) we can write

$$p' = p - \rho P_c'' = (1/i) (\partial/\partial\alpha)_{\theta, \Phi, \chi} - \rho K, \quad (3-43)$$

which can then be substituted into Eq. (3-42) with the result

$$[F(-i(d/d\alpha) - \rho K)^2 + V(\alpha)]Q(\alpha) = EQ(\alpha), \quad (3-44a)$$

$$\left[-F(d^2/d\alpha^2) + V(\alpha)\right]M(\alpha) = EM(\alpha), \quad (3-44b)$$

where $M(\alpha)$ is $e^{-i\rho K\alpha}Q(\alpha)$. Equations (3-44) are just the same as Eqs. (3-16) and (3-24) only with the scale change in ρ and F [see Eq. (2-30)]. Analogous to the function $P(\alpha)$ in Eq. (3-25) the eigenfunction $Q(\alpha)$ can be expanded in a Fourier series as

$$Q(\alpha) = \sum_{k} A_{3k+\sigma}^{Kv} e^{i(3m+\sigma)\alpha}.$$
 (3-45)

Furthermore, it can be easily seen that

$$Q_{Kv\sigma}(\alpha) = Q_{-Kv-\sigma}^{*}(\alpha),$$

$$E_{Kv\sigma} = E_{-Kv-\sigma}.$$
(3-46)

Before deriving the matrix elements of H let us consider the Hamiltonian²⁰ given in Eq. (2-31). This Hamiltonian can be divided as follows:

$$H_{0} = \frac{1}{2}(A_{a} + B_{b}'')(P_{a}'^{2} + P_{b}'^{2}) + C_{c}''P_{c}'^{2} + Fp'^{2} + V(\alpha)$$

$$H_{1} = \frac{1}{2}(A_{a} - B_{b}'')$$

$$\times [(P_{a}'^{2} - P_{b}'^{2})\cos 2\rho\alpha - (P_{a}'P_{b}' + P_{b}'P_{a}')\sin 2\rho\alpha]$$

$$+ D_{bc}''[(p_{b}'p_{c} + P_{c}'P_{b}')\cos \rho\alpha$$

$$+ (p_{a}'P_{c}' + P_{c}'P_{a}')\sin \rho\alpha]. \quad (3-47)$$

Here P_a' , P_b' , and P_c' are components of the total angular momentum along the internal rotational axes. The orientation of this axes system is described by the Eulerian angles $\theta \Phi \chi'$ where

$$\chi' = \chi + \rho \alpha,$$

[see Eq. (2-28)]. The basis functions again are chosen to diagonalize H_0 . They are

$$\psi = S_{JKM}(\theta, \Phi) e^{iK\chi'} M(\alpha'), \qquad (3-48)$$

where $M(\alpha')$ is the solution of the torsional equation (3-44b) which must satisfy the boundary conditions [see Eq. (3-20) Sec. I. B]. Furthermore, we can see that the basis functions given in Eqs. (3-41) and (3-48) are indeed identical as

$$e^{iK\chi}Q(\alpha) = e^{iK\chi'}e^{-i\rho K\alpha}Q(\alpha) = e^{iK\chi'}M(\alpha').$$

The energy matrix can then be constructed from the Hamiltonian Eq. (2-29) with Eq. (3-41) as the basis functions or from Eqs. (2-31) and (3-48). The results of these two schemes are identical.

The matrix elements of the Hamiltonian^{20,31} are as follows:

$$(Kv\sigma | H | Kv\sigma) = \frac{1}{2} (A_a + B_b'') [J(J+1) - K^2] + C_c'' K^2 + E_{Kv\sigma}, \quad (3-49a)$$

^{¶¶¶} Kilb *et al.*³⁸ calculated a V_6 term but their approximation is now realized to be inadequate because they ignored the thirdorder correction in the evaluation of the V_6 term from the splittings in the ground torsional states.

$$(Kv\sigma | H | K+1, v'\sigma) = D_{bc}''(K+\frac{1}{2}) \\ \times [J(J+1) - K(K+1)]^{\frac{1}{2}} I_{K+1,v'\sigma}^{Kv\sigma}, \quad (3-49b)$$

$$\begin{aligned} (Kv\sigma | H | K+2, v'\sigma) \\ &= -\frac{1}{4} (A_a - B_b'') [J(J+1) - K(K+1)]^{\frac{1}{2}} \\ &\times [J(J+1) - (K+1)(K+2)]^{\frac{1}{2}} I_{K+2,v'\sigma}^{Kv\sigma}, \quad (3-49c) \end{aligned}$$

where

$$I_{K'v'\sigma}{}^{Kv\sigma} = \int_{0}^{211} Q_{Kv\sigma}^{*}(\alpha) Q_{K'v'\sigma}(\alpha) d\alpha.^{****} \quad (3-50)$$

If the Hamiltonian form given in Eq. (2-26) were to be used,^{8,31} then the scale factors ρ and F would be those corresponding to the symmetric molecule, i.e., $\rho = I_{\alpha}/I_{cc}$ and $F = (\hbar^2/2)[I_{cc}/I_{\alpha}(I_{cc}-I_{\alpha})]$. Unfortunately, there are more matrix elements (those linear in p') which needed to be calculated and generally this formulation has no advantage over the other two. As a result we do not discuss it further.

2. Integrals involving the torsional functions.²⁰—In order to obtain the energy levels it is necessary first to compute the integrals given in Eq. (3-50). Evaluation of such integrals is generally quite complicated because of the difficulty involved in the determination of the torsional functions by the procedure of continued fractions. Fortunately, for the case of high barriers ($s \ge 20$), one may use the harmonic oscillator approximation for the torsional functions and the integrals can be obtained in a much simpler way.

At the limit of infinite barrier, $I_{K'v'\sigma}^{Kv\sigma}$ approaches zero for $v \neq v'$ and unity for v = v'. It is convenient then to introduce the terms

$$\delta_{K+1,v\sigma}{}^{Kv\sigma} = 1 - \int_{0}^{2\pi} Q_{Kv\sigma}^{*}(\alpha) Q_{K+1,v\sigma}(\alpha) d\alpha,$$

$$\delta_{K+2,v\sigma}{}^{Kv\sigma} = 1 - \int_{0}^{2\pi} Q_{Kv\sigma}^{*}(\alpha) Q_{K+2,v\sigma}(\alpha) d\alpha.$$
(3-51)

By using the harmonic oscillator approximation for the torsional wave function Hecht and Dennison²⁰ obtained the following formulas for the ground torsional state v=0: $\delta_{K+1,0\sigma}{}^{K0\sigma} = f(\rho/3),$ (2.52)

where

$$f(x) = \frac{1}{\sqrt{s}} x^2 + \frac{1}{2s} x^2 (1 - x^2) + \cdots$$

 $\delta_{K+2,0\sigma}{}^{K0\sigma}=f(2\rho/3),$

(3-52)

Expressions for $I_{K'v'\sigma}^{Kv\sigma}(v \neq v')$ have also been derived by Hecht and Dennison from the harmonic oscillator approximation [see Eq. (28) of reference 20]. An im-

**** Hecht and Dennison²⁰ chose the torsional function in the form of

$$M_{Kv\sigma}(\alpha) = e^{i(1-\rho)K\alpha}Q_{Kv\sigma}(\alpha),$$

which leads to the same integrals $I_{K'v'\sigma}^{Kv\sigma}$ in different forms. The form given above is the same as Itoh's.³¹

portant property of the integrals in Eq. (3-50) is their relative independence of the quantum numbers K and σ . Furthermore, unlike the case of PAM the matrix elements off-diagonal in v are usually very small and their contributions to the energy are rather unimportant.

3. Diagonalization of the energy matrix.-The diagonalization of those elements off-diagonal in v can be accomplished by a Van Vleck transformation. After this transformation the energy matrix takes on a block structure in which each block corresponds to a certain value of J with the dimensions $(2J+1) \times (2J+1)$. Both $(K|K\pm 1)$ and $(K|K\pm 2)$ elements are present in these submatrices because the coordinate axes are not principal axes. One then applies a transformation $S (=S_1S_2)$ which diagonalizes the limiting rigid rotor Hamiltonian. The off-diagonal elements of the transformed Hamiltonian now consist of only the terms containing the integrals $I_{K'v'\sigma}^{Kv\sigma}$ and $E_{Kv\sigma}$. Examples of the transformed Hamiltonian have been given by Hecht and Dennison for J=1.1111 The energy levels can then be obtained by the usual perturbation method (or a modified procedure may be recommended in case near degeneracy occurs). One may, of course, apply a transformation S' to H to bring it directly into the diagonal form. The advantage of using S instead of S' is that the former transformation matrix can be set down in a systematic fashion.

Let S be written as S_1S_2 where S_1 transforms the coordinate axes to the principal axes system and S_2 is the matrix which diagonalizes the asymmetric rigidrotor Hamiltonian (referred to principal axes) in the symmetric top representation. The elements of S_2 can be determined from the asymmetric rotor energy levels by well-known techniques.⁹⁷ The elements of S_1 can be written directly from the representation of the rotational group as given by Wigner¹¹⁷ as

$$\psi_{JKp} = \sum_{K} D^{J}(\beta)_{KpK} \psi_{JK} = \sum_{K} (S_{1})_{KpK} \psi_{JK}, \quad (3-53)$$

where K_p and K refer to the quantum number along the z principal axis and the internal axis, respectively, and

$$D^{J}(\beta)_{K_{p}K} = \sum (-1)^{n} \\ \times \frac{\left[(J+K)! (J-K)! (J+K_{p})! (J-K_{p})! \right]^{\frac{1}{2}}}{(J-K_{p}-n)! (J+K-n)! n! (n+K_{p}-K)!} \\ \times \left(\cos^{\beta}_{-2} \right)^{2J+K-K_{p}-2n} \left(\sin^{\beta}_{-2} \right)^{2n+K_{p}-K}. \quad (3-54)$$

The summation is from the larger of 0 or $(K-K_p)$ to the smaller of (J-K) or $(J-K_p)$. The angle β is the angle between the vector $\mathbf{\varrho}$ and z principal axis, i.e.,

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 $[\]dagger\dagger\dagger\dagger$ See p. 38 of reference 20. In these matrices the elements nondiagonal in v have been neglected because they do not contribute to the splittings of the A and E levels but only cause a shift in frequencies.

the angle between the c' and the z axis:

$$\sin\beta = \rho_y/\rho.$$

For small angles of β Eq. (3-54) can be expanded (to the order of β^2) with the results⁶²:

$$(S_{1})_{KK} = 1 - \frac{\beta^{2}}{4} [J(J+1) - K^{2}],$$

- $(S_{1})_{K,K+1} = + (S_{1})_{K+1,K} = \frac{\beta}{2} [(J-K)(J+K+1)]^{\frac{1}{2}},$
 $(S_{1})_{-1,1} = (S_{1})_{1,-1} = \frac{\beta^{2}}{8} J(J+1),$
 $(\beta \approx \rho_{u}/\rho, \alpha \approx \rho_{z}/\rho).$

4. Energy levels and spectra.—Since the energy matrix given in Eq. (3-49) is diagonal in σ , one may expect to have three series of energy levels corresponding to $\sigma = 0$, 1, -1. From Eq. (3-46) the energy submatrices for $\sigma = 1$ and $\sigma = -1$ are identical, therefore the energy levels for $\sigma = \pm 1$ are doubly degenerate. The eigenfunctions for $\sigma = \pm 1$ correspond to the symmetry species E of the C₃ group, and the levels with $\sigma = 0$ have the symmetry properties of the A species. Since v is nearly a good quantum number (the elements offdiagonal in v are small), a torsional level is labeled by v and σ , and associated with each torsional level one has a set of rotational energy levels characterized by the quantum numbers J, K, M.

The selection rules $\Delta \sigma = 0$ (derived in Sec. 6) predict two lines for each rotational transition associated with the ground torsional state v=0 for relatively high barriers, one from the nondegenerate torsional levels $\sigma=0$, and one from $\sigma=\pm 1$. Figure 4 shows two pairs of such transitions arising from the two K doublets of a slightly asymmetric top. The splitting of the doublets depends mainly on the tunneling, and the separation between the two pairs of doublets depends on the asymmetry. When the splitting and the separation become comparable in magnitude a mixing of states occurs such that "forbidden lines" can now occur. This is discussed in Sec. 5.

The doublet structure in the microwave spectra is characteristic of the threefold high barrier case, and when the splitting is not too large, the doublets can easily be recognized because the Stark effect is virtually identical for the two lines. Since the δ 's and the integrals I are to a good approximation independent of Kand σ , the difference between the two corresponding eigenvalues of the degenerate and nondegenerate submatrices for a given J arise only from the terms containing $E_{Kv\sigma}$. Therefore, the splittings of the doublets in the microwave spectrum depend to the first order only on $E_{Kv\sigma}$ but not $\delta_{K'v\sigma}^{Kv\sigma}$ and $I_{K'v\sigma}^{Kv'\sigma}$ which cause only a shifting in the positions of the lines. The effect of the δ 's and *I*'s can be included,²⁰ but the relations are rather complicated. After the transformation *S*, the resulting Hamiltonian contains some elements which carry the δ 's as coefficients and have the same structure as the ordinary rigid asymmetric rotor matrix elements.⁶² As a result the δ 's add a correction to the rotational constants which is the same for the degenerate and nondegenerate levels.

Since the energy levels (except K=0, $\sigma=0$) are all degenerate for symmetric tops with high barriers, it can be seen that the presence of the asymmetry splits some of these degenerate levels so that the levels with $\sigma=0$ are now nondegenerate. The splitting of the levels by asymmetry can be seen in the following way: to split a pair of degenerate levels of the unperturbed system (the symmetric molecule), say K=2, $\sigma=0$, and K=-2, $\sigma=0$, it is necessary that the perturbation (the asymmetry) offers matrix elements connecting these two levels directly or through high-order terms. In the present case these two levels do indeed interact with each other through the asymmetry terms as

$$K=2, \sigma=0 \leftrightarrow K=0, \sigma=0 \leftrightarrow K=-2, \sigma=0.$$

On the other hand, since the asymmetry terms are diagonal in σ , the pairs of levels with quantum number $K, \sigma = 1$, and $-K, \sigma = -1$ which are degenerate in the symmetric top case, can never connect each other under any high-order interaction. Consequently all the levels with $\sigma = \pm 1$ remain doubly degenerate. This is shown in Fig. 4 where the thickness of the levels was drawn to illustrate the degeneracy. Each J, K level has a weight of six from the two K levels and the three internal rotor levels.

At the limit of infinitely high barriers, the δ 's and *I*'s approach zero and the energy matrix in Eq. (3-49) reduces to that of a rigid rotor.

5. Splitting of the hindered rotation doublets.-The splittings of doublets associated with the ground torsional level are utilized to determine the barrier height. Hecht and Dennison²⁰ have given expressions for the differences between the A and E component of a rotational state in the ground torsional level up to J=3. With these formulas the barrier can be evaluated from the splittings of the low J rotational lines. For higher Jlevels the splitting of the A and E levels can be calculated as follows: A transformation S_1S_2' is applied to the Hamiltonian where S_1 corresponds to a rotation of the axes as defined previously and S_2' is the matrix which changes the basis vectors from the symmetric top wave function to the Wang symmetric and antisymmetric combinations. Note that S_2' is different from S_2 . Let the transformed Hamiltonian be written as $H_R + H_T + H_{IR}$ where H_R is the rotational part, H_T is the internal rotation part dependent on $E_{Kv\sigma}$, and H_{IR} is the internal rotation part dependent on the integrals which, as pointed out before, have little effect on the splittings of the internal rotation doublets. For slightly asymmetric tops the splittings are caused primarily by

the difference in the diagonal elements of H_T between the A and E levels provided the asymmetry splitting is not too small.

Approximate formulas for the diagonal elements in the H_T were derived by Lide and Mann⁶² for the case of small values of β . These formulas for the splitting of the energy levels follow directly from Eq. (3-55) and are given in Eq. (3-56):

$$\Delta E_{JK} = \Delta_{K} + (\beta^{2}/4) [(J+K)(J-K+1)\Delta_{K-1} \\ -2[J(J+1)-K^{2}]\Delta_{K} \\ + (J-K)(J+K+1)\Delta_{K+1}], \\ \Delta E_{J1} = \Delta_{1} + (\beta^{2}/4) [(J-1)(J+2)(\Delta_{2}-\Delta_{1})], \\ (J+K_{-1}+K_{+1} \text{ even}), \quad (3-56)$$

$$\begin{split} \Delta E_{J1} &= \Delta_1 + (\beta^2/4) [2J(J+1)\Delta_0 \\ &- (3J^2+3J-2)\Delta_1 + (J-1)(J+2)\Delta_2], \\ &(J+K_{-1}+K_{+1} \text{ odd}), \\ \Delta E_{J0} &= \Delta_0 + (\beta^2/2)J(J+1)(\Delta_1 - \Delta_0), \end{split}$$

where

$$\Delta_{K} = -\frac{1}{2} (E_{Kv1} + E_{Kv-1}) + E_{Kv0} \approx +\frac{3}{2} F a_{1} \cos\left(\frac{2\pi}{3}\rho K\right)$$
$$= \Delta_{0} \cos\left(\frac{2\pi}{3}\rho K\right), \quad (3-57a)$$

$$\Delta_0 = +\frac{3}{2}Fa_1 = +(9/4)F\Delta b.\ddagger\ddagger\ddagger \qquad (3-57b)$$

In general the off-diagonal elements of H_T should also be considered for the *E* levels especially when the asymmetry splitting is small. They connect the states corresponding to the symmetric and antisymmetric combination of the symmetric top functions and have the form of

$$(K_{+}|H|K_{-}) = \delta_{K} = +\frac{\alpha}{2}(E_{Kv\sigma} - E_{-Kv\sigma})$$
$$= +\frac{\alpha}{\sqrt{3}}\Delta_{0}\sin\left(\frac{2\pi}{3}\rho K\right), \quad (3-58)$$
where

where

$$\alpha = \rho_z / \rho = (1 - \beta^2)^{\frac{1}{2}}.$$

Both the quantities Δ_K and δ_K can be approximated by the trigonometric form only when the barrier is relatively high such that $E_{Kv\sigma}$ can be approximated accurately by the Fourier coefficients a_0 and a_1 with the neglect of the higher terms. The term δ_K is equivalent to the linear terms in P_z in the PAM and the term Δ_K is equivalent to the shift in the rotational constants, i.e., $C_{v0}-C_{v1}$.

