to the prescription

$$\sum_{\text{spins of 1 and 2}} (u_1{}^*O_1u_2)(u_2{}^*O_2u_1)$$

$$=\tfrac{1}{4}\ \text{trace}\ O_2\left(1+\frac{1}{c}\boldsymbol{\alpha}\cdot\mathbf{v}_1+\beta\frac{m_1c^2}{E_1}\right)$$

$$\times O_1\left(1+\frac{1}{c}\boldsymbol{\alpha}\cdot\mathbf{v}_2+\beta\frac{m_2c^2}{E_2}\right).$$

The indices 1 and 2 refer to the electron and neutrino and u, $\mathbf{v}$, m, E are, respectively, the four-component Dirac amplitude, velocity, mass and energy of the corresponding particle. O_1 and O_2 can be any operators of the Dirac type, $\boldsymbol{\alpha}$, β, $\boldsymbol{\sigma}$ or any product. The trace vanishes for odd powers of any Dirac operators and is 4 for a constant.

Using the commutation rules for α, β we find

$$\sum|u_1{}^*u_2|^2=1+\frac{\mathbf{v}_1\cdot\mathbf{v}_2}{c^2}+\frac{m_1m_2c^4}{E_1E_2},$$

$$\sum|u_1{}^*\beta u_2|^2=1-\frac{\mathbf{v}_1\cdot\mathbf{v}_2}{c^2}+\frac{m_1m_2c^4}{E_1E_2},$$

$$\sum|u_1{}^*\alpha_xu_2|^2=1+\frac{2v_{1x}v_{2x}-\mathbf{v}_1\cdot\mathbf{v}_2}{c^2}-\frac{m_1m_2c^4}{E_1E_2},$$

$$\sum|\sigma_x|^2=1+\frac{2v_{1x}v_{2x}-\mathbf{v}_1\cdot\mathbf{v}_2}{c^2}+\frac{m_1m_2c^4}{E_1E_2},$$

$$\sum|\beta\alpha_x|^2=1-\frac{2v_{1x}v_{2x}-\mathbf{v}_1\cdot\mathbf{v}_2}{c^2}-\frac{m_1m_2c^4}{E_1E_2},$$

$$\sum|\beta\sigma_x|^2=1-\frac{2v_{1x}v_{2x}-\mathbf{v}_1\cdot\mathbf{v}_2}{c^2}+\frac{m_1m_2c^4}{E_1E_2}.$$

The mass terms are zero when the neutrino mass is assumed to be zero. For the decay of the meson, electron and neutrino have velocities $\sim c$ in opposite directions, therefore $\mathbf{v}_1\cdot\mathbf{v}_2/c^2=-1$; and in averaging over all directions $v_{1x}v_{2x}/c^2=-1/3$. For the β-decay there is no correlation between the direction of electron and neutrino velocities and all products $\mathbf{v}_1\cdot\mathbf{v}_2$ and $v_{1x}v_{2x}$ are zero in the directional average. All sums give 1 therefore for β-decay.

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Hindered Rotation in Methyl Alcohol

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The problem of hindered rotation in methyl alcohol is discussed in relation to a model in which a rigid OH bar may rotate about the axis of a rigid pyramid representing the CH_3 group under the action of a hindering potential of the form $V=\frac{1}{2}H(1-\cos 3x)$. The wave equation is separated into a Mathieu equation governing the internal motion and a symmetrical rotator equation which describes the rotation of the whole molecule. The Mathieu functions, because of a coupling between the internal motion and the rotation of the entire system, obey quasi-periodic boundary conditions. A qualitative treatment is given of the behavior of the energy levels as the barrier height H, is raised from zero to infinity. An exact method of calculating the energy levels, the wave functions, and the transition probabilities is devised which involves finding the roots of certain continued fractions. It is shown that the levels lying well below the barrier, which may be described as vibrational levels, are each split into three components whose spread is dependent upon the penetrability of the barrier. The positions of the three components of a level are periodic functions of the variable $\sigma=KC_1/C$ (C_1 and C are moments of inertia and K is a quantum number having integral values.) Examining levels in the order of increasing energy, the levels which lie above the barrier rapidly take on the character of states found in free rotation. A set of numerical calculations of the levels and of the resulting spectrum are made with a barrier height of 770 cm^{-1}. The qualitative features of the theoretical spectrum appear to be in agreement with the observations of Borden and Barker and those of Lawson and Randall, but a comparison indicates that the barrier height is probably lower, about 470±40 cm^{-1}. Further experimental work, particularly in the far infra-red, should determine the barrier height more exactly in which case better correlation between the predicted and measured spectra may be expected.

INTRODUCTION

DURING the past few years more than a dozen papers have appeared dealing with hindered rotation in the ethane molecule.[1] The

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[1] E. Teller and B. Topley, J. Chem. Soc. 885 (1935); J. B. Howard, J. Chem. Phys. **5**, 442, 451 (1937); E. B.

interest aroused in this subject has led to the experimental investigations of Borden and Barker and of Lawson and Randall[2] on methyl alcohol. They have obtained data on that portion of the infra-red absorption spectrum which is due to changes in the internal rotation of the molecule. Methyl alcohol was chosen because it is one of the simplest molecules in which the frequencies associated with hindered rotation are active in infra-red absorption. It is the purpose of this paper to present a detailed study of hindered rotation in methyl alcohol and to make a preliminary comparison of the results of this formulation with the existing experimental data.

In methyl alcohol, not only does the whole molecule rotate in space, but the OH bar and the CH_3 pyramid also rotate with respect to one another about the $C-O$ bond. Available evidence indicates this internal rotation is not free, but that there exists an interaction between the bar and the pyramid which hinders this rotation. It is evident that any hindering potential must have the threefold symmetry of the CH_3 group.

Model Chosen

The computations made in this paper are based upon a model which has been used to represent the methyl alcohol molecule.