The asymmetry term is of the form

$$\delta_{\text{Asy}} = -\frac{1}{4} (A - B) [(J - K)(J - K - 1) \\ \times (J + K + 1)(J + K + 2)]^{\frac{1}{2}}. \quad (3-59)$$

For the K=1 levels only, the asymmetry and the offdiagonal elements of H_T compete directly with one another for the shifting of the levels. If the two effects are of the same order of magnitude, then the correction can be determined from the

$$\frac{1}{2}(4\delta_{K}^{2}+\delta_{Asy}^{\prime 2})^{\frac{1}{2}}.$$
 (3-60)

Here δ_{Asy} ' is the asymmetry splitting and not the asymmetry term (note that for K=1, they are the same). If $\delta_K \gg \delta_{Asy}$ ', the suitable zeroth-order basis functions are no longer the Wang functions but rather the symmetric rotor functions. After the transformation S_1 , the energy matrix can then be diagonalized exactly or by perturbation methods. If, on the other hand, $\delta_{Asy} > \delta_K$, then the splitting due to the off-diagonal elements of H_T must be calculated by the proper asymmetric rotor wave functions, i.e., the effects of β^2 and higher-order terms should be considered. Lide and Mann⁶² have derived expressions to the order β^2 for the frequencies of the parallel transition, J+1, $K \leftarrow J$, K.

6. General case.—The most general type of molecules, where the internal rotor is arbitrarily located with respect to the principal axes, has been considered by Pitzer and Gwinn,⁸⁴ Hecht and Dennison,²⁰ and Burkhard.⁷ The method follows in an analogous manner, only with added complications. As an aid in the computation it is usually easier to determine the molecular parameters such as ϱ and r by the PAM and then convert them to the IAM.

7. Intermediate barrier case.—If the barrier hindering internal rotation becomes too low for the high barrier approximation to be valid, the matrix elements off-diagonal in v would have appreciable effect on the energy levels. The whole matrix can then be diagonalized either exactly or approximately by using modified perturbation procedure.

Methyl alcohol, methyl amine, and methyl mercaptan are examples of molecules with intermediate barriers, i.e., low s values. Considerable work has been done on these molecules and this is discussed in Sec. 8. The low s values in these molecules are caused in part by the small reduced moment of the methyl group. With the light asymmetric frames, these molecules have only a slight symmetry. All the off-diagonal matrix elements due to asymmetry and internal rotation are small and their effect can be calculated by perturbation theory. For the main Q branch series $(\Delta J=0, \Delta K=\pm 1)$ reported, the transition positions are determined essentially by the limiting symmetric top rotational transition plus the internal rotational transition. The offdiagonal elements contribute small terms which can be expanded in a power series of J(J+1). The coefficients of these power series are the perturbation correction terms including centrifugal distortion. Usually some parallel transitions are needed in addition to aid in the structural determination.

Should the asymmetry be large, the solution of the low reduced barrier problem is quite difficult. With the

 $[\]ddagger \ddagger \ddagger$ Here, Δ_0 is the negative of Δ_0 in reference 20 because we have taken the *A* level minus the *E* level. Here Δb is the difference between the values of *b* [see Eq. (3-4)] for the Λ and *E* sublevels of a torsional state.

matrix elements given in Eq. (3-49) a diagonalization of the low J energy matrices could be made. The (v | v')connections probably could be treated to sufficient accuracy by perturbation calculations. Evaluation of the torsional functions needed for calculating the matrix elements is discussed in Appendix 2.

4. LOW BARRIER APPROXIMATIONS

The barriers of most molecules determined from the microwave spectra are in the category of a "high barrier," i.e., of the order of 0.7–5.0 kcal. Here the "high barrier approximation" (Sec. 3) can be used, in which both a rotational and a torsional equation are solved, and any interaction removed by a transformation. In the low barrier approximation the free internal rotational problem is solved exactly and then the barrier is added as a perturbation. So far two molecules have been treated by this method; they are nitromethane $(CH_3NO_2)^{106,107}$ and methyl difluoroboron $(CH_3BF_2).^{74,75}$

The possession of a sixfold symmetry in these two molecules is believed to be the cause for the low value of the barrier. Consider the case of CH_3NO_2 . The interaction of a single oxygen with the methyl group gives rise to a barrier to internal rotation in the form

$$\frac{1}{2}V_3(1-\cos 3\alpha)+\frac{1}{2}V_6(1-\cos 6\alpha)+\frac{1}{2}V_9(1-\cos 9\alpha)+\cdots$$

The second oxygen contributes another potential barrier which is 180° out of phase with the one from the first oxygen. The potential due to both oxygen atoms is then

$$V_{6}(1-\cos 6\alpha)+V_{12}(1-\cos 12\alpha)+\cdots$$

The present discussion is therefore confined primarily to molecules with sixfold symmetry. The treatment given can, in principle, be extended to the more general case though the actual analysis might become quite complicated.

I. Free Rotation

A. Symmetric Molecules

For symmetric molecules the difference between the solution by the principal axes method and the internal axis method is not as distinct as in the high barrier problems because the torsional equation with its different boundary conditions is now eliminated.

In the PAM, the Hamiltonian is¹²¹

where

$$H = A_{x}(P_{x}^{2} + P_{y}^{2}) + C_{z}P_{z}^{2} + Fp^{2} - 2C_{z}pP_{z}, \quad (4-1)$$

$$A_{x} = \hbar^{2} / 2I_{x} = \hbar^{2} / 2I_{y} = \Lambda, \qquad (4-2a)$$

$$C_z = \hbar^2 / [2(I_z - I_\alpha)], \qquad (4-2b)$$

$$F = \hbar^2 / 2r I_{\alpha} = \hbar^2 I_z / [2I_{\alpha} (I_z - I_{\alpha})]. \qquad (4-2c)$$

This equation can be rearranged to Eq. (4-3),

$$H = A \left(P_{x}^{2} + P_{y}^{2} \right) + C P_{z}^{2} + F \left(p - (I_{\alpha}/I_{z})P_{z} \right)^{2}.$$
(4-3)

But this is just Eq. (2-9) in the IAM.⁴⁸ The eigenfunctions of these two equations are

$$S_{JKM}(\theta,\varphi)e^{iK\chi}e^{im\alpha},$$
 (4-4)

where m is an integer. The eigenvalues corresponding to Eq. (4-1) and Eq. (4-3) are then, respectively,

$$E = AJ(J+1) + (C_z - A)K^2 + Fm^2 - 2C_z Km, \qquad (4-5)$$

$$E = AJ(J+1) + (C-A)K^2 + F[m - (I_{\alpha}/I_{z})K]^2. \quad (4-6)$$

However, if the IAM Hamiltonian Eq. (2-20) is used in which χ' and α' are the variables, then the eigenfunctions are

$$S_{JKM}(\theta,\varphi)e^{iK\chi'}e^{im'\alpha'}.$$
(4-7)

The choice of m' is governed by the boundary conditions, i.e., the wave function must be invariant under the transformation

$$\chi_1 \longrightarrow \chi_1 + 2\pi n_1 \quad \chi_2 \longrightarrow \chi_2 + 2\pi n_2. \tag{4-8}$$

With Eq. (2-15) and following the same method as used in Eq. (3-20) we obtain the result

$$m' = l - (I_{\alpha}/I_{z})K, \qquad (4-9)$$

where l is an integer. Consequently the eigenvalues given in Eq. (4-10) are obtained:

$$E = AJ(J+1) + (C-A)K^{2} + F[l-I_{\alpha}/I_{z})K]^{2}.$$
 (4-10)

Clearly, if we identify l with m, Eq. (4-10) is identical to Eq. (4-6).

The selection rules for the microwave spectra can be stated as $\Delta J = \pm 1$, $\Delta K = 0$, $\Delta m = 0$ (see Sec. 6) (or $\Delta l = 0$). The frequencies of the rotational transitions are

$$\nu_{J+1\leftarrow J} = 2A(J+1),$$
 (4-11)

which are exactly the same as those for a rigid symmetrical rotor. Therefore, the effect of completely free rotation in symmetric tops cannot be detected from the microwave spectra.

B. Asymmetric Molecules (CH₃NO₂ type)

If the methyl group of CH_3NO_2 were allowed to execute free rotation (zero hindering barrier), the microwave spectrum would be considerably different from a rigid molecule. The Hamiltonian may be split into that of a symmetric internal rotor plus the asymmetry term, i.e.,

 $H = H_0 + H_1$,

where

$$H_{0} = \frac{1}{2}(A+B)(P_{x}^{2}+P_{y}^{2}) + C_{z}P_{z}^{2}+Fp^{2}-2C_{z}pP_{z}, \quad (4-12a)$$

$$H_{1} = \frac{1}{2}(A-B)(P_{z}^{2}-P_{z}^{2}), \quad (4-12b)$$

By using the basis functions Eq. (4-4) which diagonal-

ize H_0 , we obtain the matrix elements

$$(JKm|H|JKm) = \frac{1}{2}(A+B)J(J+1) + [C_z - \frac{1}{2}(A+B)]K^2 + I^zm^2 - 2C_zKm,$$

$$(JKm|H|J, K\pm 2, m) = -\frac{1}{4}(A-B)[J(J+1) - K(K\pm 1)]^{\frac{1}{2}} \times [J(J+1) - (K\pm 1)(K\pm 2)]^{\frac{1}{2}}.$$
 (4-13)

The Hamiltonian is diagonal in J, m, and M and the energy matrix consists of submatrices of the order 2J+1 for a given set of J, m, and M. As different values of K are connected only in steps of two by the off-diagonal elements, each of the submatrices can be factored into

$$J = 1 \begin{vmatrix} [C_z - \frac{1}{2}(A+B)] - 2mC_z - \lambda \\ -\frac{1}{2}(A-B) \end{vmatrix}$$
$$J = 2 \begin{vmatrix} [C_z - \frac{1}{2}(A+B)] - 2mC_z - \lambda \\ -\frac{3}{2}(A-B) \end{vmatrix}$$

For each *m* there exists an identical secular equation corresponding to -m and hence the energy levels (with $m \neq 0$) are all doubly degenerate. The selection rules (see Sec. 6) for dipole radiation are identical to those of rigid asymmetric tops with the additional restriction of $\Delta m = 0$. If the dipole moment is along the *z* axis, the parity of *K* cannot change.

From the secular equations (4-14) and (4-15) the frequencies of the $J=2 \leftarrow 1$ odd K, parallel transitions $(\Delta K=0)$ are given by

$$\nu_{2 \leftarrow 1}^{\text{odd } K} = 2(A+B) + \lambda_{2} - \lambda_{1}$$

= 2(A+B) ± { [4mC_{z}^{2} + (9/4)(A-B)^{2}]^{\frac{1}{2}} - [4m^{2}C_{z}^{2} + \frac{1}{4}(A-B)^{2}]^{\frac{1}{2}} }. (4-16)

For each value of m, two lines are predicted which are symmetrically spaced with respect to the midfrequency of 2(A+B). As m increases, the separation between the pair becomes smaller and finally the transitions converge to the band head of $\nu = 2(A+B)$. This effect has been observed on CH₃NO₂ by Tannenbaum, Myers, and Gwinn^{106,107} and on CH₃BF₂ by Naylor and Wilson.^{74,75} The intensities of the higher members would tend to decrease on account of the unfavorable Boltzmann factors.

The other $J=2 \leftarrow 1$ transition which is even in K, can be treated in a similar manner. As Naylor and Wilson^{74,75} have pointed out, the J=1, K=0 eigenvalue is zero and the J=2, K=0 eigenvalue is positive, decreasing with increasing m. This group of lines therefore converge toward 2(A+B) from the high-frequency side as m increases. For large values of m the energy matrix Eq. (4-13) may be solved by second-order perturbation theory which leads to

even and odd K blocks. When m is equal to zero, the secular equation degenerates into one identical to that of a rigid asymmetric rotor with the exception that C_* is the rotational constant of the framework alone rather than the entire molecule. For $m \neq 0$, the Wang transformation does not lead to further factoring of the secular equation because of the presence of the elements linear in K. As examples, the secular determinant with odd values of K for J=1 and J=2 are given below. The terms independent of K in the diagonal elements have been omitted since they can be regarded as additive constants for a given J and m.

$$\frac{-\frac{1}{2}(A-B)}{\left[C_{z}-\frac{1}{2}(A+B)\right]+2mC_{z}-\lambda}=0$$
(4-14)

$$\frac{-\frac{3}{2}(A-B)}{[C_{z}-\frac{1}{2}(A+B)]+2mC_{z}-\lambda} = 0$$
(4-15)

$$E = \frac{1}{2}(A+B)J(J+1) + [C_z - \frac{1}{2}(A+B)]K^2 + Fm^2 - 2C_zKm + \frac{(A-B)^2}{64\{[C_z - \frac{1}{2}(A+B)](K-1) - C_zm\}} \times [J^2 - (K-1)^2][(J+1)^2 - (K-1)^2] - \frac{(A-B)^2}{64\{[C_z - \frac{1}{2}(A+B)](K+1) + C_zm\}} \times [J^2 - (K+1)^2][(J+1)^2 - (K+1)^2] + \cdots$$
(4.17)

The transitions of the type $\Delta J = \pm 1, \Delta K = 0,$ \$\$\$ $\Delta m = 0$ again give rise to a band-like structure for each given J.

II. A Low Sixfold Barrier

The sixfold potential barrier introduces to the Hamiltonian an additional term of the form

$$V(\alpha) = (V_6/2)(1 - \cos 6\alpha)$$

= $(V_6/4)(2 - e^{i6\alpha} - e^{-i6\alpha}).$ (4-18)

The first term $\frac{1}{2}V_6$ merely represents a common additive constant and can be safely dropped. The energy matrix analogous to Eq. (4-13) is

$$(JKm|H|JKm) = \frac{1}{2}(A+B)J(J+1) + [C_{z}-\frac{1}{2}(A+B)]K^{2}+Fm^{2}-2mC_{z}K (JKm|H|J, K\pm 2, m) = -\frac{1}{4}(A-B)\{[J(J+1) -K(K\pm 1)][J(J+1)-(K\pm 1)(K\pm 2)]\}^{\frac{1}{2}} (4-19) (JKm|H|JK, m+6) = -\frac{1}{2}K$$

$$(JKm|H|JK, m\pm 6) = -\frac{1}{4}V_6$$

When V_6 is small, the nondiagonality in m may be re-

^{§§§§§} In the present case K is nearly a good quantum number.

moved by a Van Vleck transformation.³⁴ To the secondorder approximation the matrix elements reduce to those given in Eq. (4-13) with the additional diagonal term

$$\frac{V_{6^{2}}}{192[C_{z}K - F(m+3)]} - \frac{V_{6^{2}}}{192[C_{z}K - F(m-3)]}$$
$$= \frac{FV_{6^{2}}}{32[(C_{z}K - Fm)^{2} - 9F^{2}]}.$$
 (4-20)

The submatrices for m and -m are still identical and the energy levels remain doubly degenerate. Calculations show that the two correction terms from the Van Vleck transformation in Eq. (4-20) have very little effect on the frequency provided $\frac{1}{4}V_6 \ll F$. The spectrum is therefore almost identical to that for free rotation. The validity of Eq. (4-20) depends, of course, on the relative magnitude of V_6 and F. When the potential barrier becomes larger it is necessary to consider the third- and fourth-order terms from the Van Vleck transformation, but it has been indicated⁷⁴ that even when the effect of the higher terms may be quite appreciable as far as the positions of the energy levels are concerned, the effect on the frequency may be negligible.

The foregoing treatment is not directly applicable to the |m|=3 levels because a near degeneracy exists and it becomes necessary to consider the m=-3 and m=3 block as a single secular equation. The matrix elements connecting 3 with 9 and -3 with -9 can, however, still be treated by the Van Vleck procedure. An example is furnished by the block corresponding to J=1, K odd:

where

$$a = \frac{1}{2}(A+B) + C_{z} + 9F - 6C_{z} - \frac{V_{6}^{2}}{192(6F-C)},$$

$$a' = \frac{1}{2}(A+B) + C_{z} + 9F + 6C_{z} + \frac{V_{6}^{2}}{192(6F+C)},$$

$$b = -\frac{1}{2}(A-B).$$

The symmetry about the antidiagonal allows this matrix to be factored through a transformation which is equivalent to choosing wave functions of the type

$$\frac{1}{\sqrt{2}} [\psi(K, m=3) \pm \psi(-K, m=-3)]. \quad (4-22)$$

The two resulting matrices are

$$\begin{bmatrix} a' & b + \frac{1}{4}V_6 \\ b + \frac{1}{4}V_6 & a \end{bmatrix},$$
 (4-23a)

$$\begin{bmatrix} a' & b - \frac{1}{4}V_6 \\ b - \frac{1}{4}V_6 & a \end{bmatrix}.$$
 (4-23b)

The double degeneracy discussed in the previous paragraph and in the free-rotor case is now split by the barrier when |m| = 3. In fact the energy levels corresponding to *m* equal to whole multiple of three are all nondegenerate (see Fig. 2). The higher the multiple of three, the higher the order of perturbation required to demonstrate the splitting. The method for calculating these splittings is very similar to that used for the λ doubling in diatomic molecules.

There are now four lines for the $J=2 \leftarrow 1$ transition with odd K and |m|=3. These four lines appear as two pairs, both symmetrically spaced about the band head $\nu=2(A+B)$ and the splittings of these two pairs of lines are extremely sensitive to the barrier height. In CH₃BF₂ the splitting of one of these pairs, which would be practically coincident at the limit of zero barrier, amounts to about 4000 Mc, for a barrier of 14 cal/mole. These splittings are what make it possible to determine the barrier height with a high degree of accuracy from the microwave spectra.

The selection rules are given approximately by

$$\Delta J=0,\pm 1; \quad \Delta K=0; \quad \Delta m=0.$$

Exact selection rules may be obtained by the group theoretical treatment (Sec. 6) or by an explicit evaluation of the transition moments.

In principle three sets of lines should be observed. The first set, which has the structure of the ordinary rigid asymmetric top spectrum, corresponds to m=0. Analysis of these lines yields the two principal moments of inertia perpendicular to the axis connecting the internally rotating groups (the C-N or C-B bond) || || || || and also the moment of inertia of the framework about this axis. The second set consists of all the lines with $m \neq 0$ and $m \neq 3$. A band structure is observed if a sufficient number of high m transitions is detected. The |m|=3 lines constitute the third set and the splittings of these lines are used to determine the barrier height accurately.

III. A Low Threefold Barrier

The problem of a low threefold potential barrier can be handled in essentially the same fashion. The paper by Wilson, Lin, and Lide¹²¹ gives a treatment for a general N-fold barrier. Here, however, there are no

 $^{\| \| \| \|}$ Nuclear spin symmetry (see Sec. 6) in CH₃NO₂ allows only those energy levels with K-m even so that the second set is also needed to determine the moments of inertia.

degenerate levels like the |m| = 3 for the sixfold barrier which are connected by matrix elements of the barrier. Therefore, the barrier height cannot be as accurately determined. Recently CH₃C=CCH₂Cl has been studied^{53b} and an estimate of the barrier height has been given.

5. CALCULATIONS OF BARRIER HEIGHTS

After the rather lengthy discussions of the high barrier approximation and the low barrier approximation for the IAM and PAM, the casual reader may be a little perplexed as to when the approximations are valid and which representation to use. Consequently, it seems desirable to give a few suggestions in regard to the analyses of microwave spectra, characteristics of the spectra, and methods of calculation.

I. Analyses of Microwave Spectra

As pointed out previously, the effects of rigid internal rotation are not observed in a symmetric top molecule. As a result, all the applications of internal rotational theory have been done on asymmetric molecules. The methods for determining the barrier heights for the symmetric top molecules from the microwave spectra are discussed in Sec. 7.

For convenience the effect of internal rotation in an asymmetric molecule can be subdivided into the following groups according to the magnitude of the parameter s as defined in Eqs. (3-4):

(1) The pseudo-rigid rotor case (s>30).—With a relatively high barrier and large asymmetry splittings,

i.e., the asymmetry splittings are larger than the internal rotation splittings, both members of a transition follow a rigid-rotor spectrum. This is especially true of the low K energy levels with the possible exception of the K=1 levels.

The splittings due to the internal torsion may be ascribed to the Δ_K term [Eqs. (3-57)] in the IAM or the ΔW term [cf. Eq. (3-38)] in the PAM. Acetyl fluoride⁸⁰ is an example of this class of molecules.

For the ground torsional state, the frequencies of the A transitions are generally somewhat higher than those of the corresponding lines of the rigid molecule while the E transitions usually have lower frequencies. The shift of the A line from the "unperturbed position" is approximately twice that of the E line. This follows from the fact that according to Eqs. (3-57) and (3-28), $\frac{1}{2}(E_{Kv1}+E_{Kv-1})$ is approximately equal to $-\frac{1}{2}E_{Kv0}$ or from Eq. (3-33) and Table II, $w_{01}^{(2)}$ is very close to $-\frac{1}{2}w_{00}^{(2)}$. Many exceptions to this rule can occur, especially for the K=1 energy levels, but generally it is a useful first approximation.

(2) A departure of the E levels from a pseudo-rigid rotor pattern (15 < s < 30).—The δ_K term in the IAM or the $w_{01}^{(1)}$ term in the PAM causes the E energy levels to depart from a rigid-rotor pattern and for a given K the two $\Delta K = 0$ transitions tend toward one another so that the spectrum becomes similar to that of a slightly asymmetric top. In other words, the internal rotation cancels out part of the asymmetry. This δ_K term is especially important for the K=1 energy levels because both the asymmetry and this "nonrigid-rotor term"



I.O Mc/sec

FIG. 5. High K transitions in propylene oxide.²⁷ The two E lines are superimposed on the left of the first transition but split in the second transition as K increases. In the third transition the E line is now under the A line and finally comes out the other side on the last transition.

connect the same pair of levels. If either the asymmetry term or the internal rotation term dominates to a large degree, the other can be treated as a perturbation.⁶² If the two terms are of the same order of magnitude, then a 2×2 matrix must be solved (cf. Sec. V).

(3) High K energy levels.—The high K energy levels of an asymmetric rotor are nearly degenerate even for very large values of asymmetry, so the internal rotational splittings often dominate the asymmetry splittings. These high J, high K energy levels are very similar to symmetric rotor levels except for a shift due to the asymmetry. For the parallel type transitions $(\Delta K=0)$ very little splittings are observed, but for the perpendicular transitions $(\Delta K=\pm 1)$ a triplet is observed consisting of an A symmetry line and two E symmetry lines. This is explained in Sec. 6 II. B. Propylene oxide²⁷ is an example of this group and some of these triplets are shown in Fig. 5.

(4) Intermediate barrier heights (s < 15).—When the internal rotational splittings are of the order of the spacings between different rotational levels, then the various approximations used in the high barrier case are not generally valid. This is true especially for the perpendicular transitions. Consequently, a more detailed calculation is needed. The IAM is usually recommended for the intermediate barrier problem, especially for the slightly asymmetric molecules, e.g., methyl alcohol. As a guide to the first analysis, the low Jparallel transitions should be used to obtain the approximate barrier height and molecular structure since these lines are relatively barrier insensitive. A more detailed analysis of the perpendicular transitions is then made to determine the barrier height more accurately. For molecules with large asymmetry (such as acetic acid¹⁰⁵) many times the PAM is more convenient.

(5) Low barrier heights (s < 2).—For barrier heights in this region the low barrier approximation given in Sec. 4 is recommended. A considerable number of lines will be observed with all the possible *m* values. Naturally the Boltzmann factor eventually decreases the intensity of the high *m* lines.

Generally, the m=0 lines should be analyzed first, followed by the low m (except |m|=3) transitions which are relatively barrier insensitive. Then an accurate barrier height can be obtained from the |m|=3 levels which are widely split by the sixfold potential energy term.

Finally, in the analysis of the spectra, regardless of the *s* values, the choice of the axis of quantization is gauged by the axis of internal rotation in both the IAM and PAM. This follows directly for the IAM. In the PAM the principal axes closest to the top axes are used as the *z* axes even if this does not conform to the best choice for the solution of asymmetric rotor energy levels.⁴¹



FIG. 6. A rotational line in the ground state and excited vibrational (or torsional) states. (a) The rotational lines of the ground state and first two excited vibrational levels (or torsional levels without internal rotational splitting). (b) The same pattern including internal rotational splitting into the A and E lines. The observed spectrum is from propylene oxide.²⁷

II. General Characteristic of the Spectra

While the most intense part of the spectrum for molecules with a relatively high barrier arises from the transitions in the ground torsional state, the rotational transitions in the excited torsional states are usually observable. For example, at room temperature the intensities of the spectral lines from the first excited state could be reduced by a factor of two or three and those from the second excited states by a factor of about ten. These weaker lines (known as satellites) are shifted from the main line associated with the ground torsional state because of the influence of the vibration of the molecule. This total effect is taken into account by using effective rotational constants B_i which are related to the actual rotational constants B_e as $B_i = B_e - \Sigma_i$ $\times (v_i + \frac{1}{2}) \alpha_i$. The splittings between the A and E satellite lines in the "heavy" molecules are, however, rather insensitive to the effect of molecular vibrations and, to a first approximation, are caused by the internal rotation only. The general formulas for the A and Esplittings developed in Sec. 3 are applicable to the rotational lines in the excited torsional states provided that such torsional levels are far below the top of the potential barrier. As the internal rotation splittings become magnified in the excited torsional states, the potential barrier many times can be determined from the splittings of the satellites.²² In propylene oxide^{27,101} the same barrier can account for the splittings of the rotational lines in the three lowest torsional levels (see Fig. 6). In the lighter molecules, such as methyl alcohol and methyl silane,⁴² the splittings of the satellite rotational lines cannot be completely ascribed to the internal rotation. This is because the effects of molecular vibrations contribute appreciably to the splittings as well as the frequency shifts of the rotational lines in the excited states.

In the identification of microwave transitions, a rigid

model of the molecule can be used in order to first locate the approximate positions of the lines. The Stark effect can be used in a similar manner as in a rigid asymmetric molecule. The A symmetry levels can be thought of as those of a rigid molecule possessing torsional oscillations. The E symmetry levels, on the other hand, can exhibit some first-order Stark effect (see Sec. III), but this is usually quite small for cases of high barrier and large asymmetry. However, in other cases the E transition can be distinguished from the A transition by the Stark effect. The nuclear spin weights can also aid in the identification. For the normal methyl group, the intensity ratio of A and E is 1:1; but in a deuterated methyl group, the ratio is 11:16 with the E level stronger³⁸ (see Sec. 6).

With the identification of the various transitions, approximate unperturbed rotational constants can be determined by using either the average position of the A and E doublet or else two-thirds the doublet separation from the A line. The latter method is a better approximation except for the K=1 levels. With the approximate rotational constants one can determine the structure of the molecule which along with the A-Esplittings may be used to obtain the barrier height. Successive iterations lead to more accurate results.

III. Stark Effect

For the case of free rotation, the lines with m=0show a second-order Stark effect (first order if accidental degeneracy exists) which is a characteristic of a rigid-rotor spectrum. When *m* is not equal to zero the situation is different. As stated before, the Wang combinations of the *K* and -K symmetric top functions are no longer the proper zeroth-order wave functions because of the presence of the linear *K* terms in the secular equation. For example, an eigenfunction for J=1 and odd values of *K* may be written as

$$\Psi = a\psi(K=1) + b\psi(K=-1), \quad (5-1)$$

where a and b are not identical. The expectation values of the direction cosines between the electric field and the body-fixed z axis is then

$$\int \Psi^* \cos \theta \Psi d\tau = \frac{(a^2 - b^2)KM}{J(J+1)}.$$
 (5-2)

This leads us to the conclusion that, in general, a firstorder Stark effect is observed provided m, K, and M are all different from zero. For example, with $J=1 \leftarrow 0$ only $\Delta K=0$ and $\Delta M=0$ are allowed and the transitions have a second-order Stark lobe while the Stark effect of the $J=2 \leftarrow 1$ transitions (with odd K) is first order for $M=\pm 1$ and second order for M=0.

When the barrier is $low^{75,107}$ the Stark patterns of the lines with $|m| \neq 3$ are practically identical to those for free rotation as the Van Vleck transformation offers only minor modifications to the wave functions. How-

ever, for the case of |m|=3, the transformation [see Eq. (4-22)] eliminates the diagonal elements of $\cos\theta$. The resulting off-diagonal elements then give rise to a second-order Stark effect with a large Stark coefficient analogous to the case of near degeneracy in rigid asymmetric tops. This serves as a means for identifying the |m|=3 lines.

When the barrier becomes higher, the asymmetry has a larger influence. The coefficients a and b in Eq. (5-1) depend on δ_K and δ_{Asy}' (defined in Sec. 3) as

$$a^{2} - b^{2} = \pm 2\delta_{K} (4\delta_{K}^{2} + \delta_{Asy}^{2})^{-\frac{1}{2}}.$$
 (5-3)

Since δ_K is very barrier sensitive, the first-order Stark effect rapidly vanishes as the barrier height is increased.

IV. High Barrier Case

In the symmetric top case, the energy associated with the internal rotation for the IAM is expanded in a Fourier series [Eq. (3-27)] while for the PAM it is expanded in a power series [Eq. (3-13)] as

$$E_{Kr\sigma} = F \left[a_0 + a_1 \cos \frac{2\pi}{3} (\rho K - \sigma) + a_2 \cos \frac{4\pi}{3} (\rho K - \sigma) + \cdots \right], \quad (5-4)$$

$$E_{Kv\sigma} = F[w_{v\sigma}^{(0)} + w_{v\sigma}^{(1)}\rho K + w_{v\sigma}^{(2)}(\rho K)^2 + \cdots].$$
 (5-5)

In Fig. 7, the various Fourier coefficients are plotted from s=10 to s=100 on a semilogarithmic scale, and in Fig. 8, the coefficients of the power series in Eq. (5-5) are given. From Eqs. (5-4) and (5-5) the connecting relations between these two types of coefficients can easily be established. They are given in Table III.

TABLE III. The relations between the Fourier coefficients and the power series coefficients [see Eqs. (5-4) and (5-5)].

Factor N ² /4	<i>a</i> ₀	<i>a</i> 1	<i>a</i> 2	<i>a</i> 3	<i>a</i> 4	<i>a</i> 5
$b(\pi)$	1	1	1	1	1	1
$b(2\pi)$	1	1	1	-1	1	-1
$b(3\pi)$	1	$-\frac{1}{2}$	$-\frac{1}{2}$	1	$-\frac{1}{2}$	$-\frac{1}{2}$
$b(4\pi)$	1	0	-1	0	1	Ō
$b(6\pi)$	1	$\frac{1}{2}$	$-\frac{1}{2}$	-1	$-\frac{1}{2}$	$\frac{1}{2}$
$(N^2/4)b(\pi x)$	a_0	$+a_1 \cos$ $+a_3 \cos$	$(2\pi/x)$	$+a_2\cos(4)$	$\frac{1}{4\pi/x}$	
Threefold case (A	V = 3)			•		
$\frac{3}{2} \left[b(\pi) - b(3\pi) \right]$		1	1	0	1	1
$(9/8)[b(\pi) - b(2\pi)]$)]	1	0	1	0	1
$-2\sqrt{3}p_{vv}/\pi = \sqrt{3}w$	$v_1^{(1)}/\pi$	1	-2	0	4	-5
$-9w_{v0}^{(2)}/2\pi^2$		1	4	9	16	25
$+9w_{v1}^{(2)}/\pi^2$		1	4	-18	16	25
$-3\Delta w_{v}^{(2)}/\pi^{2}$		1	4	0	16	25
$(w_{v1}^{(2)} + \frac{1}{2}w_{v0}^{(2)})/$	$(3\pi^2)$	0	0	-1	0	0
$-27\sqrt{3}w_{v1}^{(3)}/2\pi^{3}$		1	-8	0	64	-125
$+243w_{v0}^{(4)}/2\pi^4$		1	16	81	256	625
$-243w_{r1}{}^{(4)}/\pi^4$		1	16	-162	256	625
e.g., $(N^2/4)b(3\pi) = -[9w_{v0}^{(2)}/2\pi^2] =$	$a_0 - \frac{1}{2}a_1 = a_1 + 4a$	$-\frac{1}{2}a_2+$ $+9a_3-$	$-a_3 - \frac{1}{2}a_4 + 16a_4 + $	$a_4 - \frac{1}{2}a_5 = a_5 - 25a_5 + \cdots$	and	



FIG. 7. The Fourier coefficients as a function of the reduced barrier height s for the various torsional levels [see Eq. (5-4)]. --, v=0; ---, v=1; ----, v=2.

Although these formulas were derived for the symmetric top molecules, they are also applicable to the asymmetric molecules with the necessary modification of F and ρ .

Each of the coefficients (except a_0) are very barrier sensitive, as shown in Figs. 7 and 8. They approximate

a functional form of the type $As^{-B} \exp(-C\sqrt{s})$.^{20,99} Empirical formulas for the coefficients in Eqs. (5-4) and (5-5) determined by curve fitting are displayed in Table IV. For the high barriers only the Fourier coefficient a_1 is needed from which all the perturbation coefficients of the PAM can be calculated. The domi-



FIG. 8. The power series coefficients as a function of the reduced barrier height s for the various torsional levels [see Eq. (5-5)]. In order to distinguish the various perturbation terms the following notation is used: $w^{(1)} = -2\xi$, $w^{(2)} = \eta$, $w^{(3)} = \zeta$, $w^{(4)} = \tau$. The first subscript denotes the torsional state v, and the second denotes the sublevel σ . --, v = 0; ---, v = 1; ---, v = 2.

nance of a_1 is seen in Table IV by the fact that the empirical constants B and C have all about the same value for v=0. The small deviations are caused by the low s values.

For low values of J, K, and ρ , the agreement between the IAM and PAM is very good. The splittings of the J=1 energy levels are given as a comparison in Table V. These results become identical if ρK is small and the

barrier is high. Under such circumstances Eq. (5-4) can be approximated by the first two terms and $\sin(2\pi/3)\rho K$ may be replaced by $(2\pi/3)\rho K$. A similar agreement between the IAM and PAM is found for the higher Jlevels.

These connecting relations also indicate the limitations of the two methods: the IAM is restricted to low J because of computational difficulties, and the PAM is restricted to low values of ρK . If J and ρK are large and the asymmetry is small, a method of solution similar to that used by Burkhard and Dennison⁸ on methyl alcohol probably would be the best. If $J, \rho K$, and the asymmetry are all large, both the PAM and IAM involve a considerable amount of calculation. As the barrier is lowered, more expansion terms in Eqs. (5-4) and (5-5) are needed to determine the energy levels.

V. Sample Calculation on the Spectrum of Acetaldehyde (CH_3CHO)

Some of the points previously discussed in regard to the determination of the barrier height from the observed spectrum are illustrated by considering acetaldehyde³⁸ as an example. The values of the parameters obtained in this section differ slightly from the reported values by Kilb et al.,³⁸ because our calculation is not performed to the same refinement as that of reference 38.

Four of the transitions reported in reference 38 for the normal isotopic species are given in Table VI. The estimated unperturbed frequency given in Table VI was taken as $\frac{2}{3}$ of the doublet separation from the A line. For the $2_{12} \leftarrow 1_{11}$ transition and the $2_{11} \leftarrow 1_{10}$ transition, this procedure is not valid because of the δ_1 term. Here the unperturbed position was estimated from the A line alone. For the $2_{12} \leftarrow 1_{11}$ transition twothirds of the $1_{01} \leftarrow 0_{00}$ splitting was subtracted from the A line; for the $2_{11} \leftarrow 1_{10}$ transition three times this amount was subtracted from the A line. This procedure follows directly from the PAM (see Table I).

In order to evaluate the barrier height from the internal rotation splittings, the bond lengths and the bond angles of the molecule must be known. These can best

TABLE IV. Approximate formulas (threefold case). $Log X = log A + B log s - C(s)^{\frac{1}{2}} + Ds.$

x	v	Range of s	Error	A	В	С	D
$-a_1$	0	20-80	0.1%	0.84469	0.92376	0.89751	8.46×10-4
$-a_1$	1	36-100	0.1%	1.21631	1.89036	0.95594	20.55×10-4
$-a_1$	2	60-100	0.1%	0.66776	3.45716	1.09452	50.19×10-4
$-\Delta b$	0	2080	0.3%	0.68248	0.85539	0.87703	
$-\frac{1}{2}w_{01}^{(1)}$	0	20-80	0.3%	0.83388	0.83347	0.87430	
w ₀₀ ⁽²⁾	0	20-80	0.3%	1.18418	0.87348	0.87918	
$-w_{01}^{(2)}$	0	20-80	0.3%	0.89533	0.85530	0.87658	
$\Delta w_0^{(0)}$	0	2080	0.3%	1.36463	0.86703	0.87825	
w01 ⁽³⁾	0	20-80	0.3%	1.02871	0.79882	0.87022	

TABLE V. Comparison of the splitting formulas for an asymmetric molecule with a plane of symmetry.