First, the model molecule will be taken to consist of a rigid OH bar and a rigid CH_3 pyramid; the only internal degree of freedom allowed in the model will be a rotation of the OH bar and the CH_3 group with respect to one another about the axis of the molecule. This assumption will not introduce any large errors into these considerations because, while the fundamental frequency associated with hindered rotation appears at 270 cm^{-1}, all of the other fundamental vibrational frequencies appear above 850 cm^{-1}. Thus, in a normal coordinate treatment, if those force constants which are not associated with internal rotation are increased to infinity (thereby making the molecule rigid) the hindered rotation will not be materially affected, because of the initial lack of resonance.

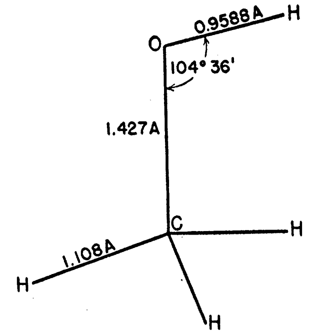

FIG. 1. Numerical values of moments of inertia and the molecular dimensions. Estimates made by Borden and Barker, reference 2.

Second, the hindering potential in the model molecule will be taken to be:

$$V=\tfrac{1}{2}H\{1-\cos 3x\},$$

where H is the height of the barrier and x is the angle measuring the rotation of the OH bar with respect to the CH_3 pyramid. The work of Dennison and Uhlenbeck[3] on the double minima problem has shown that the results of such a calculation as is contemplated here are very little influenced by the exact form of the potential used, but depend considerably on the area under the potential barrier. The above potential function is one of the simplest having the desired flexibility and the necessary symmetry properties.

Third, the molecule will be taken to be a symmetric rotator; it will be assumed that the principal C axis lies along the geometric axis of the molecule, and that the center of gravity lies on this axis. The slight asymmetry of the actual methyl alcohol molecule is due to the relatively light hydrogen atom in the OH bar. Borden and Barker have shown that the moments of inertia A and B differ in methyl alcohol by 4 percent from their average value. This difference will produce practically unobservable changes in the J and K spacings of the perpendicular bands resulting from internal rotation, these changes amounting to 0.06 cm^{-1} for both J and K spacings. The numerical values of the moments of inertia and of the molecular dimensions which we shall use are based on the plausible estimates made by Borden and Barker and are indicated in Fig. 1.

In the next sections the problem will be set up from our model of the molecule. The wave

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Wilson, Jr., J. Chem. Phys. **6**, 740 (1938); F. Stitt, J. Chem. Phys. **7**, 297 (1939). These papers give references to others which have appeared on this problem.

[2] A. Borden and E. F. Barker, J. Chem. Phys. **6**, 553 (1939); J. R. Lawson, Thesis; J. R. Lawson and H. M. Randall (to appear shortly).

[3] D. M. Dennison and G. E. Uhlenbeck, Phys. Rev. **41**, 313 (1932).

equation will be obtained and separated; finally we will examine the boundary conditions which the various portions of the wave function must satisfy.

THE WAVE EQUATION

In order to obtain the wave equation describing the rotation and internal motion of this model molecule, it is necessary to know the classical formulae for the kinetic and potential energies of the system. The kinetic energy associated with the precession of our model, written in terms of the usual Euler angles, is just that of a symmetric rotator;

$$2T_J = A\{\dot{\theta}^2 + \dot{\psi}^2 \sin^2\theta\},$$

where A is the moment of inertia of the entire molecule about an axis perpendicular to the axis of the molecule. If C_1 is the moment of inertia of the OH bar about the axis of the molecule and C_2 is the moment of inertia of the CH_3 group about this same axis, the portion of the kinetic energy associated with rotations about the axis of the model is:

$$2T_{K_1K_2} = C_1\{\dot{\psi}\cos\theta + \dot{\phi}_1\}^2 + C_2\{\dot{\psi}\cos\theta + \dot{\phi}_2\}^2,$$

where ϕ_1 and ϕ_2 describe the position of the OH bar and the CH_3 pyramid, respectively, with regard to rotations around the axis of the model. The total kinetic energy is the sum of these two energies:

$$2T = A\{\dot{\theta}^2 + \dot{\psi}^2 \sin^2\theta\} + C_1\{\dot{\psi}\cos\theta + \dot{\phi}_1\}^2 + C_2\{\dot{\psi}\cos\theta + \dot{\phi}_2\}^2.$$

The wave equation can now be written down at once. The procedure is well known and is equivalent to the writing out of the Laplacian in a curvilinear coordinate system for which the metric is given by $2T$. Inserting the hindering potential, the result is:

$$\frac{1}{A\sin\theta}\frac{\partial}{\partial\theta}\left\{\sin\theta\frac{\partial u}{\partial\theta}\right\} + \frac{1}{A\sin^2\theta}\frac{\partial^2 u}{\partial\psi^2} + \left\{\frac{1}{C_1} + \frac{\cos^2\theta}{A\sin^2\theta}\right\}\frac{\partial^2 u}{\partial_1\phi^2} + \left\{\frac{1}{C_2} + \frac{\cos^2\theta}{A\sin^2\theta}\right\}\frac{\partial^2 u}{\partial\phi_2{}^2}$$
$$-\frac{2\cos\theta}{A\sin^2\theta}\left\{\frac{\partial^2 u}{\partial\psi\partial\phi_1} + \frac{\partial^2 u}{\partial\psi\partial\phi_2}\right\} + \frac{2\cos\theta}{A\sin^2\theta}\frac{\partial^2 u}{\partial\phi_1\partial\phi_2} + \frac{2}{\hbar^2}\left[W - \frac{H}{2}(1-\cos 3\{\phi_1-\phi_2\})\right]u = 0.$$