PAM $\Delta E(1_{01}) = \Delta B = F \rho_x^2 \Delta w_v^{(2)}.$ $\Delta E(1_{11}) = \Delta C - \frac{(Q_z w_{v1}^{(1)})^2}{A - B} = F \rho_z^2 \Delta w_{v2}^{(2)} - \frac{\delta_1^2}{A - B}$ $\Delta E(1_{10}) = \Delta B + \Delta C + \frac{(Q_z w_{v1}^{(1)})^2}{A - B} = F \rho^2 \Delta w_{v2}^{(2)} + \frac{\delta_1^2}{A - B}.$ IAM

$$\Delta E(\mathbf{1}_{01}) = \Delta_0 + \beta^2 (\Delta_1 - \Delta_0) \approx \Delta_0 - \frac{2\pi^2}{9} \rho_x^2 \Delta_0.$$

$$\Delta E(1_{11}) = \Delta_1 - \beta^2 (\Delta_1 - \Delta_0) - \frac{\delta_1^2}{A - B} \approx \Delta_0 - \frac{2\pi^2}{9} \rho_z^2 \Delta_0 - \frac{\delta_1^2}{A - B}$$
$$\Delta E(1_{10}) = \Delta_1 + \frac{\delta_1^2}{A - B} \approx \Delta_1 - \frac{2\pi^2}{9} \rho^2 \Delta_0 + \frac{\delta_1^2}{A - B}.$$

Connecting relations

$$\beta^{2} = \frac{\rho_{x}^{2}}{\rho^{2}}, \quad \alpha^{2} = \frac{\rho_{z}^{2}}{\rho^{2}},$$

$$F \Delta w_{v}^{(0)} = F \Delta b = F (b_{A} - b_{E}) = (4/9) \Delta_{0} = \frac{2}{3} F a_{1},$$

$$-F \Delta w_{v}^{(2)} = \frac{2\pi^{2}}{9} \Delta_{0} = \frac{\pi^{2}}{-3} F a_{1},$$

$$\Delta_{1} - \Delta_{0} = \Delta_{0} \left(\cos \frac{2\pi\rho}{3} - 1 \right) \approx -\Delta_{0}^{2} - \frac{2\pi^{2}}{-2} \rho^{2},$$

$$\delta_{1} = + \frac{\alpha \Delta_{0}}{\sqrt{3}} \sin \frac{2\pi}{3} \rho \approx + \frac{2\pi}{3\sqrt{3}} \rho_{z} \Delta_{0} = \frac{\pi}{\sqrt{3}} \rho_{z} F a_{1} = F \rho_{z} w_{v1}^{(1)}$$

$$= Q_{z} w_{v1}^{(1)} = -2Q_{z} \rho_{vv}.$$

be determined from the rotational constants of a number of isotopic species of the molecule.38 In this sample calculation, however, we use an approximate assumed structure for acetaldehyde. The various molecular parameters calculated from this assumed structure are shown in Table VI.

A. IAM Calculations on Acetaldehyde

From Eqs. (3-56), (3-57), (3-28), and (3-4) we can obtain the expressions for the splitting of the various transitions. For the $J = 1_{01} \leftarrow 0_{00}$ transition a splitting of +3.0 Mc was measured. The approximate formula for this transition is as follows:

$$\nu_A - \nu_E = \Delta \nu = \beta^2 (\Delta_1 - \Delta_0) = -0.22134 \Delta_0 \beta^2$$

= - (9/4)F \Delta b \beta^2 (0.22134) = -678.5 \Delta b Mc.

By equating this to 3.0 Mc, we obtain a value of -0.004422 for Δb . From the formulas in Table IV, from the curve in Fig. 7 for a_1 ($\Delta b = \pm 2a_1/3$), or from references 3b and 104, the corresponding s value can be determined. A value of 22.943 was obtained which corresponds to a barrier height of 407.7 cm⁻¹ (1166 cal/mole). The calculations for the $2_{02} \leftarrow 1_{01}$ follow in a similar manner.

TABLE VI. Parameters for acetaldehyde.

1.	Spectrum		
		Obs frequency	Estimated unperturbed frequency
	$1_{01} - 0_{00}$	19 265.3 (A) 19 262.3 (E)	19 263.3
	$2_{12} - 1_{11}$	37 464.6 (A) 37 687.2 (E)	37 462.6
	2 ₀₂ -1 ₀₁	38 512.3 (A) 38 506.4 (E)	38 508.4
	211-110	39 594.9 (A) 39 362.5 (E)	39 588.9
2.	Rotational constants C (A) 56.9 kMc B (B) 10 163.2 Mc A (C) 9100.0 Mc The rotational constant nota	tion in parenthe	sis refers to
3.	Assumed molecular structure		
	$\begin{array}{ccc} d_{\rm CH} & 1.09 \ A \ ({\rm methyl \ group}) \\ d_{\rm CC} & 1.54 \\ d_{\rm CO} & 1.21 \\ d_{\rm CH} & 1.09 \ ({\rm aldehyde \ group}) \end{array}$	<hch <cch <cco< td=""><td>108°15′ 120° 120°</td></cco<></cch </hch 	108°15′ 120° 120°
4.	Moments of inertia		
	$\begin{array}{l} I_x & 55.553 \text{ amu } A^2 \\ I_y & 49.742 \\ I_z & 8.890 \\ I_\alpha & 3.079 \end{array}$	$I_{aa} \\ I_{bb} \\ I_{cc} \\ I_{bc}$	55.553 43.176 15.086 14.563
5.	Internal rotation parameters $\lambda_y = 0.3910$ $\lambda_z = 0.9204$ r = 0.6931 $\beta^2 = 0.00583$ $\alpha = 0.31941$	$F = 236.9 \text{ kMc} = \Delta_1 = 0.77866\Delta_0$ $\Delta_2 = 0.21262\Delta_0$ $(2\pi/3) e^{-K} = 28.94$	= 17.77 cm ⁻¹
	φ 0.01711	$(2\pi/3)pn = 30.00$	JA

In the calculations of the barrier height from the $2_{12} \leftarrow 1_{11}$ transition and the $2_{11} \leftarrow 1_{10}$ transition, the δ_1 term must also be considered. For the 2_{12} and 2_{11} energy levels we have the following 2×2 matrix (formed by the K and -K state) with the eigenvalues $\pm \lambda_2$:

$$\begin{bmatrix} 190 \ 400 \Delta b & 1594.8 \\ 1594.8 & -190 \ 400 \Delta b \end{bmatrix},$$

where

$$\delta_1 = (1/\sqrt{3})\Delta_0 \sin(2\pi/3)\rho K = 190\ 400\Delta b\ Mc$$

from Eq. (3-58);

$$\delta_{\text{Asy}} = -\frac{1}{4}(A-B)J(J+1) = \frac{1}{4}(1063.2)J(J+1),$$

from Eq. (3-59)

and for the 1_{10} and 1_{11} energy levels we have the following matrix with eigenvalues $\pm \lambda_1$:

$$\begin{bmatrix} 190 \ 400\Delta b & 531.6 \\ 531.6 & -190 \ 400\Delta b \end{bmatrix}.$$

Here, terms on the diagonal which are common to both states have been omitted. The expression for the splitting in $2_{12} \leftarrow 1_{11}$ transitions from Eq. (3-56) is then

$$\Delta \nu = \beta^2 (\Delta_2 + 2\Delta_0 - 3\Delta_1) + \delta_1 \text{ terms} \\= 378.01 \Delta b + (\lambda_2 - 1594.8) - (\lambda_1 - 531.6).$$

By equating this to the observed splitting of -222.6Mc we obtain a Δb of -0.003993 after successive approximations. This leads to a value of 23.56 for s and 418.7 cm⁻¹ (1197 cal/mole) for the barrier height. In a similar manner the expression for the $2_{11} \leftarrow 1_{10}$ transition is

$$\Delta \nu = \beta^2 (\Delta_2 - \Delta_1) + \delta_1 \text{ terms}$$

= -1759.0\Delta b - (\lambda_2 - 1594.8) + (\lambda_1 - 531.6).

By equating this to the observed splitting of +232.4Mc we obtain a Δb of -0.00405. A value of 23.48 is obtained for s and 417.2 cm⁻¹ (1193 cal/mole) for the barrier height. These results are compared in Table VII with the results obtained in reference 38 and by the PAM.

B. PAM Calculations on Acetaldehyde

From Table II and Eq. (3-33) we can obtain the expressions for the splittings of the various transitions. The equation for the $1_{01} \leftarrow 0_{00}$ transition is

$$\Delta \nu = \Delta B = \frac{h}{8\pi^2} \frac{\lambda_y^2 I_\alpha}{r I_y^2} \Delta w_0^{(2)} = 138.74 \Delta w_0^{(2)}.$$

By using the approximate formulas in Table IV or the curves in Fig. 8 we obtain an s value of 22.95 and a barrier height of 407.8 cm⁻¹ (1166 cal/mole). The transition $2_{02} \leftarrow 1_{01}$ follows in a similar manner.

In order to obtain the splittings for the $2_{12} \leftarrow 1_{11}$ transition and the $2_{11} \leftarrow 1_{10}$ transition it is necessary to diagonalize two 2×2 matrices because of the linear terms in K. These matrices are

$$\begin{bmatrix} -151\ 040\ p_{00} + 7680\ w_{01}^{(3)} & 1594.8\\ 1594.8 & 151\ 040\ p_{00} - 7680\ w_{01}^{(3)} \end{bmatrix},$$

and

$$\begin{bmatrix} -151\ 040p_{00} + 7680w_{01}^{(3)} & 531.6\\ 531.6 & +151\ 040p_{00} - 7680w_{10}^{(3)} \end{bmatrix}$$

TABLE VII. Barrier height in acetaldehyde by various methods.

	IAM	РАМ	KLW (38)
$\begin{array}{c} 1_{01} - 0_{00} \\ 2_{02} - 1_{01} \\ 2_{12} - 1_{11} \\ 2_{11} + 1_{10} \\ \delta_1 \\ V_3 \text{ (av)} \end{array}$	407.7 cm ⁻¹ 409.7 418.7 417.2 765 Mc 414 cm ⁻¹	407.8 410.1 418.0 418.0 -763 Mc ^a	408.9 6 417.3 419.0 -760 Mc°

The third-order correction included.
 No individual value was reported for this transition in reference 38.
 A sixfold potential energy term was included. See the footnote at the end of Sec. 3 II.A3(b).

Here the third-order terms have been included. The expressions for the $2_{12} \leftarrow 1_{11}$ transition and for the $2_{11} \leftarrow 1_{10}$ transition from Table II are

$$\Delta \nu = \Delta B + (\lambda_2 - 1594.8) - (\lambda_1 - 531.6)(2_{12} \leftarrow 1_{11}),$$

$$\Delta \nu = 3\Delta B - (\lambda_2 - 1594.8) + (\lambda_1 - 531.6)(2_{11} \leftarrow 1_{10}).$$

By equating these to the observed splittings we obtain the following parameters after successive approximations:

$$p_{00} = 5.46 \times 10^{-3}$$
 $Q_z w_{01}^{(1)} = -824.7$ Mc
 $\Delta w_0^{(2)} = 1.92 \times 10^{-2}$ $\Delta B = 2.66$ Mc
 $w_{01}^{(3)} = 8.10 \times 10^{-3}$ $F(O_2/F)^3 w^{(3)} = 62.2$ Mc.

From the curves in Fig. 8 or the approximate formulas in Table IV, a value of 23.52 is obtained for s which corresponds to a barrier height of 418.0 cm⁻¹ (1195 cal/mole). The results are summarized in Table VII.

6. SELECTION RULES AND NUCLEAR SPIN STATISTICS

I. Selection Rule for Symmetric Molecules

The selection rules for symmetric molecules can be derived easily from the wave function of the internal rotor. Consider, for instance, the wave function obtained from the IAM

$$S_{JKM}(\theta,\varphi)e^{iK\chi}e^{-i\rho K\alpha}P_{Kv\sigma}(\alpha).$$

Since the orientation of the dipole moment is independent of the angle α , the usual selection rules for the dipole radiation of a rigid symmetric rotor are applicable, i.e.,

$$\Delta J = 0, \pm 1; \quad \Delta K = 0.$$

In addition, it may be shown from Eq. (3-25) that the transition moments are different from zero only when $\Delta \sigma = 0$.

II. Selection Rules for Asymmetric Molecules

The selection rules for an asymmetric molecule in the quantum number J is $\Delta J=0,\pm 1$. This follows from the fact that the total angular momentum for a rotating molecule remains a good quantum number even when internal rotation is present. The selection rules governing the changes of the other quantum numbers are more complicated. In general, these rules can be derived by group-theoretical methods.

The general selection rules are derived from symmetry considerations. Application of these rules to the cases of high barrier and low barrier are then discussed in detail.

A. General Selection Rules

The Hamiltonian of a rigid asymmetric rotor is invariant under the operations

$$E: P_x \to P_x, P_y \to P_y, P_z \to P_z,$$

$$C_z: P_x \to -P_x, P_y \to -P_y, P_z \to P_z,$$

$$C_x: P_x \to P_x, P_y \to -P_y, P_z \to -P_z,$$

$$C_y: P_x \to -P_x, P_y \to P_y, P_z \to -P_z,$$
(6-1)

and therefore has the symmetry of the four group $\P\P\P\P V$.

When the effect of internal rotation is included, the Hamiltonian is no longer invariant under the operations given in (6-1) because of the cross terms between the *P*'s and p [e.g., Eq. (2-25) or Eq. (2-37)] or between the *P*'s and functions of the angle α [e.g., Eq. (2-29) or Eq. (2-31)]. The group properties of the various types of molecules are discussed in the following sections.

1. Molecules with a planar frame.—The Hamiltonian Eq. (2-31) or Eq. (2-37) (with $Q_x=0$) is invariant under the following operations:

$$E: P_{x, y, z} \to P_{x, y, z}, \alpha \to \alpha(p \to p),$$

$$C_{x}: P_{x} \to P_{x}, P_{y, z} \to -P_{y, z}, \alpha \to -\alpha(p \to -p),$$

$$C_{3}: P_{x, y, z} \to P_{x, y, z}, \alpha \to \alpha + (2\pi/3)(p \to p),$$

$$C_{3}^{2}: P_{x, y, z} \to P_{x, y, z},$$

$$\alpha \to \alpha + (4\pi/3) = \alpha - (2\pi/3)(p \to p).$$
(6-2)

(The operations C_xC_3 and $C_xC_3^2$ follow directly from these operations.) These symmetry operations satisfy the properties of the group D_3 , and therefore the wave functions have the symmetry of the species A_1 , A_2 , or E.

For this type of molecule the dipole moment lies on the plane of the framework and has the transformation properties of A_2 . The selection rules for the dipole transitions are then²⁰

$$A_1 \leftrightarrow A_2, \quad E \leftrightarrow E$$

2. Molecules with no symmetry in their framework.— For this class of molecules only the operations E, C_3, C_3^2 leave the Hamiltonian unaltered. The energy states then fall into the species A or E of the C_3 group. Since the dipole moment has the symmetry property of A, the selection rules can be summarized as $A \leftrightarrow A, E \leftrightarrow E$.

3. Molecules with a frame of C_{2v} symmetry (CH₃NO₂ type).¹²¹—The group properties are of particular interest because the cross term between **P** and *p* appears only as pP_z . The Hamiltonian is now invariant under the following operations:

$$E: P_{x, y, z} \to P_{x, y, z}, \alpha \to \alpha(p \to p),$$

$$C_{x}: P_{x} \to P_{x}, P_{y, z} \to -P_{y, z}, \alpha \to -\alpha(p \to -p),$$

$$C_{y}: P_{y} \to P_{y}, P_{x, z} \to -P_{x, z}, \alpha \to -\alpha(p \to -p),$$

$$C_{z}: P_{z} \to P_{z}, P_{x, y} \to -P_{x, y}, \alpha \to \alpha(p \to p).$$
(6-3)

Because of the sixfold symmetry, the Hamiltonian is also invariant under the operation $\alpha \rightarrow \alpha + (2n\pi/6)$.

^{¶¶¶¶} The operation $P_x \to -P_x$, $P_y \to P_y$, $P_z \to P_z$, does not alter the Hamiltonian but does change the commutation relations between the three components of the angular momentum, so it is not considered to be a symmetry operation.

TABLE VIII. Character table for the point group D_{6h} .

	Ε	2C3	3CzCz	C₂	2 <i>C</i> zC 2	3 <i>C</i> ₽C ₽	C_2	2 <i>C</i> 6	3 <i>C</i> _x C ₆	C2C2	2 <i>Cz</i> C8	3 <i>Cy</i> C6
A.	1	1	1	1	1	1	1	1	1	1	1	1
Bze	1	1	-1	1	1	-1	1	1	-1	1	1	-1
E_{1e}	2	-1	0	2	-1	0	2	-1	0	2	-1	0
Bre	1	1	1	-1	-1	-1	1	1	1	-1	-1	-1
B_{ye}	1	1	-1	-1	-1	1	1	1	-1	-1	-1	1
E_{2e}	2	-1	0	$^{-2}$	1	0	2	-1	0	-2	1	0
A_0	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1
B_{z0}	1	1	-1	1	1	-1	-1	-1	1	-1	-1	1
E_{10}	2	-1	0	2	-1	0	-2	1	0	-2	1	0
B_{x0}	1	1	1	-1	-1	-1	-1	-1	-1	1	1	1
B_{y0}	1	1	-1	-1	-1	1	-1	-1	1	1	1	-1
E_{20}	2	-1	0	-2	1	0	-2	1	0	2	-1	0

These six operations are denoted by E, C_6 , $C_6^2(C_3)$, $C_6^3(C_2)$, $C_6^4(C_3^2)$, and C_6^5 , where the operation C_6 represents $\alpha \to \alpha + (\pi/3)$. These six operations along with the "four-group" operations form a new group of twenty-four elements which is isomorphous to the point group D_{6h} . The character table of this group is given in Table VIII.

The dipole moment for this model would ordinarily be along the z axis. If this is the case, the transition moment will have symmetry B_{ze} . The selection rules for dipole absorption will then be $A_{e} \leftrightarrow B_{ze}$, $B_{ze} \leftrightarrow B_{ye}$, $E_{1e} \leftrightarrow E_{1e}$, $E_{2e} \leftrightarrow E_{2e}$, $A_{0} \leftrightarrow B_{z0}$, $B_{x0} \leftrightarrow B_{y0}$, $E_{10} \leftrightarrow E_{10}$, $E_{20} \leftrightarrow E_{20}$.

B. Selection Rules for High Barrier

Molecules with a planar frame may be considered as an example. The limiting rigid-rotor Hamiltonian belongs to the four-group. As the operation C_x is common to both the D_3 group (of the torsional rotor) and the four-group, the A_1 species of the D_3 group corresponds to A and B_x in the four-group while the A_2 levels of the hindered rotor reduces to the B_y or B_z levels of the limiting rigid molecule. As shown before, the selection rules for the rotational states associated with the nondegenerate torsional levels are $A_1 \leftrightarrow A_2$. In terms of the transitions for the limiting rigid rotor these correspond to $A, B_x \leftrightarrow B_y, B_z$, which are indeed the selection rules for a rigid asymmetric top molecule with dipole moment on the yz plane. Hence, for the internal rotor with high barriers the selection rules governing the transitions between the rotational levels belonging to the nondegenerate torsional levels (the pseudo-rigid rotor lines) may simply be taken as those for the corresponding rigid molecules.

In the case of degenerate torsional levels, according to the general symmetry selection rule $E \leftrightarrow E$, transitions between all the *E* levels are, in general, possible. This can be understood by considering the effective rotational Hamiltonian for a given torsional level. For the *E* levels the nonrigid-rotor terms, δ_k , tend to eliminate the asymmetry and the transitions approach those of a symmetric rotor. The eigenfunctions no longer have the symmetry of the four-group, and the symmetry selection rules for the wave functions associated with these symmetry species are not applicable. For the case of high barriers and low K, it may be expected that the transitions in the hindered rotor which are forbidden for the limiting rigid rotor are usually weak. However, if transitions involving higher K values are observed, the effect of the internal rotation can now exceed the asymmetry splitting even in the case of relatively high barriers, and the spectrum becomes very interesting. Consider the perpendicular type transition $(\Delta K = \pm 1)$ between two groups of four energy levels corresponding to the A and E levels of a K doublet. At low values of K four lines are expected (two doublets) similar to those shown in Fig. 4. As K increases, all four E transitions are possible and six lines appear (two A and four E). At high values of K the wave function may be approximated by the symmetric top wave function. When this is the case the two A levels of a given K become nearly degenerate and the two A lines merge into a single line. The two E levels, however, remain separated because of the linear term P_z in the effective Hamiltonian Eq. (3-33), and two of the four E lines now become forbidden so that for large values of K one observes a group of three spectral lines—(one A and two E). Such a transition from four lines (low K) to three lines (for high K) has indeed been found by Herschbach and Swalen.²⁷ In the transition region between these two patterns all four E transitions are observed. Those transitions forbidden in the limit of a rigid rotor can be seen to increase in intensity at the expense of the rigid-rotor lines until finally the triplet pattern results (see Fig. 5).

C. Selection Rules for Low Barrier

So far the only molecules which have been found by the methods of microwave spectroscopy to have low potential barriers to internal rotation are CH_3NO_2 and $CH_3BF_2^{*****}$; our present discussion is confined mainly to this class of molecules. The symmetry selection rules have been given in Sec. A3. In order to apply these rules to the analysis of the microwave spectrum it is necessary to establish some correlation between the symmetry properties and the rotational quantum numbers.

1. Limiting free rotator.—The Hamiltonian and the energy levels were discussed in Sec. 4. Since the quantum number m is diagonal, the wave function can be expressed as a product of $e^{im\alpha}$ and a function of θ , Φ , and χ . This function may be determined from the transformation matrix which diagonalizes the energy matrix in Eq. (4-13). An inspection of the structure of this matrix reveals the fact that a typical wave function has one of the following forms:

$$\Psi_m^{\text{even }K} = e^{im\alpha} \sum_{\text{even }K} a_K S_{JKM}(\theta, \varphi) e^{iK\chi}, \quad (6-4)$$

$$\Psi_m^{\text{odd }K} = e^{im\alpha} \sum_{\text{odd }K} a_K S_{JKM}(\theta, \varphi) e^{iK\chi}, \qquad (6-5)$$

^{*****} Recently $\rm CH_3C\!=\!\rm CCH_2Cl^{53a}$ has been studied and reported to have a low barrier.

where $S_{JKM}(\theta,\varphi)e^{iK\chi}$ denotes the symmetric top wave function and the summation in K in Eqs. (6-4) and (6-5) extends only from -J to J. As explained in Sec. 4, each energy level with $m\neq 0$ is doubly degenerate. This double degeneracy occurs because the energy matrix Eq. (4-13) remains unchanged when m and K are replaced by -m and -K. Now those energy levels where m is a multiple of three (and not zero) are associated with the pairs of symmetry species: A_e , B_{ze} ; A_0 , B_{z0} ; B_{ze} , B_{ye} ; or B_{z0} , B_{y0} . Here each pair constitutes the double degeneracy which would be split by a barrier. Those energy levels where m is not a multiple of three are associated with the symmetry species: E_{1e} , E_{2e} , E_{10} , E_{20} . Here the degeneracy is not split by the barrier.

Consideration of the C_z operation $(\chi \to \chi + \pi)$ shows that the wave function Eq. (6-4) remains unchanged, but the wave function Eq. (6-5) changes sign. For the C_6^3 operation $(\alpha \to \alpha + \pi)$ both Eq. (6-4) and Eq. (6-5) remain unchanged if *m* is even but change sign if *m* is odd. With the aid of the character Table VI, the symmetry properties of the energy levels characterized by different *m* and *K* may be summarized as follows:

$$\begin{array}{ccc} m \left(m \neq 0 \right) & K \\ A_{e}, B_{ze}, E_{1e} & \text{even} & \text{even} \\ B_{xe}, B_{ye}, E_{2e} & \text{even} & \text{odd} \\ A_{0}, B_{z0}, E_{10} & \text{odd} & \text{even} \\ B_{x0}, B_{y0}, E_{20} & \text{odd} & \text{odd} \end{array}$$

The selection rules for m and K are such that the parity is not changed. For the quantum number m the selection rule is even more restricted in the case of free rotation. Since the dipole moment is independent of α and neither wave function Eq. (6-4) nor Eq. (6-5) involve states of different m, we have the selection rule $\Delta m=0$. For the K quantum number, the selection rule is $\Delta K=0, \pm 2,$ ± 4 , etc. Here K is nearly a good quantum number and the transitions with $\Delta K=0$ will in general be stronger than those with $\Delta K=\pm 2, \pm 4$, etc. These latter types of transitions result from a mixing of the K levels in Eqs. (6-4) and (6-5). Note, however, that the Wang functions are no longer the appropriate zero-order wave functions because of the linear term in K on the diagonal of the energy matrix.

The discussion presented above pertains to the energy levels with $m \neq 0$ only. When m=0, the exponential factor $e^{im\alpha}$ in Eqs. (6-4) and (6-5) and also the linear term in K in the energy matrix disappear. The secular equation degenerates into that of a rigid rotor. Since the expressions in Eqs. (6-4) and (6-5) with m=0 are invariant under the operation C_{6^3} and C_3 , the energy levels with m=0 have the symmetry properties of A_{e} , B_{ze} , B_{ye} , or B_{ze} . The selection rules for the transitions with this series of energy levels are identical to those for a rigid asymmetric top, i.e., $A_e \leftrightarrow B_{ze}$ and $B_{ze} \leftrightarrow B_{ye}$.

2. Low barrier.—As explained in Sec. 4, the addition of a small barrier term $\frac{1}{2}V_0(1-\cos6\alpha)$ to the Hamiltonian of a free internal rotor does not greatly alter the spacing of the rotational energy levels except for the ones with m equal to whole multiples of three. The nondiagonal elements in m may be removed by a Van Vleck transformation so that the secular equation can be factored approximately into blocks corresponding to different values of m. The basis functions for this effective energy matrix (for $m \neq 3n$) are then

$$(e^{im\alpha} + ae^{i(m+6)\alpha} + be^{i(m-6)\alpha} + \cdots)S_{JKM}(\theta,\varphi)e^{iK\chi}.$$
 (6-6)

The coefficients a and b do not depend critically on K. The final composite wave functions are taken as linear combinations of such basis functions. The structure of the secular Eq. (4-19) again is such that the basis functions of odd and even K do not combine in forming the final wave function. Furthermore, since the coefficients a, b are usually very small, one may still use m as the labeling index for the energy states. The selection rule for m is Δm equals a whole multiple of 6. Since the $\Delta m \neq 0$ transitions are weak and usually beyond the microwave region, the selection rules for the dipole transitions may be given approximately as $\Delta m = 0$, $\Delta K = 0, \Delta J = 0, \pm 1$. Here again it is assumed that K is nearly a good quantum number. Remembering that each energy level characterized by (m,K) is degenerate with the one by (-m, -K), one may easily show that the selection rules $\Delta m = 6n$ (*n* being an integer) are equivalent to those derived from the symmetry consideration.

For m=3 (or whole multiple of three) the solution of the secular equation becomes more complicated as discussed in Sec. 4 II. As an example the block in the secular equation corresponding to J=1, m=3, odd Kwas given in Eq. (4-21). This secular equation can be factored by choosing as the basis functions the type of linear combination given in Eq. (4-22) i.e.,

$$\psi(K, m=3) \pm \psi(-K, m=-3).$$
 (6-7)

To the zeroth-order approximation these functions may be expressed as

$$e^{3i\alpha}S_{JKM}(\theta,\varphi)e^{iK\chi}\pm e^{-3i\alpha}S_{J-KM}(\theta,\varphi)e^{-iK\chi}.$$
 (6-8)

These two linear combinations have the symmetry property of the A_0 and B_{z0} when K is even; and B_{x0} and B_{y0} for odd K. In the case of the example in Eq. (4-21) the energy eigenfunctions arising from the secular Eq. (4-23a) have the symmetry of B_{z0} while those corresponding to the determinant Eq. (4-23b) belong to A_0 species. The approximate wave functions for these four states are

$$\begin{split} \Psi_{++} &= a [\psi(1,3) + \psi(-1, -3)] \\ &+ b [\psi(-1, 3) + \psi(1, -3)], \\ \Psi_{+-} &= - b [\psi(1,3) + \psi(-1, -3)] \\ &+ a [\psi(-1, 3) + \psi(1, -3)], \\ \Psi_{-+} &= c [\psi(1,3) - \psi(-1, -3)] \\ &+ d [\psi(-1, 3) - \psi(1, -3)], \\ \Psi_{--} &= - d [\psi(1,3) - \psi(-1, -3)] \\ &+ c [\psi(-1, 3) - \psi(1, -3)]. \end{split}$$
(6-9)

Here the first and second number inside the parentheses of the functions refer to the values of K and m, respectively. For CH₃NO₂ the difference between the two diagonal elements in Eq. (4-23a) and Eq. (4-23b) are roughly ten times greater than the off-diagonal terms; so the ratios of the coefficients a, b, c, and d in Eq. (6-9) may be estimated by perturbation methods as $|a/b| \approx |c/d| \approx 10$. One may construct four approximate wave functions similar to Eq. (6-9) for the states with J = 2, m = 3, and odd K. The coefficients a, b, c, etc., here are somewhat different from those in Eq. (6-9), but the ratios of these coefficients are still of the same order of magnitude as those for J=1. In accordance with the symmetry selection rules $A \leftrightarrow B_z$, $B_x \leftrightarrow B_y$, $o \leftrightarrow o, e \leftrightarrow e$, derived previously, there are eight possible transitions for $J=2 \leftarrow 1, m=3$ with odd K. Among these eight lines, four are much more intense than the others, and indeed only the four strong lines are observed in the microwave spectrum. These transitions are

$$\Psi_{++} \leftrightarrow \Psi_{++}, \quad \Psi_{+-} \leftrightarrow \Psi_{+-}, \quad \Psi_{-+} \leftrightarrow \Psi_{-+}, \quad \Psi_{--} \leftrightarrow \Psi_{--}.$$

Similar results are also found in the microwave spectrum of CH_3BF_2 .

The selection rules for the transitions involving the energy levels with m=0, are $A_e \leftrightarrow B_{ze}$, and $B_{xe} \leftrightarrow_{ye}$.

III. Nuclear Spin Weight

To obtain the relative intensities of the components of the internal rotation multiplets (such as the doublet for the high barrier case), the correct combinations of nuclear spin functions ψ_s with the internal torsional function ψ_t must be found. The method for finding such appropriate nuclear spin functions has been given by Wilson.¹¹⁸ This procedure will be applied to the various types of nonsymmetric molecules.

A. Molecules with No Symmetry

By following Wilson,¹¹⁸ we observe that for the protons in the methyl radical, the group of permutation operations which are equivalent to the internal rotations of the molecules is isomorphous with the group C_3 , as is the group derived from the internal rotation operations. For CH₃ there are eight nuclear spin functions which can be schematically represented by specifying the quantum number m_s for each nucleus as follows:

$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	(one)
12	$\frac{1}{2}$	$-\frac{1}{2}$ etc.	(three)
$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$ etc.	(three)
$-\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	(one)

These eight spin functions form a reducible representation of the C_3 group. The characters of this representation are $\chi(E)=8$, $\chi(C_3)=2$, $\chi(C_3^2)=2$. This reducible representation then belongs to the species $4A+2E_1$ $+2E_2$.³⁸ The over-all wave function must be antisymmetric to the interchange of protons, i.e., of species A with respect to the operations of C_3 . Since the nondegenerate torsional function is of species A, the symmetry of the composite wave functions is $A \cdot (4A+2E_1+2E_2)=4A+2E_1+2E_2$; therefore, the statistical weight is four. For the degenerate torsional sublevel the reducible representation formed by the total wave function is $(E_1+E_2) \cdot (4A+2E_1+2E_2)=4A$ $+6E_1+6E_2$. Consequently the members of a torsional doublet (in the case of high barriers) of a particular rotational transition should have equal intensity.

The twenty-seven nuclear spin states for a CD_3 group form a representation of species $11A + 8E_1 + 8E_2$.³⁸ Thus the nondegenerate levels yield $A \cdot (11A + 8E_1 + 8E_2)$ $= 11A + 8E_1 + 8E_2$, whereas the degenerate levels give rise to $(E_1 + E_2) \cdot (11A + 8E_1 + 8E_2) = 16A + 19E_1 + 19E_2$. The relative intensity of the two members of a doublet is therefore 11/16.

This discussion is also applicable to the molecules with a planar frame such as acetaldehyde.

B. CH₃NO₂ Type Molecules

The method outlined in the previous section may also be applied to find the statistical weights of the degenerate and the nondegenerate levels for this type of molecule. When the barrier is low the separation between the nondegenerate level and a degenerate level say between a level with m=0 and one with m=1—is of the order 2Fm which may be comparable to kT. Hence the relative intensity of the various members of the multiplet arising from the internal rotation is not simply equal to the ratio of the statistical weights. Rather, the Boltzmann factor must be taken into consideration.

In addition, for the case of $\text{CH}_2\text{NO}_2^{16}$ the wave function must be even with respect to the interchange of the two oxygen (I=0). This operation is $C_zC_6^3$. Thus, only the levels with symmetry properties of A_e , B_{ze} , E_{1e} , B_{x0} , B_{y0} , E_{20}^{107} can exist in $\text{CH}_3\text{NO}_2^{16}$. For CH_3BF_2 these species will have one-third the statistical weight of the others because of the fluorine nuclear spin $(I=\frac{1}{2})$ and the requirement of antisymmetry for exchange of the two fluorine nuclei.^{121 75}.

7. VIBRATION-TORSION-ROTATION INTERACTION

The methods for the determination of the potential barrier described in Secs. 3 and 5 utilize the splittings between the same rotational transitions corresponding to the two ground torsional levels. These methods, however, fail when the splittings of the rotational lines vanish as in the case of symmetric tops (see Fig. 4) or fall below the limit of resolution of the spectrograph for very high barriers. The latter difficulty may be overcome, at least partially, by measuring the splittings of the rotational lines in the excited torsional levels (satellites) which are considerably larger than those in the ground torsional state. Because of the influence of the molecular vibrations on the internal torsion and the over-all rotation, these satellites are shifted from the "main lines" (the lines associated with the ground torsional state). Furthermore, the splittings of the satellites sometimes contain sizeable contributions from the effect of molecular vibration (cf. Sec. 5 II) as well as the internal rotation. With a careful analysis of the interaction of vibration, torsion, and over-all rotation, it is possible to determine the barrier height either from the splittings of the satellites or from the shifts of the satellites from the main line. The latter procedure is particularly significant because it is applicable to symmetric top molecules.

Besides the frequency shifts, the intensities of the satellites are decreased by the Boltzmann factor. From the intensity ratios between the satellites and the main line, one can calculate the energy differences between the ground and excited torsional states from which the barrier height may be determined.

In the present section two methods—the satellite frequency pattern and the relative intensities—for determining potential barriers are presented. Neither of these methods gives as accurate results as the "splitting method" described in the previous sections. Therefore, these methods are used only when the splitting method fails to yield the barrier height or when an analysis of the torsional satellites is desired to study torsion-rotation interaction.

I. Satellite Frequency Pattern

In the discussion of the theory of internal rotation in Sec. 2 the effects of molecular vibration have not been considered. This is justified if the torsional frequency is well below the frequencies of the other vibrations. Since the moments of inertia do not depend directly on the torsional normal coordinate, the only way the torsional mode can affect the moments of inertia is by means of higher-order interactions via the other vibrations of the molecule.42 When the nonrigidity of the two halves of the molecule is taken into account, some interesting results are obtained. Consider first the symmetric molecules such as methyl silane, CH₃SiH₃. Classically, as the CH₃ group oscillates about its equilibrium position, the centrifugal force produces a slight change in the molecular dimensions. Because both the angular velocity and the potential energy are functions of the internal angles α , the instantaneous configuration of the molecule depends also on α . The rotational constant B determined from the microwave spectra is actually related to the average value of the reciprocal of the moment of inertia for a given torsional and vibrational state. One would expect that the rotational constants and thus the rotational lines associated with the different excited torsional states would be shifted by different amounts (even for the case of a symmetric top). From the pattern of these lines one can then determine the height of the potential barrier. Furthermore, this type of internal torsion-vibration interaction also gives rise to an additional splitting of the pairs of lines associated with the A and E sublevels of a given torsional level; but as shown by Kivelson,⁴² such a splitting for the ground torsional state of CH₃SiH₃ is less than 0.05 Mc which is experimentally unobservable.