This equation is the same as that used by H. H. Nielsen[4] in his discussion of the torsion oscillator. In his paper Nielsen carries out the separation of the wave equation. We will merely describe his results. The coordinates:

$$\phi = (C_1\phi_1 + C_2\phi_2)/C, \quad \text{and} \quad x = \phi_1 - \phi_2,$$

in which $C = C_1 + C_2$, are introduced into the equation. It is then observed that ϕ and ψ are ignorable coordinates and the differential equation which results from the use of this information is seen to be separable into an equation involving x alone and an equation involving θ only. Writing out the results:

$$u = (1/2\pi)e^{iK\phi}e^{iM\psi}\Theta(\theta)\mathfrak{M}(x), \tag{1}$$

where Θ and $\mathfrak{M}$ satisfy the equations:

$$\frac{1}{\sin^2\theta}\frac{d}{d\theta}\left\{\sin\theta\frac{d\Theta}{d\theta}\right\} - \left[\frac{1}{\sin^2\theta}\{M - K\cos\theta\}^2 - J(J+1) + K^2\right]\Theta = 0, \tag{2}$$

$$d^2\mathfrak{M}/dx^2 + \{R + S\cos 3x\}\mathfrak{M} = 0. \tag{3}$$

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[4] H. H. Nielsen, Phys. Rev. 40, 445 (1932).

In these equations:

$$W = W_\alpha + W_\beta, \qquad (1/A)[J(J+1) - K^2] = 2W_\beta/\hbar^2 - K^2/C$$

or

$$W_\beta = \left[\frac{J(J+1)}{A} + K^2\left(\frac{1}{C} - \frac{1}{A}\right)\right]\frac{\hbar^2}{2}, \qquad S = \frac{C_1C_2}{C}\frac{2}{\hbar^2}\frac{H}{2}, \qquad R = \frac{C_1C_2}{C}\frac{2}{\hbar^2}\left\{W_\alpha - \frac{H}{2}\right\}.$$

From the form of these equations it is evident that the motion can be described as the rotation of the whole top, together with an internal motion of the two ends of the molecule relative to one another. The whole top motion is given by the symmetric top equations in ϕ, ψ and θ while the internal motion is described by the Mathieu equation in x.

BOUNDARY CONDITIONS

We have seen that the wave function for the problem is:

$$u = (1/2\pi)e^{iK\phi}e^{iM\psi}\Theta(\theta)\mathfrak{M}(x).$$

Since the wave function must be single valued in ψ, it is clear that M must be an integer. The solutions must also be periodic in θ with period 2π. Let us now consider the boundary conditions obeyed by ϕ and x. These coordinates describe the rotation of the whole top about the axis of the molecule and the internal motion which takes place about the same axis; they have been chosen in a way which avoids a cross product term in the kinetic energy between $\dot{\phi}$ and $\dot{x}$. The coupling, however, still exists and is now apparent in the boundary conditions. We will next examine these boundary conditions. Floquet[5] has shown that solutions of Mathieu equations can be written in the form:

$$\mathfrak{M}(x) = e^{i\sigma x}P(x),$$

where $P(x)$ is periodic with period 2π and the coefficient $i\sigma$ in the exponential has been chosen imaginary so that the wave function will be everywhere finite. We now make the following transformations on the entire wave function:

$$\phi_1 \to \phi_1 + 2\pi n_1, \quad \phi_2 \to \phi_2 + 2\pi n_2,$$

where n_1 and n_2 are integers. It is clear that since the physical system remains unchanged under these transformations, the wave function describing the system also remains unchanged. Hence:

$$u(\phi_1\phi_2) = u(\phi_1 + 2\pi n_1,\ \phi_2 + 2\pi n_2).$$

Considering only those portions of the wave function which contain ϕ_1 and ϕ_2, this means that:

$$e^{iK\phi}e^{i\sigma x}P(x) = e^{iK\phi}e^{i\sigma x}P(x)$$
$$\times \exp\left[2\pi i\{K(n_1C_1 + n_2C_2)/C + \sigma(n_1 - n_2)\right].$$

Thus:

$$K(n_1C_1 + n_2C_2)/C + \sigma(n_1 - n_2) = n,$$

where n is an integer. This equation can only hold for all n_1 and n_2 if K is an integer and if $\sigma = s - KC_1/C$ where s is an integer whose value depends only on the definition of σ. It is convenient to let $s=0$ and thus, $\sigma = -KC_1/C$. The internal wave function is therefore:

$$\mathfrak{M}(x) = P(x)\exp\left[-iKC_1x/C\right] \qquad (4)$$

and must obey the following boundary condition:

$$\mathfrak{M}(x+2\pi) = \mathfrak{M}(x)\exp\left[-2\pi iKC_1/C\right].$$

Thus the coupling between the ϕ and x motions appears through the dependence of the boundary conditions of the internal motion on the angular momentum of the whole rotator about the axis of the molecule as given by K. The apparent asymmetry in the moments of inertia C_1 and C_2 is merely a result of the particular way in which the equations have been written here.

In the next sections of the paper we will devote most of our attention to a consideration of the internal motion. We will only mention the whole rotator briefly when we wish to obtain certain rotational spacings in the various types of bands which occur. We will first consider the internal motion in the limiting case in which the two ends of the molecule rotate freely with respect to one another. This will be followed with a discussion of the other limiting case in which the bar

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[5] E. T. Whittaker and G. N. Watson, *Modern Analysis*, fourth edition, p. 412.

and the pyramid are tightly bound together and can only vibrate slightly against one another. The internal energy levels are then qualitatively connected across from the free to the bound case by using symmetry considerations. Finally exact calculations suitable to the intermediate case are made.

FREE CASE

Let us first consider the internal motion when the internal energy is very much greater than the hindering potential ($W_\alpha \gg H$). The differential equation for the internal motion becomes:

$$d^2\mathcal{M}/dx^2 + R\mathcal{M} = 0.$$

Hence:

$$\mathcal{M} = (1/2\pi)^{\frac{1}{2}} \exp\left[\pm iR^{\frac{1}{2}}x\right].$$

It is evident that:

$$P(x) = (1/2\pi)^{\frac{1}{2}} \exp\left[imx\right],$$

where m is an integer and:

$$\mathcal{M} = (1/2\pi)^{\frac{1}{2}} \exp\left[i(m - KC_1/C)x\right].$$

Comparing the two $\mathcal{M}$'s:

$$\pm R^{\frac{1}{2}} = (m - KC_1/C).$$

The value of the internal energy resulting from this relation is:

$$W_\alpha = \frac{H}{2} + \frac{\hbar^2}{2}\frac{C}{C_1C_2}\left(m - K\frac{C_1}{C}\right)^2. \tag{5}$$

Note that if both K and m change sign W_α remains unchanged. That is, if we reverse the direction of rotation of the whole top and of the internal motion, the internal energy must remain invariant.

The selection rules for the free case have been given by Borden and Barker and are, $\Delta J = 0, \pm 1$, $\Delta m = \pm 1$ and $\Delta(K - m) = 0$. The physical meaning of these rules is interesting. $K\hbar$ denotes the component of the total angular momentum of the system along the axis of the molecule and is composed of two parts; $m\hbar$, the angular momentum of the OH bar and $(K - m)\hbar$ the angular momentum of the CH_3 pyramid. Since the component of the electric moment perpendicular to the axis, which is responsible for these transitions, depends upon the rotation of the OH bar but not upon that of the CH_3 pyramid, it is clear that the quantum number m must change while $(K - m)$ does not.

The appearance of the spectrum for the free case has been sketched by Borden and Barker and should consist of a set of bands separated by $h/4\pi^2cC_1$ which for methyl alcohol is about 39 cm^{-1}. Each set of bands is composed of lines with a spacing of $h/4\pi^2cA$ or about 1.57 cm^{-1}. This last spacing is not affected by the internal rotation and is associated with the precession of the molecule. It will be shown that even in the general case, bands of the "free" type will appear in the short wave-length end of the internal rotation spectrum.

BOUND CASE

We will next consider the case where the internal energy is much less than the barrier height ($W_\alpha \ll H/2$). For this case the internal motion is a torsional oscillation of the OH bar and the CH_3 pyramid with respect to one another, the two ends rotating against one another through small arcs about the axis of the molecule in the region of one of the potential minima.

We will first consider vibrations about the minimum at x equals zero. Expanding the hindering potential about this point in a Taylor's series we obtain:

$$d^2\mathcal{M}/dx^2 + \{\lambda - \xi^2x^2\}\mathcal{M} = 0, \quad -\tfrac{1}{3}\pi \leqslant x \leqslant \tfrac{1}{3}\pi,$$

where:

$$\lambda = \frac{2}{\hbar^2}\frac{C_1C_2}{C}W_\alpha, \quad \xi^2 = \frac{9C_1C_2H}{2\hbar^2C}.$$

We have seen that:

$$\mathcal{M}(x) = P(x) \exp\left[-iK(C_1/C)x\right].$$

For small values of K and for large values of the barrier height the motion will take place within such a small range of x that the exponential will be practically constant in this region. On the other hand $P(x)$ will vary rapidly in this region. We can therefore insert for the exponential, the value which it has at $x = 0$. Thus:

$$\mathcal{M}(x) = P(x) \qquad -\tfrac{1}{3}\pi \leq x \leq \tfrac{1}{3}\pi.$$

If the barriers are sufficiently high and wide, the energies and wave functions will be just those of the linear harmonic oscillator:

$$W_{\alpha n}=3\hbar(CH/2C_1C_2)(n+\tfrac{1}{2}),$$
$$\mathfrak{M}_n(x)=N_n \exp\left[-\tfrac{1}{2}\xi x^2\right]H_n(\xi^{\frac{1}{2}}x), \qquad \tfrac{1}{3}\pi\leqq x\leqq\tfrac{1}{3}\pi. \tag{6}$$

$H_n(\xi^{\frac{1}{2}}x)$ is the nth Hermite polynomial and N_n is the normalization factor. There will be two other states having this same energy; they are the states in which the system is executing an exactly similar vibration about the minimum at $2\pi/3$ or the one at $4\pi/3$. The wave functions will be just the one given above except that they will be centered at a different minimum and will have a phase factor characteristic of that minimum. For example, the harmonic oscillator function describing vibrations about the minimum at $2\pi/3$ will be written in terms of the variable $(x-2\pi/3)$ and will be multiplied by the phase factor $\exp[-\frac{2}{3}\pi iKC_1/C]$.

The three wave functions described above are not the correct zeroth-order wave functions for our threefold hindering potential. The correct linear combinations of these wave functions can be found from group theory or by performing a degenerate perturbation calculation. Let us consider, for a given K, the three wave functions of the degenerate states whose energy is $h\nu_0(n+\frac{1}{2})$. If we call the harmonic oscillator wave functions centered about 0, $2\pi/3$, $4\pi/3$ simply $H_n{}^1(x)$, $H_n{}^2(x)$, $H_n{}^3(x)$, respectively, and if we write the phase factor for all of these wave functions as a common factor, we find for the correct zeroth-order wave functions:

$$\begin{aligned}\mathfrak{M}_n{}^a&=(1/3)^{\frac{1}{2}}\exp\left[-iKC_1x/C\right]\\&\qquad\times\left[H_n{}^1+H_n{}^2+H_n{}^3\right],\\\mathfrak{M}_n{}^b&=(2/3)^{\frac{1}{2}}\exp\left[-iKC_1x/C\right]\\&\qquad\times\left[H_n{}^1-\tfrac{1}{2}(H_n{}^2+H_n{}^3)\right],\\\mathfrak{M}_n{}^c&=(1/2)^{\frac{1}{2}}\exp\left[-iKC_1x/C\right]\left[H_n{}^2-H_n{}^3\right].\end{aligned}\tag{7}$$

A perturbation treatment shows that if $K=0$ the threefold potential will cause the triply degenerate state to split into two states, the a state splitting away from the other two. If $K\neq 0$, in general, all three states will separate.