The quantum-mechanical treatment can be carried out in this way: The Hamiltonian, including the rotation, internal torsion, and vibration,^{†††††} according to Kivelson,^{42,45b} is written as

$$H = \frac{1}{2} \sum_{ij} \mu_{ij} P_i P_j + H_T + H_v, \tag{7-1}$$

where P_i is the component of the total angular momentum along the *i* principal axis, μ_{ij} is the *ij* component of the inverse of the instantaneous inertia tensor and H_T and H_v represent the part of the Hamiltonian connected with the internal torsion and vibration, respectively. A Van Vleck transformation³⁴ similar to that used by Howard and Wilson¹²⁰ is applied to remove the nondiagonality in the vibrational quantum number v. The results may be expressed approximately as

$$H = W_v + \frac{1}{2} \sum_{ij} (v |\mu_{ij}|v) P_i P_j + (v | H_T | v) + \sum_{v'} (v | \frac{1}{2} \sum_{ij} \mu_{ij} P_i P_j + H_T | v') |^2 (W_v - W_{v'})^{-1}.$$
(7-2)

The first term W_v , the vibrational energy, represents merely an additive constant and can be safely dropped. If only the splittings of the rotational lines in various torsional states are desired, then the terms independent of the rotational quantum numbers can be neglected. Finally, the terms corresponding to the ordinary centrifugal distortion effect can usually be ignored. By using Eq. (7-2) as the Hamiltonian, Kivelson⁴² calculated the effective rotational constant *B* for a symmetric rotor and arrived at the equation

where p' is the angular momentum associated with the torsional motion as defined in Eq. (2-8), B_v is the effective rotational constant averaged over the vibrational functions, and F_v , G_v , and L_v are empirical constants which depend on the interaction of the vibrations and the internal torsion. It is now possible to modify Eq. (7-3) slightly in order to see clearly the difference between this expression and the familiar one for ordinary vibrations. The torsional equation in reduced form is

$$\left[p'^{2} + \frac{9_{s}}{8}(1 - \cos 3\alpha)\right] P_{Kv\sigma} = (9/4)b_{v\sigma}P_{Kv\sigma}.$$
 (7-4)

titt Here the word "vibration" means all the internal modes of motion other than the hindered rotation.

titti Kivelson⁴² used the quantum number *m* for $Kv\sigma$ and Π_2 for $p' = p - \rho P_2$.

In this equation the kinetic and potential energy may be identified

$$\langle T \rangle = (Kv\sigma | p'^2 | Kv\sigma)$$

$$\langle V \rangle = \frac{9s}{8} (Kv\sigma | 1 - \cos 3\alpha | Kv\sigma).$$

For K = 0 Eq. (7-3) becomes

$$B_{v\sigma} = B_v + F_v' \langle V \rangle + G_v \langle T \rangle, \qquad (7-5)$$

where

$$F_v'=8F_v/9s;$$

or

$$B_{v\sigma} = B_v - \beta_1 \langle H \rangle - \beta_2 [\langle T \rangle - \langle V \rangle], \qquad (7-6a)$$

$$=B_{v}-(9/4)\beta_{1}b_{v\sigma}-\beta_{2}x_{v\sigma}, \qquad (7-6b)$$

where

$$\begin{aligned} \beta_1 &= -\frac{1}{2} (G_v + F_v'), \quad x_{v\sigma} &= \langle T \rangle - \langle V \rangle, \\ \beta_2 &= -\frac{1}{2} (G_v - F_v'), \quad \langle H \rangle &= \langle T \rangle + \langle V \rangle = (9/4) b_{v\sigma}. \end{aligned}$$

Now for harmonic vibrations

$$\langle T \rangle = \langle V \rangle,$$

and the asymptotic form for b_v as $s \to \infty$ is $b_v \sim 2(s)^{\frac{1}{2}} \times (v + \frac{1}{2})$. It follows that

$$B_{v\sigma} = B_v - \alpha_T (v + \frac{1}{2}), \qquad (7-7)^{29}$$

where

$$\alpha_T = (9/2)(s)^{\frac{1}{2}}\beta_1.$$

For the $J = 1 \leftarrow 0$ transition of CH₃SiH₃ Kivelson found

$$F_{v} = -65.322 \text{ Mc}$$
 and $G_{v} = -0.8824 \text{ Mc}$,
 $s = 30.22 \ (\alpha = 17.0 = \frac{9}{16}s)$,

and therefore $F_{v}' = -1.9212$ Mc, $\beta_1 = +1.4018$ Mc, $\beta_2 = -0.5194$ Mc, and $\alpha_T = +34.68$ Mc. For an ordinary vibration, the constant α is of the order B_e^2/ω which is ~ 22 Mc. Consequently, we see that this analysis is very similar to that for ordinary vibration rotation interaction; only the extreme departure from harmonicity must be corrected by the β_2 term.

Kivelson's method of analysis has also been extended to include asymmetric molecules^{43,44,45b} and the Stark effect.^{45a} Application of this theory has been made in the study of the vibration-torsion interaction of methyl alcohol,⁷⁷ methyl mercaptan^{49,50a} and propylene oxide²⁷ (cf. Fig. 6).

Hecht and Dennison²¹ have also investigated the nonrigidity effects in methyl alcohol. In addition to the centrifugal stretching, these authors point out that the effect of Coriolis force (from the internal motion) on the distortion of the equilibrium configuration of the molecule should also be considered. While the OH group executes the internal torsion, the Coriolis force arising from the end-over-end rotation of the entire molecule causes the hydrogen atom to rock back and

forth on the COH plane. The effect is to produce a change in the average moments of inertia (over one external revolution) which, analogous to the distortion by centrifugal force described in the beginning of this section, depends on the torsional state. Hecht and Dennison²¹ also take into account the fact that the height of the barrier is a function of the molecular dimension.⁴³ Inasmuch as the origin of the barrier is not clearly understood, the dependence of the barrier height on the displacements of the atoms cannot be calculated in any simple way; it can best be described in a parametric form as

$$V = V_3 \begin{bmatrix} 1 + \sum_i \alpha_i \delta_{q_i} + \cdots \end{bmatrix}$$
(7-8)

where the δ_{q_i} are the displacements of the atoms. A rigorous theoretical treatment which takes into consideration the effects of centrifugal and Coriolis forces on the average rotational constants as well as the change of potential barrier height could become very lengthy because of the large number of normal vibrations which could effect the moments of inertia through Coriolis interaction. Hecht and Dennison²¹ carried out the calculation in two steps. They first examined the interaction between the rotation and the normal vibration in which the O-H bar moves in its own plane relative to the methyl group. In other words, they used a relatively simple model for CH₃OH which has five degrees of freedom-three for over-all rotation, one for internal torsion, and one for the O-H rocking. All the other modes of vibration were considered to be frozen. In the second step the remaining normal vibrations were introduced as perturbation and the effects of these additional terms on the energy levels were investigated with the aid of appropriate approximations. As the vibrational frequencies of methyl alcohol can be obtained from the vibrational spectrum, and the potential barrier height has been determined from the rotational transitions in the ground torsional states, the only parameter that needs to be introduced is the one which describes the variation of the potential barrier height with respect to the vibrational coordinate. Hecht and Dennison²¹ have been able to explain quantitatively some thirty splittings of lines of normal methyl alcohol and five other isotopes using only six empirical parameters.

This treatment can, in principle, be applied to determine the potential barrier of symmetric top molecules for which the methods described previously (PAM and IAM) fail. However, the force constants for most of the symmetric top molecules are usually not known to a sufficient degree of accuracy and therefore it becomes necessary to introduce several empirically determined parameters. A reliable result on the barrier height is obtained only if a sufficiently large number of lines in the excited torsional levels can be observed.

Recently, Swan and Strandberg¹⁰³ reanalyzed the results on methyl alcohol considering vibration rotation interaction more completely. By using the observed

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infrared vibrational spectrum for the normal frequencies they diagonalized the vibration-rotation-internal rotation matrix, i.e., they attempted to calculate the empirical constants F_v , G_v , etc., from the vibrational wave functions. As Hecht and Dennison point out, this procedure can, at present, only be used to verify constants but not calculate good values for them. This is borne out in Swan and Strandberg's results in which the quantitative fit of the calculated frequencies to the observed is only fair. Nevertheless, this type of calculation is valuable, and with improved wave function and energy values a better quantitative agreement on molecules might be obtainable.

II. Intensity Method

The ratio of the intensity (I_1/I_0) of given rotational transitions in the first excited torsional state to the ground torsional state is equal to the relative population in the two torsional states, i.e.,

$$I_1/I_0 = (g_1/g_0)e^{\Delta E_v/kT}, \qquad (7-9)$$

where g_0 and g_1 are the statistical weights of the ground and the excited torsional states and ΔE_r is the difference in energy between these two states. Since the ratio of g_1 and g_0 can be determined from group-theoretical consideration, a measurement of the relative intensities between a rotational line and its satellite gives the torsional frequency which, with the aid of the Mathieu tables,^{36,104} leads to a determination of the potential barrier. Where there are uncertainties as to the ratio of the statistical weights of the two levels, the relative intensity can be measured at several different temperatures.

One of the first molecules studied by this technique was CH_3CF_3 .^{14,72} The barrier heights of a number of other molecules obtained by this procedure are summarized in Table X. The main virtue of the intensity method lies on its simplicity and its applicability to the case of very high barrier in which the splitting between the A and E lines are undetectably small. However, the experimental error involved in the relative intensity measurement is rather large—usually 10 to 20% or even higher. It is therefore not surprising that some of the resulting barrier heights obtained represent little more than estimates.

Baird and Bird² studied the problem of the measurement of relative intensities in the microwave region. They propose a procedure by which one can obtain an improvement in accuracy and reproducibility of the intensity ratio. Unfortunately, their technique or one comparable has generally not been used in the work reported in Table X. Recently, Verdier and Wilson¹¹¹ obtained more refined measurement on the relative intensities for the spectral lines of CH₃CHO and CH₃CH₂F using a Stark-modulated cavity. Their results on the barrier height compare favorably with those obtained by the "splitting methods" (see Table

IX). They point out some limitations of the intensity method.

First, the quantity measured is usually the ratio of the peak absorption heights. The absorption coefficient of a line at its center for a Van Vleck-Weisskopf line shape is given in Eq. $(7-10)^{108}$:

$$\alpha(\nu_0) = (16\pi^3 n_0 |\mu_{mn}|^2 \nu_0 \tau) / 3kcT, \qquad (7-10)$$

where n_0 is the number of molecules per unit volume in the lower level of the transition, μ_{mn} is the matrix element of the dipole moment between the upper and the lower level, and τ is the mean interval between collisions. In order to compare the peak absorption coefficients of two lines ν_0 , μ_{mn} , τ , and T must be the same, otherwise any difference will contribute to a correction term in the intensity ratio. The temperature T will undoubtedly be the same for the two lines. The correction for the difference in ν_0 can be made easily. However, the two are usually so nearly equal that this correction is negligible. The transition moment μ_{mn} may be different, because the asymmetry parameter could change from the ground to the excited state. For certain transitions in nearly symmetric tops, μ_{mn} may be quite sensitive to a small change in the asymmetry parameter and in such case an appropriate correction in Eq. (7-10) should be applied. The variation in τ between torsional levels should normally be within the limit of experimental accuracy.

The second difficulty which might arise is that the A and E lines are not resolved, and yet the separation between these lines is about the same order of magnitude as the line width; the measured peak intensity then does not correspond to Eq. (7-10). For example, it may happen that the A and E lines are resolved in the excited torsional state but overlap (with only one peak) in the ground state. In this case serious error would result if a correction were not applied to the measured intensity ratio. In order to correct for this effect, one can measure the integrated intensity of these lines instead of the peak value. The integrated intensity of the resolved A or E line is then one-half of that of the composite line. Alternatively, if the splitting of the unresolved doublet is calculated from theory, then a relation between the actual and apparent peak absorption can be derived by adding two Van Vleck-Weisskopf shaped lines separated by a frequency equal to the splitting of the doublet.

8. EXPERIMENTAL RESULTS

Table IX gives the experimental values for the barrier heights determined from frequency measurements of the microwave spectra. If more than one value is available in the literature, the best value according to our opinion is reported.§§§§§

^{§§§§§} The major references on each molecule are listed and the one which gave the best value for the barrier as shown in Table IX is underlined.

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TABLE I	\mathbf{X} .	Barriers	by	the	frequency	method.
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Compound	Formula	V (cm ⁻¹)	V (cal/mole)	Method	References
Threefold barriers					
Methyl alcohol	CH3OH	374.8	1070	IAM	8, <u>32</u> , 77
				PAM	98
				nonrigidity	21, 77, 103
				experimental	10, 12, 28,
					30, 109, 110
Methyl amine	CH₃NH₂	691.1	1976	IAM	$\frac{31}{10}, \frac{78}{10}, \frac{79}{10}$
				experimental	28, 56-58
					88-91
	CD_3NH_2	684.7 ± 2	1958	IAM	$\frac{59}{10}, \frac{40}{10}$
Methyl mercaptan	CH ₃ SH	444 ± 10	1270	IAM	49, 50, 35
Acetic acid	CH3COOH	169	483 ± 25	PAM	105
Acetaldehyde	CH3CHO	406	1150 ± 30	PAM	38
Acetal fluoride	CH ₃ COF	378	1080	PAM	80
Acetal chloride	CH3COC1	472	1350	PAM	93
Acetal cyanide	CH3COCN	444	1270 ± 30	PAM	52
Methyl formate	HCOOCH3	416	1190 ± 40	PAM	11b
Ethyl bromide	CH ₃ CH ₂ Br	1248	3567 ± 30	IAM 1st	66a
Ethyl chloride	CH ₃ CH ₂ Cl	1245	3560 ± 12	IAM 1st	66a
Ethyl fluoride	CH ₃ CH ₂ F	1158	3306	PAM 1st	22
1,1 difluoroethane	CH ₃ CHF ₂	1112	3180	PAM 1st	22
Methyl silane	CH ₃ SiH ₃	558 ± 17	1595	nonrigidity	42
		595	1700 ± 100	PAM	39
Methyl fluorosilane	CH ₃ SiH ₂ F	545	1560	PAM	81a
Methyl difluorosilane	CH ₃ SiHF ₂	439	1255	PAM	102
Methyl germane	CH ₃ GeH ₃	433	1239 ± 25	PAM	53a
Methyl allene	$CH_{3}CH = C = CH_{2}$	550 ± 2	1589 ± 0	IAM	03
Propylene	$CH_{3}CH = CH_{2}$	692 ± 6	1978 ± 17	IAM	62
1-fluoropropylene	CH ₃ CH=CHF	752	2150 ± 150	PAM	92
2-fluoropropylene	$CH_3CF = CH_2$	848	2424 ± 25	PAM	81c
Propylene oxide	CH ₃ CH—CH ₂	895 ± 25	2560 ± 70	PAM	$101, \underline{27}$
	\mathbf{b}			IAM	
1-chlorobutyne 2	CH ₂ C≡CCH ₂ Cl	<30	<100		53b
Vinyl silane	CH ₂ CHSiH ₂	523 + 18	1495 ± 50	PAM	81d
Ethyl jodide	CH ₃ CH ₂ I	839	2400	PAM	33c
Sixfold barriers					
Nitromethane	CH ₃ NO ₂	2.11	6.03 ± 0.03	low barrier	106, 107
	CD ₃ NO ₂	1.82	5.19 ± 0.03	low barrier	107
Methyl boron difluoride	CH_3BF_2	4.82	13.77 ± 0.03	low barrier	75
Two threefold barriers					
Acetone	(CH ₃) ₂ CO	266 ± 20	760	PAM	100
Dimethyl ether	(CH ₃) ₂ O	950 ± 50	2720	PAM	33b
Dimethyl silane	(CH ₃) ₂ SiH ₂	582	1665	PAM	81b
Twofold barriers					
Hydrogen perovide	H.O.	113	373	TAM	70 71
Phenol	C.H.OH	1100 - 100	3140		$\frac{70}{50}$ b
I HEHOI		1100 ±100	0110		500

As discussed in Secs. 3, 4, and 5, the ratio V_3/F is determined from the analysis of a microwave spectrum. In general, this ratio can be determined to an accuracy of two percent or better. Uncertainties in the molecular structure and limitations in the approximations are the two main sources of error. The spectra of molecules with lower *s* values are influenced to a much larger extent by the internal rotation and usually these can be analyzed to give somewhat more accurate values for the ratio V_3/F . Structural errors, in regard to the reduced moment of inertia of the methyl group, cause a large share of the error in the barrier. In our opinion, the barrier heights reported in Table IX are accurate to somewhere between 2% and 5%.

The spectra of methyl alcohol and methyl amine have been studied very thoroughly in the microwave region. Furthermore, a considerable amount of work has been done on their theoretical interpretation using the IAM given in Sec. 3. To a lesser extent methyl mercaptan has also been studied. These three molecules are of the class of an intermediate barrier molecule with slight asymmetry. Mainly the perpendicular $(\Delta K = \pm 1)$ Q branch lines $(\Delta J=0)$ have been analyzed for the barrier height. The effects of the asymmetry and the off-diagonal internal rotational matrix elements are calculated by second-order perturbation. Methyl amine has the additional complication of inversion similar to ammonia.

Also the $J = 1 \leftarrow 0$, K = 0 transition has been analyzed for methyl alcohol^{21,77,103} including the effects of nonrigidity. The splittings of the internal rotation doublets are caused by the rigid internal torsion as well as the molecular vibration, but the division between these two effects is not known accurately since it depends rather critically on the structure of the molecule. Slight shifts in the methyl group axis affect this division. With six empirical constants a good agreement between the theory and experiment was obtained for the frequency shifts of the excited states transitions for a number of isotopes of methyl alcohol. Nishikawa⁷⁷ obtained a good fit of the spectrum with only the three symmetric top constants. Attempts have been made¹⁰³ to calculate these "empirical constants" from the vibrational wave functions and qualitative agreement between the calculated and observed values has been obtained.

The results of the barrier height of methyl alcohol and methyl amine obtained by various methods are all in good agreement. However, for methyl mercaptan the situation is somewhat confusing. Intensity work by Solimene and Dailey⁹⁵ gave a value of 371 cm⁻¹. Kilb³⁵ determined a value of 246 cm⁻¹ by rigid hindered theory (PAM to second order) on the $J=1 \leftarrow 0$ transitions of a large number of isotopic species measured by Solimene and Dailey.95 Kojima and Nishikawa first obtained a barrier49 of 280 cm-1, but subsequently they revised their value⁵⁰ to 444 cm⁻¹. Also the $J = 1 \leftarrow 0$ lines of the isotopic species C12H3SH, C13H3SH, C12D3SH, and C¹²H₃SD were analyzed by the symmetric top nonrigidity theory. According to Kojima and Nishikawa the $J=1 \leftarrow 0$ of C¹²H₃SD was incorrectly assigned by Solimene and Dailey. The results of Kojima and Nishikawa⁵⁰ are probably more accurate because their analysis was carried out to a higher order of approximation.