In the truly bound case, the spectrum resulting from changes in the internal motion would be an ordinary perpendicular band and would consist of a series of zero branches with the spacing $(1/C-1/A)h/4\pi^2c=6.57$ cm⁻¹. Each zero branch is the center of positive and negative branches whose lines are spaced $h/4\pi^2cA=1.57$ cm⁻¹. These latter lines would no doubt blur together to form a background of absorption.

Connection Between the Free and Bound Cases

The qualitative behavior of the energy levels as the barrier height is gradually raised from zero to infinity may be inferred from the following arguments. The presence of the three identical hydrogen nuclei in the CH_3 pyramid leads to the well-known result that the levels of the system may be divided into the symmetry classes α, β and $(\gamma\delta)$. A wave function belonging to the α class is invariant under an interchange of any two of the hydrogen nuclei while a β-wave function changes sign under this operation. The degenerate classes $(\gamma\delta)$ always occur together and the levels cannot be separated by any order of perturbation. The symmetry class of a wave function is of course not altered by changing the barrier height. We now determine the symmetries of the wave functions of the free rotator and also those of the bound oscillator. The connections between the two may then be made uniquely for it has been shown by Strutt[6] that, for a given σ (or K), the solutions of the Mathieu equation which are subject to the boundary condition $\mathfrak{M}(x+2\pi)=e^{2\pi i\sigma}\mathfrak{M}(x)$ can be ordered by the number of zeros which the wave functions possess in the interval 0 to 2π. This means that the levels will not cross as we raise the barrier height.

The symmetry characters of the wave functions of the free internal rotator are easily found by adapting the arguments employed in finding the symmetries of the rotating molecule YX_3 to our case.[7] The significant point is that the symmetry is determined by the quantum number $(K-m)$ rather than by K since it is the former which represents the rotation of the CH_3 group. Thus if $(K-m)=0$ the level is either α or β depending upon whether the total angular momentum number J is even or odd. If $(K-m)$ is not a multiple of 3, we have the degenerate pair $(\gamma\delta)$ while if $(K-m)$ is a multiple of 3 there are two levels one of which is α and the other β.

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[6] M. J. O. Strutt, Ergebn. Der. Math. u. Ihrer Grenz. I, No. 3, p. 14 (1932).

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

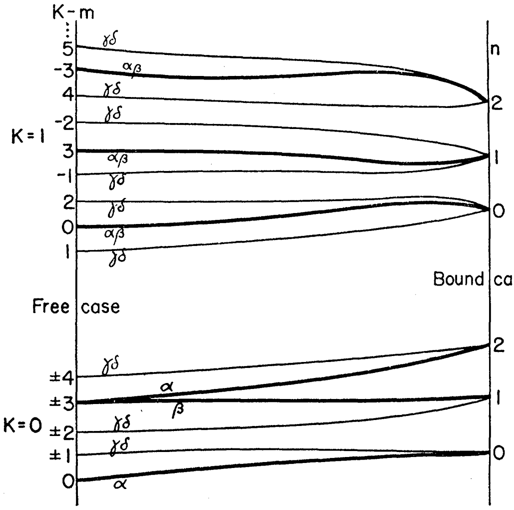

FIG. 2. Splitting of energy levels.

When the barrier is infinitely high (the bound case) the wave functions may be written as the product of the vibrational functions (Eq. (7)) and the wave functions of a symmetrical rotator. For each vibrational level, n, there are, as has been seen, three functions whose symmetry is easily shown to be α, $(\gamma\delta)$ for n even and β, $(\gamma\delta)$ for n odd. The symmetry classes of the rotational wave functions are well known and may be stated as follows. For $K=0$, the level is α or β as J is even or odd. For K not a multiple of 3 we have a degenerate pair $(\gamma\delta)$ while for K a multiple of 3 we have the two levels α and β. The symmetry of the total wave function may then be found from the usual multiplication rules,

$$\alpha\cdot\alpha=\beta\cdot\beta=\alpha,\quad \alpha\cdot\beta=\beta,\quad \alpha\cdot(\gamma\delta)=\beta\cdot(\gamma\delta)=(\gamma\delta),$$
$$(\gamma\delta)\cdot(\gamma\delta)=\alpha,\ \beta,\ (\gamma\delta).$$

The results of these considerations are shown diagramatically in Fig. 2 for the typical cases of $K=0$ and $K=1$, both for J even. No attempt has been made to draw the levels to scale (this will be done later in Fig. 3) but only to show the manner in which the levels of the free rotator connect with those of the bound oscillator. In constructing such a diagram it is important to notice that the order of the levels on the "free" side for $K\neq 0$ depends upon the ratio of the moments of inertia C_1/C and will alter as K increases.

EXACT METHODS—INFINITE DETERMINANTS

We will now consider the internal motion for intermediate values of the barrier height, examining the equations of motion first with the aid of infinite determinants, and in the following section considering the equations of motion when they are written as infinite continued fractions. The two descriptions are equivalent.

The internal equation of motion can be written in the form:

$$d^2\mathfrak{M}/dx^2+\{R+2\alpha\cos 3x\}\mathfrak{M}=0,$$

where:

$$\mathfrak{M}(x)=e^{i\sigma x}P(x)$$

and:

$$\sigma=-KC_1/C.$$

We can now expand $P(x)$ in a Fourier series. Thus:

$$\mathfrak{M}(x)=e^{i\sigma x}\sum_{\tau=-\infty}^{\infty}a_\tau e^{i\tau x},\tag{8}$$

where τ is an integer. If we substitute this into the differential equation, multiply through by $e^{i\tau' x}$, and integrate from zero to 2π we will obtain the following recursion formula:

$$\frac{\alpha}{\{R-(\sigma+\tau)^2\}}a_{\tau-3}+a_\tau+\frac{\alpha}{\{R-(\sigma+\tau)^2\}}a_{\tau+3}=0.\tag{9}$$

The necessary and sufficient condition that this infinite set of linear homogeneous equations shall have solutions other than $a_\tau=0$ (for all τ) is that the determinant of the coefficients should vanish. We have written out a few terms of the determinant below:

$$D_I(\sigma, R)=0$$

$$=\begin{vmatrix} 1 & 0 & 0 & \frac{\alpha}{\{-3\}} & & \\ 0 & 1 & 0 & 0 & \frac{\alpha}{\{-2\}} & \\ 0 & 0 & 1 & & & \frac{\alpha}{\{-1\}} \\ \frac{\alpha}{\{0\}} & 0 & & 1 & & \\ & \frac{\alpha}{\{1\}} & & & 1 & \\ & & \frac{\alpha}{\{2\}} & & & 1 \end{vmatrix}\tag{10}$$

where

$$\{\tau\}=\{R-(\sigma+\tau)^2\}.$$

The vanishing of this determinant is the relation which yields the eigenvalues of the problem (R) in terms of σ and α. It is evident that the determinant converges. It is also clear that the determinant can be factored into three infinite determinants a few terms of which we have written below:

$$D_I=D_1D_2D_3, \tag{11}$$

$$D_1(\sigma,R)=0=\left|\begin{array}{cccccc}
1 & \frac{\alpha}{\{-9\}} & & & & \\
\frac{\alpha}{\{-6\}} & 1 & \frac{\alpha}{\{-6\}} & & & \\
 & \frac{\alpha}{\{-3\}} & 1 & \frac{\alpha}{\{-3\}} & & \\
 & & \frac{\alpha}{\{0\}} & 1 & \frac{\alpha}{\{0\}} & \\
 & & & \frac{\alpha}{\{3\}} & 1 & \frac{\alpha}{\{3\}} \\
 & & & & \frac{\alpha}{\{6\}} & 1
\end{array}\right|$$

$$D_2(\sigma,R)=0=\left|\begin{array}{cccccc}
1 & \frac{\alpha}{\{-7\}} & & & & \\
\frac{\alpha}{\{-4\}} & 1 & \frac{\alpha}{\{-4\}} & & & \\
 & \frac{\alpha}{(-1)} & 1 & \frac{\alpha}{\{-1\}} & & \\
 & & \frac{\alpha}{\{2\}} & 1 & \frac{\alpha}{\{2\}} & \\
 & & & \frac{\alpha}{\{5\}} & 1 & \frac{\alpha}{\{5\}} \\
 & & & & \frac{\alpha}{\{8\}} & 1
\end{array}\right| \tag{12}$$

$$D_3(\sigma,R)=0=\left|\begin{array}{cccccc}
1 & \frac{\alpha}{\{-8\}} & & & & \\
\frac{\alpha}{\{-5\}} & 1 & \frac{\alpha}{\{-5\}} & & & \\
 & \frac{\alpha}{\{-2\}} & 1 & \frac{\alpha}{\{-2\}} & & \\
 & & \frac{\alpha}{\{1\}} & 1 & \frac{\alpha}{\{1\}} & \\
 & & & \frac{\alpha}{\{4\}} & 1 & \frac{\alpha}{\{4\}} \\
 & & & & \frac{\alpha}{\{7\}} & 1
\end{array}\right|$$

Thus the threefoldness of the problem expresses itself in these three determinants, the vanishing of each yielding a different group of eigenvalues and eigenfunctions of the internal motion.

Using a remarkable theorem discovered by G. W. Hill[8] we can now state the dependence of these determinants on σ precisely. Writing out this theorem for our cases, we have:

$$D_I(\sigma, R) \equiv D_I(0, R) - \sin^2 \pi\sigma / \sin^2 \pi R^{\frac{1}{2}}.$$

Thus our eigenvalues are given by:

$$D_I(0, R) = \sin^2 \pi\sigma / \sin^2 \pi R^{\frac{1}{2}}.$$

Similarly, in the case of the three factors one finds:

$$D_1(0, R_1) = \sin^2 \tfrac{1}{3}\pi\sigma / \sin^2 \tfrac{1}{3}\pi R^{\frac{1}{2}},$$

$$D_2(0, R_2) = \frac{\frac{1}{2} - \cos \frac{2}{3}\pi(\sigma + \frac{1}{2})}{\frac{1}{2} + \cos \frac{2}{3}\pi R_2^{\frac{1}{2}}},$$

$$D_3(0, R_3) = \frac{\frac{1}{2} - \cos \frac{2}{3}\pi(\sigma - \frac{1}{2})}{\frac{1}{2} + \cos \frac{2}{3}\pi R_3^{\frac{1}{2}}}.$$

These, then, are the three equations yielding the three different types of eigenvalues denoted by R_1, R_2, and R_3. We can, however, proceed further. Upon examination the three infinite determinants of the above equations prove to be simply related to one another. It can be shown that:

$$D_2(0, R) = D_3(0, R) = \frac{\frac{3}{4} - D_1(0, R) \sin^2 \frac{1}{3}\pi R^{\frac{1}{2}}}{\frac{3}{4} - \sin^2 \frac{1}{3}\pi R^{\frac{1}{2}}}.$$

From this relation the three equations yielding the roots become:

$$D_1(0, R_1) = \sin^2 \tfrac{1}{3}\pi\sigma / \sin^2 \tfrac{1}{3}\pi R_1^{\frac{1}{2}}, \tag{13}$$

$$D_1(0, R_2) = \sin^2 \tfrac{1}{3}\pi(\sigma - 1) / \sin^2 \tfrac{1}{3}\pi R_2^{\frac{1}{2}}, \tag{14}$$

$$D_1(0, R_3) = \sin^2 \tfrac{1}{3}\pi(\sigma + 1) / \sin^2 \tfrac{1}{3}\pi R_3^{\frac{1}{2}}. \tag{15}$$