The molecules acetaldehyde (CH₃CHO), acetyl fluoride (CH₃COF), acetyl chloride (CH₃COCl), acetyl cyanide (CH₃COCN), propylene (CH₃CH=CH₂), 1 fluoropropene (CH₃CH=CHF), methyl allene (CH₃CH = C=CH₂), methyl silane (CH₃SiH₃), methyl fluorosilane (CH₃SiFH₂), and methyl difluorosilane (CH₃SiF₂H) are examples of molecules with relatively high barriers. A pseudo-rigid rotor splitting was used to determine the barrier height. In some cases transitions up to J=12were analyzed using the PAM. Also in the near symmetric top molecules the first-order (nonrigid rotor) terms produced a large effect. This was especially true

in acetaldehyde³⁸ (see Sec. 5) and methyl silane, mono-, and di-deuterated.³⁹ Methyl silane has been analyzed by nonrigidity theory⁴² and all of the determined barrier heights agree very well with one another.

The barrier heights in ethyl fluoride,²² 1,1-difluoroethane,²² ethyl chloride,^{66a} and ethyl bromide^{66a} were determined by the splittings in the first excited torsional state since the ground state splittings were too small to observe. To a good approximation the splittings of the satellites of the first excited torsional state are caused entirely by the hindered rotation (but not the molecular vibrations) because of the high barrier.

In propylene oxide²⁷ the barrier was determined by the splittings in the ground and first two excited torsional states. The agreement is exceedingly good indicating the validity of using excited state splittings for the determination of barrier heights in molecules of high barriers. No effects of a V_6 potential were observed.

Acetic acid¹⁰⁵ is a molecule with an intermediate barrier and large asymmetry. Unusual difficulty was encountered in the analysis, but, by using the PAM to fourth order, Tabor was able to assign a number of higher J lines. The assignment was one of the more difficult aspects of this problem. The IAM would have been very difficult to use in this particular case because of the relatively high J transitions necessary for its analysis.

Low barriers have been observed in nitromethane and methyl boron difluoride. Here the m=3 lines give an accurate determination of the barrier height. In the low barrier problem the initial assignment is quite difficult and an extensive searching of the lines is needed. The accuracy of these barrier heights is exceedingly good and generally better than that in the high barrier case. This results from the wide splittings of the order of 1000 Mc as compared with small splittings of a few Mc of the high barrier problems. The very low barrier obtained in these two cases for a sixfold potential seem to indicate that the ratio of V_3 to V_6 is generally of the order of 100. 1-chloro butyne-2 is another molecule with a low barrier which has been recently studied.53b Only an upper limit of the barrier height has been obtained.

The barriers have been determined for a number of molecules by the intensity method of Sec. 7. These are listed in Table X. Generally, an error of 10 to 20% can by assigned to these determined barrier heights. It is interesting to compare some of the results in Table X with the more accurate values of Table IX. Ethyl bromide^{115,116} is 21% low; ethyl chloride^{112,114}, 4.5% low; ethyl fluoride¹¹¹ is in agreement; and 1,1-difluoroethane⁹⁴ is 12% high. By taking into account a 5% error in the values in Table IX, we can see that 10–20% error in the values of Table X is quite realistic.

It is interesting to compare the results of the barrier heights obtained by microwave spectroscopy with those from other means, particularly the thermodynamic methods (see Sec. 1). While detailed examinations of

Compound	Formula	V (cm ⁻¹)	V (cal/mole)	References
Acetaldehvde	CH ₃ CHO	386	1103 ± 60	111
Ethyl bromide	CH ₃ CH ₂ Br	980	2800 ± 500	115, 116
Ethyl chloride	CH ₃ CH ₂ Cl	1190	3400 ± 600	112, 114
Ethyl cyanide	CH ₃ CH ₂ CN	1150 ± 100	3280 ± 290	54
Ethyl fluoride	CH ₃ CH ₂ F	1160	3310 ± 210	111, 51
1,1 Difluoroethane	CH ₃ CHF ₂	1250 ± 200	3570 ± 580	94
1,1,1 Trifluoroethane	CH ₃ CF ₃	1200	3480	14, 72
Methyl mercaptan	CH ₃ SH	371 ± 43	1060 ± 120	95 -
Methyl silane	CH ₃ SiH ₃	460 ± 80	1315	60
Methyl trifluorosilane	CH ₃ SiF ₃	420	1200	72, 73, 87
1 Trifluoro butyne-2	$CH_3 - C \equiv C - CF_3$	<100	<300	$3, 4a, 6\overline{1}$
Isobutane	(CH ₃) ₃ CH	1360	3900	65
t-Butyl fluoride	(CH ₃) ₃ CF	1500	4300	65
Trimethyl phosphine	(CH ₃) ₃ P	910	2600	65
Trimethyl amine	$(CH_3)_3N$	1530	4400	64
Methyl germane	CH ₃ GeH ₃	585	1673	4b

TABLE X. Barriers by the intensity method.

the thermodynamic results are beyond the scope of this paper, it may be stated that the barrier heights determined by the splitting methods are usually more accurate than those obtained from the thermodynamic properties of the molecules. On the other hand, the intensity and thermodynamical methods yield results of comparable accuracy (ten to twenty percent uncertainty). With careful experimental measurements and in favorable cases, this error may be somewhat lower for both of these methods. In the absence of any frequency work on a given molecule, a careful investigation of the specific experimental difficulties is required in order to decide whether the thermodynamic results or the microwave intensity results are more reliable.

In addition to the barrier heights, the equilibrium configuration has been obtained for a number of molecules listed in Table XI. These equilibrium configurations are valuable because they supply additional information which, besides the barrier heights, any theory of the origin of barriers must explain. Ethyl chloride

TABLE XI. Equilibrium configuration.

Compound	Formula	Configuration	Refer- ence
Acetaldehyde	CH2DCHO CHD2CHO	Methyl group eclipses O and staggers H	38
Acetyl chloride	CH2DCOCl CHD2COCl	Methyl group eclipses O and staggers Cl	93
Acetyl cyanide	CH2DCOCN CHD2COCN	Methyl group eclipses O and staggers CN	52
Acetal fluoride	CH2DCOF CHD2COF	Methyl group eclipses O and staggers F	80
Propylene	$CH_2DCH = CH_2$	Methyl group eclipses the double bond and	26
Ethyl chloride	CH ³ D ~CH ³ Cl	staggered	113
Methyl silane	CH ₂ D –SiH ₂ D CH ₂ D –SiHD ₂	staggered	39
Methyl fluorosilane	CH2D-SiH2F	staggered	81a
1,1-Difluorosilane	CH2DSiHF2 CHD2SiHF2	staggered	25c

monodeuterated¹¹³ was the first molecule in which the staggered configuration was confirmed by microwave spectroscopy. The tunneling rate is much slower than the measurement time in the microwave region so the two different configurations are observed : the deuterium gauche and trans to the chlorine atom. Each of these was observed. Even with only an approximate structure these observed rotational constants would be inconsistent with an eclipsed configuration.

Finally, a few molecules have been studied recently with two internal rotors. Although the theory, an extension of the work of Sec. 3, is not covered here [see references 84, 40, 100, and 33(b)], the results on acetone, dimethyl ether, and dimethyl silane are given in Table IX. The theory of internal rotation for molecules with an asymmetric internal rotor is not covered in this review, but two molecules, hydrogen peroxide,⁷⁰ and phenol,^{50b} have been studied and analyzed approximately as a symmetric top. References 6, 9, and 86 give some of the theoretical work.

9. CONCLUSIONS

After the various discussions on the interactions of internal rotation and over-all rotation, one naturally questions what causes these potential barriers and whether the values reported in Sec. 8 can be explained quantitatively in terms of the electronic structure of the molecules. Furthermore, can unknown barrier heights be predicted satisfactorily? Numerous attempts have been made (see Bibliography—Theoretical and Empirical Methods of Barrier Height Estimation) to provide answers to these questions, but the results do not seem very encouraging. This is understandable since the potential barrier represents only a very small fraction of the binding energy of the molecule. It seems highly impractical at this time to make any serious attempt to evaluate the barrier heights by the direct and rigorous approach, i.e., from the difference in energy of the entire molecule for the two extreme configurations corresponding to the eclipsed form ($\alpha = 60^{\circ}$) and the staggered form ($\alpha = 0^{\circ}$).

In order to offer a simple picture for the nature of the hindering potential, various mechanisms such as Van der Waals forces,^{012,016} direct electrostatic interactions,^{03,010,013} overlap, and exchange force,⁰¹⁴ have been proposed for the intramolecular interaction. Recently, Wilson^{017,018} has made a critical examination of these various hypotheses and found that none of the existing theories can account for the experimental results of the barrier heights of the various molecules. He⁰¹⁷ suggests that the potential barrier could be an inherent property of the axial bond itself and that it is is not due to the direct forces between the attached atoms to any great extent or to the electronic distribution in the attached bonds which are at any considerable distance. Pauling,⁰¹⁴ on the other hand, hypothesizes that exchange interactions of the electrons in the attached bonds, as determined by the overlap of these attached bonds which extend in the direction of the axial bond toward one another, are responsible for the potential barrier. By the use of higher orbitals, d and f, he makes a rough estimate of this nonbonding interaction which is in the right order of magnitude for the observed potential barriers. Although the absolute values are only fortuitous, a number of interesting relative values are presented. From his hypothesis, unshared electron pairs, which do not hybridize with the f orbitals, would not contribute to the potential barrier, i.e., methyl alcohol would have a barrier approximately one-third of that in ethane and methyl amine would have a barrier approximately two-thirds of that of ethane. Another interesting point is the existence of the very low barriers in molecules such as nitromethane. A sixfold barrier would require i orbitals with an azimuthal quantum number l=6. Because of the large promotional energy these probably would not contribute much to the hybrid bond orbitals and hence we would predict a low barrier.

Which of these various mechanisms, or combination of mechanisms, correctly accounts for the potential barriers measured in molecules is still unanswered. It is hoped that this review will stimulate further research toward the understanding of the origin of the potential energy hindering internal rotation. Nevertheless, from the viewpoint of molecular dynamics, the problem of internal rotation in molecules, i.e., the effect of the internal rotation on the energy levels, is quite well understood. The agreement between the theory and the observed spectra, including all the fine details, is particularly outstanding. Furthermore, the study of the microwave spectra offers a method, which is by far the most accurate at the present time, for determining the height and the shape of the hindering barrier.

APPENDIX 1

Derivation of Kinetic Energy and Angular Momentum

In Fig. 9, O and C represent, respectively, the center of mass of the entire molecule and of the top alone. Two vectors \mathbf{r}_i and $\boldsymbol{\sigma}_j$ are drawn to a typical atom in the top from the respective centers of mass O and C. The position vector (with O as origin) for an atom in the framework will be denoted by \mathbf{r}_i . If $\boldsymbol{\varrho}$ denotes the vector from O to C, one can readily see that

$$\sigma_j = \varrho + \sigma_j. \tag{A1-1}$$

The kinetic energy can be written as

$$T = \frac{1}{2} \sum_{i} m_{i} (\partial \mathbf{r}_{i} / \partial t) \cdot (\partial \mathbf{r}_{i} / \partial t) + \frac{1}{2} \sum_{j} m_{j} (\partial \mathbf{r}_{j} / \partial t) \cdot (\partial \mathbf{r}_{j} / \partial t).$$
(A1-2)

By remembering that

$$(\partial \mathbf{r}_i/\partial t) = \omega \times \mathbf{r}_i, \quad (\partial \mathbf{r}_j/\partial t) = \omega \times \mathbf{r}_j + (\partial \alpha/\partial t) \times \boldsymbol{\sigma}_j,$$

where ω is the angular velocity of the over-all rotation of the molecule, one can rewrite (A1-2) in the form of

$$T = \frac{1}{2} \sum_{i} m_{i} (\boldsymbol{\omega} \times \mathbf{r}_{i})^{2} + \frac{1}{2} \sum_{j} m_{j} [(\boldsymbol{\omega} \times \mathbf{r}_{j}) + (\partial \alpha / \partial t \times \boldsymbol{\sigma}_{j})]^{2}$$

$$= \frac{1}{2} \sum_{i} m_{i} [\boldsymbol{r}_{i}^{2} \omega^{2} - (\boldsymbol{\omega} \cdot \mathbf{r}_{i})^{2}] + \frac{1}{2} \sum_{j} m_{j} [\boldsymbol{r}_{j}^{2} \omega^{2} - (\boldsymbol{\omega} \cdot \mathbf{r}_{j})^{2}]$$

$$+ \frac{1}{2} \sum_{j} m_{j} [\boldsymbol{\sigma}_{j}^{2} \dot{\boldsymbol{\alpha}}^{2} - (\boldsymbol{\sigma}_{j} \cdot \partial \alpha / \partial t)^{2}]$$

$$+ \sum_{j} m_{j} (\boldsymbol{\omega} \times \mathbf{r}_{j}) \cdot (\partial \alpha / \partial t \times \boldsymbol{\sigma}_{j}). \quad (A1-3)$$

The first two terms obviously represent the kinetic energy of the over-all rigid rotation of the molecule with angular velocity $\boldsymbol{\omega}$, and can be written as $\frac{1}{2}\boldsymbol{\omega}^+ \cdot \mathbf{I} \cdot \boldsymbol{\omega}$ where \mathbf{I} is the usual inertia tensor of the entire molecule. The third term may be expressed as $\frac{1}{2}I_{\alpha}\dot{\alpha}^2$ where I_{α} is the moment of inertia of the top about its own axis of symmetry. The last term may be simplified as

$$\begin{split} \sum_{j} m_{j}(\boldsymbol{\omega} \times \mathbf{r}_{j}) \cdot (\partial \alpha / \partial t \times \boldsymbol{\sigma}_{j}) \\ &= \sum_{j} m_{j} \{ \left[(\boldsymbol{\varrho} + \boldsymbol{\sigma}_{j}) \cdot \boldsymbol{\sigma}_{j} \right] (\boldsymbol{\omega} \cdot \partial \alpha / \partial t) \\ &- (\boldsymbol{\omega} \cdot \boldsymbol{\sigma}_{j}) \left[(\boldsymbol{\varrho} + \boldsymbol{\sigma}_{j}) (\partial \alpha / \partial t) \right] \} \\ &= \sum_{j} m_{j} \left[\sigma_{j}^{2} (\boldsymbol{\omega} \cdot \partial \alpha / \partial t) - (\boldsymbol{\omega} \cdot \boldsymbol{\sigma}_{j}) (\boldsymbol{\sigma}_{j} \cdot \partial \alpha / \partial t) \right]. \quad (A1-4) \end{split}$$

FIG. 9. The position vectors of typical atoms in a molecule with an attached internal rotor. The O position and C position represent the centers of mass of the whole molecule and the internal rotor, respectively. The vectors \mathbf{r}_i and \mathbf{r}_i are vectors from the center of mass O to typical atoms in the frame of the molecule and the internal rotor.



The last step follows from the relation

$$\sum_{j} m_{j} \sigma_{j} = 0.$$

By using a coordinate system attached to the top with the z axis along the axis of symmetry, and the origin located at the center of mass of the top, one has

and

$$\sum_{j} m_{j} x_{j} z_{j} = \sum_{j} m_{j} y_{j} z_{j} = 0.$$

 $\boldsymbol{\sigma}_{j} = x_{j} \hat{\boldsymbol{\imath}} + y_{j} \hat{\boldsymbol{\jmath}} + z_{j} \hat{\boldsymbol{k}},$

Equation (A1-4) then takes the form of

$$\sum_{j} m_{j} [(x_{j}^{2}+y_{j}^{2}+z_{j}^{2})(\omega \cdot \partial \alpha/\partial t) -(\omega_{x}x_{j}+\omega_{y}y_{j}+\omega_{z}z_{j})z_{j}|\partial \alpha/\partial t|] =\sum_{j} m_{j} [(x_{j}^{2}+y_{j}^{2}+z_{j}^{2})(\omega \cdot \partial \alpha/\partial t)-\omega_{z}z_{j}^{2}|\partial \alpha/\partial t|] =\sum_{j} m_{j}(x_{j}^{2}+y_{j}^{2})(\omega \cdot \partial \alpha/\partial t)=I_{\alpha}(\omega \cdot \partial \alpha/\partial t).$$

The kinetic energy finally becomes

$$T = \frac{1}{2}\omega^{+} \cdot \mathbf{I} \cdot \omega + \frac{1}{2}I_{\alpha}\dot{\alpha}^{2} + I_{\alpha}(\omega \cdot \partial \alpha/\partial t). \quad (A1-5)$$

The classical angular momentum is given by

$$\mathbf{P} = \sum_{i} m_{i} (\mathbf{r}_{i} \times \partial \mathbf{r}_{i} / \partial t) + \sum_{j} m_{j} (\mathbf{r}_{j} \times \partial \mathbf{r}_{j} / \partial t)$$

$$= \sum_{i} m_{i} [\mathbf{r}_{i} \times (\boldsymbol{\omega} \times \mathbf{r}_{i})]$$

$$+ \sum_{j} m_{j} [\mathbf{r}_{j} \times \{ (\boldsymbol{\omega} \times \mathbf{r}_{j}) + (\partial \boldsymbol{\alpha} / \partial t \times \boldsymbol{\sigma}_{j}) \}]$$

$$= \sum_{i} m_{i} [\mathbf{r}_{i} \times (\boldsymbol{\omega} \times \mathbf{r}_{i})] + \sum_{j} m_{j} [\mathbf{r}_{j} \times (\boldsymbol{\omega} \times \mathbf{r}_{j})]$$

$$+ \sum_{j} m_{j} [\mathbf{r}_{j} \times (\partial \boldsymbol{\alpha} / \partial t \times \boldsymbol{\sigma}_{j})]. \quad (A1-6)$$

The first two terms stand for the angular momentum of the over-all rigid rotation of the entire molecule which can be written as $\mathbf{I} \cdot \boldsymbol{\omega}$. In order to simplify the last term, use is made of the fact that $\boldsymbol{\sigma}_j$ is a vector measured from the center of mass of the top and that the axis of the top is a principal axis of the top. It follows that

$$\sum m_{j} [\mathbf{r}_{j} \times (\partial \alpha / \partial t \times \sigma_{j})] = \sum m_{j} [(\mathbf{\varrho} + \sigma_{j}) \times (\partial \alpha / \partial t \times \sigma_{j})] = \sum m_{j} [\mathbf{\sigma}_{j} \times (\partial \alpha / \partial t \times \sigma_{j})] = \sum m_{j} [\mathbf{\sigma}_{j}^{2} \partial \alpha / \partial t - (\mathbf{\sigma}_{j} \cdot \partial \alpha / \partial t) \mathbf{\sigma}_{j}] = \sum m_{j} [\mathbf{\sigma}_{j}^{2} \hat{k} |\partial \alpha / \partial t| - z_{j}^{2} \hat{k} |\partial \alpha / \partial t|] = I_{\alpha} \partial \alpha / \partial t$$

Equation (A1-6) then reduces to

$$\mathbf{P} = \mathbf{I} \cdot \boldsymbol{\omega} + I_{\alpha} \partial \alpha / \partial t.$$

APPENDIX 2

Continued Fraction

The substitution of Eq. (3-9) or Eq. (3-23) into Eq. (3-3) or Eq. (3-16), followed by the multiplication by $e^{-i(3k+\sigma)\alpha}$ and integration leads to a recursion formula among the A's:

$$A_{3(k-1)+\sigma} + (\lambda - M_k) A_{3k+\sigma} + A_{3(k+1)+\sigma} = 0,$$
 (A2-1)

where

$$\lambda = \frac{4}{s} \left(b - \frac{s}{2} \right)$$
 and $M_k = \frac{16}{9s} (3k + \sigma)^2$.