Using these equations one finds that the eigenvalues transform into one another in a very beautiful manner. We see that:

$$R_1(\sigma + 3l) = R_1(\sigma),$$
$$R_1(\sigma + 3l + 1) = R_3(\sigma),$$
$$R_1(\sigma + 3l + 2) = R_2(\sigma)$$

and, noting that l is an integer:

$$R_2(\sigma + 3l) = R_2(\sigma),$$
$$R_2(\sigma + 3l + 1) = R_1(\sigma),$$
$$R_2(\sigma + 3l + 2) = R_3(\sigma).$$

The way in which the cyclic permutations are made should now be obvious. If one now examines the determinants and the recursion formulae it is clear that the determinants and the wave functions also depend upon σ in just the same way. For example:

$$\mathfrak{M}_1(\sigma + 3l, R_1) = \mathfrak{M}_1(\sigma, R_1),$$
$$\mathfrak{M}_1(\sigma + 3l + 1, R_1) = \mathfrak{M}_3(\sigma, R_1), \text{ etc.}$$

From these discussions concerning the case where the potential is $\frac{1}{2}H \cos 3x$ one can immediately see the extensions appropriate for the case where the potential is $\frac{1}{2}H \cos Nx$ (where N is an integer).

Exact Methods—Continued Fractions

We will now write the equations describing the internal motion in terms of continued fractions. The actual numerical calculations were made with continued fractions. We have obtained the recursion formula:

$$\frac{\alpha}{\{\tau\}} a_{\tau-3} + a_\tau + \frac{\alpha}{\{\tau\}} a_{\tau+3} = 0,$$

where:

$$\{\tau\} = \{R - (\sigma + \tau)^2\}.$$

Using the methods discussed by Poole[9] we can eliminate the a_τ by using convergence requirements, thus obtaining the following three equations which give the three types of eigenvalues:

$$1 - \cfrac{\frac{\alpha^2}{\{0\}\{3\}}}{1 - \cfrac{\frac{\alpha^2}{\{3\}\{6\}}}{1 - \cfrac{\frac{\alpha^2}{\{6\}\{9\}}}{1 - \text{etc.}}}} = - \cfrac{\frac{\alpha^2}{\{0\}\{-3\}}}{1 - \cfrac{\frac{\alpha^2}{\{-3\}\{-6\}}}{1 - \text{etc.}}} \qquad (16)(R_1)$$

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[8] E. T. Whittaker and G. N. Watson, *Modern Analysis*, fourth edition, p. 415.

[9] E. G. C. Poole, *Introduction to the Theory of Linear Differential Equations*, p. 182.

$$1-\cfrac{\dfrac{\alpha^2}{\{-1\}\{2\}}}{1-\cfrac{\dfrac{\alpha^2}{\{2\}\{5\}}}{1-\cfrac{\dfrac{\alpha^2}{\{5\}\{8\}}}{1-\text{etc.}}}}=-\cfrac{\dfrac{\alpha^2}{\{-1\}\{-4\}}}{1-\cfrac{\dfrac{\alpha^2}{\{-4\}\{-7\}}}{1-\text{etc.}}} \qquad (17)(R_2)$$

$$1-\cfrac{\dfrac{\alpha^2}{\{1\}\{4\}}}{1-\cfrac{\dfrac{\alpha^2}{\{4\}\{7\}}}{1-\cfrac{\dfrac{\alpha^2}{\{7\}\{10\}}}{1-\text{etc.}}}}=-\cfrac{\dfrac{\alpha^2}{\{1\}\{-2\}}}{1-\cfrac{\dfrac{\alpha^2}{\{-2\}\{-5\}}}{1-\text{etc.}}} \qquad (18)(R_3)$$

It can be seen that these continued fractions converge very rapidly. The convergence becomes worse if we increase α, the barrier height, or if we go to larger values of the internal energy (if we increase R).

Having found an R which satisfies one of these equations, we can proceed to calculate the a_τ which determine the corresponding internal wave function. To do this we will need the equations which connect successive a_τ in each of the three types of wave functions. These relations, which appear during the process of eliminating the a_τ from the recursion equations, are:

$$a_\tau=-\cfrac{\dfrac{\alpha}{\{\tau\}}a_{\tau-3}}{1-\cfrac{\dfrac{\alpha^2}{\{\tau\}\{\tau+3\}}}{1-\cfrac{\dfrac{\alpha^2}{\{\tau+3\}\{\tau+6\}}}{1-\text{etc.}}}} \qquad \text{for positive } \tau \qquad (19)$$

and

$$a_\tau=-\cfrac{\dfrac{\alpha}{\{\tau\}}a_{\tau+3}}{1-\cfrac{\dfrac{\alpha^2}{\{\tau\}\{\tau-3\}}}{1-\cfrac{\dfrac{\alpha^2}{\{\tau-3\}\{\tau-6\}}}{1-\text{etc.}}}} \qquad \text{for negative } \tau. \qquad (20)$$

The Fourier coefficients are now determined as follows: Suppose that we have found an R_1. The a_{3l} are then calculated in terms of some initial coefficient from the above equations. Suppose a_0 is the initial coefficient: We calculate a_3 and a_{-3} in terms of a_0 using these equations: then a_6 and a_{-6} are determined by substituting these values of a_3 and a_{-3} into the equations relating a_6 with a_3 and a_{-6} with a_{-3}: and so on. The wave function is normalized by choosing the initial coefficient. For an R_2 the a_{3l-1} are calculated in terms of a_{-1}. For an R_3 the a_{3l+1} are calculated in terms of a_1.