This defines an infinite set of homogeneous equations. In order to have a nontrivial solution it is necessary that the determinant of the coefficients vanish. This infinite determinant can be factored into 3 different subdeterminants, one for each σ value. Koehler and Dennison⁴⁸ have shown that Eq. (A2-1) leads to a continued fraction. This can easily be seen by dividing the recursion relation Eq. (A2-1) by $A_{3k+\sigma}$:

$$\frac{A_{3(k+1)+\sigma}}{A_{3k+\sigma}} = (M_k - \lambda) - \frac{A_{3(k-1)+\sigma}}{A_{3k+\sigma}}, \qquad (A2-2)$$

and inverting

$$A_{3k+\sigma}$$

 $A_{3(k+1)+\sigma}$

$$= \frac{1}{M_{k} - \lambda - \frac{A_{3(k-1)+\sigma}}{A_{3k+\sigma}}} = \frac{1}{M_{k} - \lambda - \frac{1}{M_{k-1} - \lambda - \dots}} = G_{k}^{-1}$$

also
$$\frac{A_{3k+\sigma}}{A_{3(k-1)+\sigma}} = \frac{1}{M_{k} - \lambda - \frac{1}{M_{k+1} - \lambda - \dots}} = G_{k}^{+}.$$

By substituting back into Eq. (A2-1), one obtains a continued fraction equation,

$$\lambda = M_k - G_{k+1} - G_{k-1}. \tag{A2-3}$$

A trial value of λ is substituted into G^+ and G^- leading to a first approximation of λ . By successive iteration a consistent value of the eigenvalue, λ , is obtained. The continued fraction does not always converge very rapidly and can even diverge. The use of a Newton Raphson approximation⁶⁹ is recommended to avoid this difficulty. By letting

$$f(\lambda) = M_k - \lambda - G_{k+1} + (\lambda) - G_{k-1} - (\lambda) = 0,$$

and expanding at the *n*th approximation of the eigenvalue (denoted by λ^n), one obtains

$$f(\lambda) = f(\lambda^n) + (\lambda - \lambda^n) f'(\lambda^n)$$

= $\lambda^{n+1} - \lambda^n + (\lambda - \lambda^n) f'(\lambda^n) = 0.$

 $\lambda = \lambda^n + \frac{\lambda^{n+1} - \lambda^n}{-f'(\lambda^n)}, \qquad (A2-4)$

where

Then

$$-f'(\lambda^{n}) = 1 + G_{k+1}^{+2} [1 + G_{k+2}^{+2}(1 + \cdots)] + G_{k-1}^{-2} [1 + G_{k-2}^{-2}(1 + \cdots)].$$

Since the G's are determined in the calculation of the eigenvalue, the derivative $f'(\lambda^n)$ is readily calculated. Care must also be taken to insure that the initial approximation is not separated from the desired eigenvalue by a pole. A pole occurs between each eigenvalue by a pole.

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value. If one exists between the first approximation and the desired root, the continued fraction converges to the adjacent root.

With the desired eigenvalue determined, a substitution into Eq. (A2-1) leads to a recursion relation between the A's. By solving these relations and normalizing, one obtains the eigenfunctions. These eigenfunctions are used to determine the matrix elements and integrals for the IAM and PAM if the approximations given are not sufficiently accurate. The eigenfunctions are tabulated for the periodic solutions.^{104,37} For the nonperiodic solutions σ is replaced by $\sigma + \rho K$ in all the previous expressions.

APPENDIX 3

Tabulations Related to Mathieu Equations

The most recent and complete tabulations are listed in Table XII. References 36 and 104 are the most useful

TABLE XII. Mathieu function tabulations.

Reference	Period in x	Range in V	Range in s	Accuracy
Mathieu Functions ^{a.o}	π, 2π	0(1)8 9(1)14	0(1)100 ^b 0(2)100	1×10-8
Kilbe, d, e	3π	0(1)5	2(1)30(2)52(4)100	1 × 10 ⁻¹⁰
Stejskalf	$\pi \cdot 3\pi$	0(1)4	100(15)205	1 X10-7
Blanch and Rhodes ^g	π, 2π	0(1)15	100 ^h	1 × 10 ⁻⁸
Pexton ⁱ	4π	0(1)9	1(1)40	1 ×10 ⁻⁶

a See reference 104.
b A close tabulation is given for the low s values.
a Eigenfunctions are also tabulated.
d Copies are available from E. B. Wilson, Jr., Department of Chemistry, Harvard University. Herschbach's tables are also available.
a See reference 36.
see reference 96.

See reference 5.

^b Tabulated in terms of $t \ 0\ (0.002)\ 0.1$ where $s = 1/t^2$. ⁱ Tabulated in Li and Pitzer reference 55. Notation: $4\theta = s, \ \theta_0 = b - \frac{1}{2}s$.

and complete for the threefold potential case. Also, by the use of Eq. (3-29) and these tables, the eigenvalues for s > 30 for other periodicities can readily be determined. A number of older references are given in reference 104.

Recently, Herschbach²³ tabulated the matrix elements $p, p^2, p^3, \cos 6\alpha$, the perturbation sums to fourth order for use in the PAM, and the Fourier coefficients for use in the IAM.^{25b} Herschbach gives a complete introduction explaining the use of the tables to solve the internal rotation problem. These tables are of great assistance in the computation for barrier problems.

APPENDIX 4

Notation

a	IAM "a" coordinate axis	Į
a, a_K	expansion coefficients	į
a, a'	low barrier diagonal elements $ m = 3$	
a_k	Fourier coefficient in potential energy	(
a_n	Fourier coefficient in IAM internal	
	energy	(
amu	atomic mass units	1

A	symmetry species in C_3 group
$A, A_a, A_{v\sigma}, A_x$	rotational constants
$A_{3k+\sigma}^{v}, A_{3k+\sigma}^{Kv}$	wave function expansion coefficients
А	Angstrom unit
b	IAM "b" coordinate axis
b	expansion coefficients
b	low barrier off-diagonal element $ m = 3$
$b, be, bo, b_i, b(N\pi)$	Mathieu eigenvalues
$B, B_b, B_{v\sigma}, B_y$	rotational constants
B_{e}	equilibrium rotational constants
B, B_x, B_y, B_z	symmetry species
С	IAM "c" coordinate axis
Ck	Fourier coefficient of Mathieu's func- tion
$C, C_c, C_{v\sigma}, C_z$	rotational constants
C_2, C_3, C_6, C_x	rotational symmetry operations
d	reducing factor, r , times $(I_x I_y I_z)$
d_k	Fourier coefficient of Mathieu's func- tion
d_{XY}	interatomic distance from atom X to atom Y
D_{bc}, D_{ij}	Hamiltonian cross terms between
	components of the total angular momentum
De, Do	Fourier coefficients of Mathieu's function
$D^{J}(\beta)_{KpK}$	rotational transformation matrix element
E	symmetry species, degenerate
E	energy
$E(\kappa)$	reduced rigid rotor energy
E_{JKM}	rotational energy
$E_{v\sigma}, E_{Kv\sigma}$	torsional energy: PAM and IAM
$E(JKMv\sigma)$	total energy: rotation and torsion
f	Mathieu parameter (Floquet's theo- rem)
f(x)	IAM approximate integral function
$f(\lambda)$	continued fraction function of the λ eigenvalue
F	reduced rotational constant of the internal rotor
F_v	nonrigidity potential energy expan- sion coefficient
g_0, g_1	statistical weight factors
g ⁺ , g ⁻	correction terms in the PAM rota- tional energy
G_v	nonrigidity kinetic energy expansion coefficient
G_k^+, G_k^-	continued fraction terms
ħ	Planck's constant divided by 2π

H, H_0	Hamiltonian	$\mathbf{r}_{i,i}, \mathbf{r}_{j}$	position vector of the i th (j) atom
H_{IR}	coupling term in Hamiltonian	$r_a, r_b, r_c, r_x, r_y, r_z$	position vector components
H_R	rotational Hamiltonian	S	reduced barrier height
H_T	torsional Hamiltonian	S_1	rotational transformation matrix
H_{v}	vibration Hamiltonian, harmonic os-	S_2	asymmetric transformation matirx
	cillator function	Se, So	Mathieu functions
H_1	asymmetry term in Hamiltonian	$S_{JKM}(heta,arphi)e^{iKoldsymbol{\chi}}$	symmetric rotor function
$H_{v\sigma}$	rotational Hamiltonian for the $v\sigma$	Т	kinetic energy
	torsion state	Т	temperature
î	unit vector	$U_{\boldsymbol{v}\boldsymbol{\sigma}}(\boldsymbol{\alpha})$	PAM torsional function
Ι	moment of inertia tensor	v	torsional quantum number
$I_a, I_b, I_c, I_{aa}, I_{bb}$	moments of inertia	$V(\alpha), V_N, V_3, V_6,$	V_{12} potential energy (subscript de-
$I_{cc}, I_g, I_x, I_y, I_z, I$, jk		notes periodicity)
Ια	moment of inertia of the internal	$W_{v\sigma}^{(n)}$	PAM perturbation terms
	rotor about its symmetry axis	W, W_r	rigid rotor energy
I_{bc}, I_{jk}	products of inertia	x	x principal axis
ĵ	unit vector	$x_{v\sigma}$	nonrigidity term
J	quantum number of the total angular	ν	y principal axis
	momentum	z	z principal axis
k	Boltzmann's constant	α	internal angle
ĥ	unit vector	α	direction cosine of \mathbf{o} to \mathbf{z} principal
k^{+}, k^{-}	correction terms in the PAM rota-		axis
	tional energy	ά	internal angular velocity
K	quantum number of the total angular momentum along the molecular z axis	α_t, α_i	first term in the vibration rotation ex-
l	free rotation quantum number	Q	direction agains of a to u principal
L_v	nonrigidity angular momentum ex-	β	axis
***	free rotation quantum number	eta_1,eta_2	nonrigidity expansion terms
m m	mass of the <i>i</i> th atom	Δ_0	IAM splitting of internal sublevels
M	quantum number of the total angular		for $K = 0$
111	momentum along the space axis	Δ_K	IAM splitting of internal sublevels for Kth level
$M_{Kv\sigma}(\alpha)$	IAM nonperiodic torsional function	ΔE_{JK}	internal rotational splitting of the
M(x)	Mathieu function		J, K rotational level
Mc	megacycles/second	$\Delta E(J_{K-1}K_{+1})$	internal rotational splitting of the
M_k	continued fraction term		$J\kappa_{-1}\kappa_{+1}$ rotational level
N	periodicity of the hindering potential	δ_{Asy}	asymmetry splitting of K and $-K$
Þ	internal angular momentum		rotational levels
Pvo, v'o	PAM matrix element of the internal angular momentum	ðκ	nonrigid-rotor internal rotor split-
$P_a(P_a, P_b, P_c, P_i, P_i)$	$_{k}, P_{x}, P_{y}, P_{z}$) the gth components of the	$\delta_{K'v'\sigma}^{Kv\sigma}$	IAM integrals
	angular momentum	δq_i	displacement coordinate
P_{a}^{ij}	the gth component of the total angu-	θ	Eulerian angle
•	lar momentum with the independent	κ	asymmetry parameter
	variables i and j constant	λ	eigenvalue of a secular determinant
$P_{Kv\sigma}(\alpha)$	IAM torsional function for a sym- metric molecule	$\lambda_{g}, (\lambda_{x}, \lambda_{y}, \lambda_{z})$	direction cosine of the internal rotor to the g principal axis
O_i	PAM Hamiltonian term	μ_{mn}	dipole matrix element
$O_{K_{n\sigma}}(\alpha)$	IAM torsional function for an asym-	ν	frequency
C	metric molecule	П	dot product of the total angular mo-
r	reducing factor		mentum vector and the vector p

0	(a) direction of the internal axis such that the internal angular momentum vanishes	σ_j	position vector of a top atom from the center of mass of the top (in- ternal rotor)
ρ _a σ	(b) position vector of the center of mass of the top from the center of mass of the whole molecule (Ap- pendix 1) component of ϱ along the g axis torsional sublevel quantum number	au $arphi, \Phi$ $\chi, \chi_1, \chi_2, \chi'$ Ψ, ψ ω $\omega_g (\omega_a, \omega_b, \omega_c, \omega_x, \omega_z)$	mean life time Eulerian angles Eulerian angles wave function total angular velocity vector v_y, ω_z) component of the total angular velocity along the g axis

APPENDIX 5	
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Comparison of the Notation of Various Authors (Grouped Where Possible)

Present notation	A	Ь	٥	d
Ig, Iij	A, B, C, C_1, D	I_{xx}, I_{yy}, I_{zz}	A, B, C, C_1, I_{jk}	I_x, I_y, I_z
Ια	C_2	I_1	C_2	Iα
ρ	$(C_2/C)^*$	•••	λ	(ρ)
	$(BC_1 - D^2)$		$(BC_1 - D^2)$	
ť	$(BC-D^2)$	•••	$(BC-D^2)$	r, d
σ	τ^{e}	•••	μ	σ(A,E), к
m	k	k_1	• • •	m
$w_{v\sigma}^{(1)}$	• • •	•••	•••	$-2p_{vv}$
$w_{v\sigma}^{(2)}$	•••		•••	$1+4F\rho$
$E_{Kv\sigma}, E_{v\sigma}$	$E_{K\tau n}$	•••	$E^{K_{\mu n}}$	Err
$\Delta E(J\kappa_{-1}\kappa_{+1})$	$(J\kappa_{-1}\kappa_{+1}), K$	•••	•••	$\Delta A, \Delta W$
Pg	P_{g}	J_{g}	P_{g}	P_{g}
Þ	p_x	L_1	P	Þ
α	x	φ	x	α
ρ_y/ρ	$\sin\!\beta \sim\! \beta$	•••	λ_{η}/λ	
S	H'	•••	α	S
$M_{Kv\sigma}(\alpha), P_{Kv\sigma}(\alpha),$				
$Q_{Kv\sigma}(\alpha), U_{v\sigma}(\alpha)$	$P_{Krn}(x)$	•••	$Q^{K\mu n}$	$U_{\boldsymbol{v}\boldsymbol{\sigma}}(\alpha)$
υ	n	•••	n	v

Dennison, Koehler, Burkhard, Ivash, Hecht, Lide, and Mann.
 Gwinn, Myers, and Tannenbaum.
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^d Wilson, Lin, Lide, Kilb, Swalen, and Herschbach. • $[K+\tau-\sigma=1 \pmod{3}].$

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SUBJECT^a

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75		TX	CH ₃ BF ₂
76		T	IAM sym.
77		T	CH ₃ OH IAM nonrigidity
78		TX	CH ₃ NH ₂ IAM
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80		TX	CH ₃ COF PAM
81s		TX	CH ₃ SiH ₂ F PAM
81b		TX	(CH ₃) ₂ SiH ₂
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82		T	Asymasym.
83		Review	v
84		T	IAM
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86 87 88 89 90	 Donna Price, J. Chem. Phys. 9, 807 (1941); 10, 80 (1942). J. Sheridan and W. Gordy, J. Chem. Phys. 19, 965 (1951). K. Shimoda and T. Nishikawa, J. Phys. Soc. Japan 8, 133 (1953). K. Shimoda and T. Nishikawa, J. Phys. Soc. Japan 8, 425 (1953). Shimoda, Nishikawa, and Itoh, J. Phys. Soc. Japan 9, 974 (1954). 	T XI X X X X	Asymasym. CH ₃ SiF ₃ CH ₃ NH ₂ CH ₃ NH ₂ CH ₃ NH ₂
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92		X	$CH_3CHCHF PAM$
93		TX	$CH_3COCI PAM$
94		X	CH_3CHF_2 intensity
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97		T	Microwave spectroscopy
98		T	CH ₃ OH PAM
99		T	Approx formula PAM
100		TX	(CH ₃) ₂ CO PAM
101 102	 J. D. Swalen and D. R. Herschbach, J. Chem. Phys. 27, 100 (1957). J. D. Swalen and B. P. Stoicheff, J. Chem. Phys. 28, 671 (1958). 	TX TX	CH ₃ CH–CH ₂ PAM O CH ₃ SiHF ₂ PAM
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104		T	Mathieu
105		TX	CH ₃ COOH PAM
106		TX	CH ₃ NO ₂
107		TX	CH ₂ NO ₂
108 109 110 111	 C. H. Townes and A. L. Schawlow, <i>Microwave Spectroscopy</i> (McGraw-Hill Book Company, Inc., New York, 1955). Venkateswarlu, Edwards, and Gordy, J. Chem. Phys. 23, 1195 (1955). P. Venkateswarlu and W. Gordy, J. Chem. Phys. 23, 1200 (1955). P. H. Verdier and F. B. Wilson, J. L. Chem. Phys. 29, 340 (1058). 	T X X TVI	Microwave spectroscopy CH ₂ OH CH ₂ OH
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115		XI	CH ₃ CH ₂ Br
116		XI	CH ₃ CH ₂ Br
117		T	Group theory
118		T	Symmetry
119 120 121	 E. B. Wilson, Jr., Chem. Revs. 27, 17 (1940). E. B. Wilson, Jr. and J. B. Howard, J. Chem. Phys. 4, 260 (1936). Wilson, Lin, and Lide, J. Chem. Phys. 23, 136 (1955). 	T T T	PAM Mathieu Vibration rotation interaction PAM

^a T, theoretical paper; X, experimental paper; I, intensity method.

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