Let us next examine the transition probability between two states of motion of the molecule. We will assume the OH bar to be a permanent dipole. The components of this dipole along the $x_1y_1z_1$ axes will be $(d, 0, f)$. These axes are fixed in the bar. The projections of the dipole moment upon the axes fixed in space at the center of gravity of the molecule are:

$$\mu_X=d\{\cos\psi\cos\phi_1-\cos\theta\sin\psi\sin\phi_1\}+f\sin\theta\sin\psi,$$

$$\mu_Y=d\{\sin\psi\cos\phi_1+\cos\theta\cos\psi\sin\phi_1\}-f\sin\theta\cos\psi,$$

$$\mu_Z=d\sin\theta\sin\phi_1+f\cos\theta.$$

The spectral lines resulting from the terms in f are just the ordinary far infra-red lines due solely to changes in the precessional motion. Taking only terms in d and using the fact that:

$$\phi_1=\phi+C_2x/C,$$

the above formulae become:

$$\mu_X=d[\{\cos\psi\cos\phi-\cos\theta\sin\psi\sin\phi\}\cos C_2x/C-\{\cos\psi\sin\phi+\cos\theta\sin\psi\cos\phi\}\sin C_2x/C],$$

$$\mu_Y=d[\{\sin\psi\cos\phi+\cos\theta\cos\psi\sin\phi\}\cos C_2x/C-\{\sin\psi\sin\phi-\cos\theta\cos\psi\cos\phi\}\sin C_2x/C],$$

$$\mu_Z=d[\sin\theta\sin\phi\cos C_2x/C+\sin\theta\cos\phi\sin C_2x/C].$$

The matrix elements are now given by:

$$(\mu_i)_{J'K'M'}^{JKM} = \int\int\int\int F^*(\theta\phi\psi)^{J'K'M'}\mathfrak{M}^*(x)^{K'}\mu_i\mathfrak{M}(x)^{K}F(\theta\phi\psi)^{JKM}dxd\phi d\psi \sin\theta d\theta,$$

where $i = X$, Y, or Z. Carrying out the integration over x we find:

$$\int_0^{2\pi}\mathfrak{M}^*(x)^{K'}\begin{Bmatrix}\cos C_2x/C\\ \sin C_2x/C\end{Bmatrix}\mathfrak{M}(x)^K dx = \begin{Bmatrix}\frac{1}{2}[\delta_{K'}{}^{K+1}\sum_{-\infty}^{\infty} a_\tau a_{\tau+1} + \delta_{K'}{}^{K-1}\sum_{-\infty}^{\infty} a_\tau a_{\tau-1}]\\ \\ \frac{1}{2i}[-\delta_{K'}{}^{K+1}\sum_{-\infty}^{\infty} a_\tau a_{\tau+1} + \delta_{K'}{}^{K-1}\sum_{-\infty}^{\infty} a_\tau a_{\tau-1}]\end{Bmatrix},$$

where the δ are Kronecker deltas. Note that the nonvanishing integrals over x will have the same value if K is replaced by minus K.

Let us consider the case where K' is $K-1$. If we carry out the integrals over x an examination of the remaining portions of the matrix elements shows that we are evaluating the symmetric rotator matrix elements of a dipole fixed in the whole rotator. In a set of coordinates fixed in the whole rotator so that their z axis lies along the axis of the molecule and their x axis lies along the ϕ direction the components of the whole rotator dipole are

$$\left(\frac{d}{2}\sum_{-\infty}^{\infty} a_\tau a_{\tau-1},\quad \frac{d}{2i}\sum_{-\infty}^{\infty} a_\tau a_{\tau-1},\quad 0\right).$$

The integrals over the whole rotator coordinates θ, ϕ, and ψ will be just the symmetric rotator matrix elements which one obtains in the calculation of the intensities of lines appearing in the negative side of an ordinary perpendicular band. Here, as in the case of the symmetric rotator, we can square the matrix elements and sum over the three directions X, Y, Z. This operation gets rid of all imaginary numbers. We can also sum over the $(2J+1)$ allowed values of M and over the two values $+K$ and $-K$. The resulting transition probabilities contain as one factor just those amplitudes which give the intensities of the lines in the negative side of a perpendicular band. The integrals over x contribute, if we include the dipole strength, the factor:

$$(I_{K-1}{}^{K})^2 = d^2\left(\sum_{-\infty}^{\infty} a_\tau a_{\tau-1}\right)^2. \tag{21}$$

The same procedure can be carried out for the case where K' is $K+1$. The symmetric rotator amplitudes which result are those encountered on the positive side of a perpendicular band. The factor multiplying them which results from the internal motion is:

$$(I_{K+1}{}^{K})^2 = d^2\left(\sum_{-\infty}^{\infty} a_\tau a_{\tau+1}\right)^2. \tag{22}$$

The selection rules for the whole motion are of course:

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

The selection rules for the internal motion can be deduced by noting which classes of the a_τ can appear together in the $I_{K+1}{}^{K}$. For example, in $I_{K-1}{}^{K}$ if the a_τ are a_{3l} then the $a_{\tau-1}$ are a_{3l-1}. Thus the frequency absorbed involves a transition from a state of the first kind to one of the second kind. Let us call such a frequency:

$$\nu^1_2.$$

Then the selection rules state that in the case where $K\rightarrow K-1$ the internal transitions are of the following types:

$$\nu^1_2,\quad \nu^2_3,\quad \nu^3_1.$$

In case $K\rightarrow K+1$ the internal transitions are of the following types:

$$\nu^1_3,\quad \nu^2_1,\quad \nu^3_2.$$

It is well to note that these rules say nothing about the relative intensities of fundamentals, overtones, etc. This information can only be obtained by actual calculation of the a_τ.

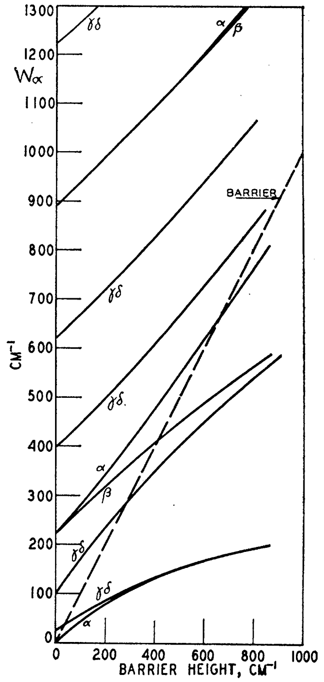

FIG. 3. W_α as a function of barrier height ($K=0$).

NUMERICAL CALCULATIONS

A series of numerical calculations of the energy levels and wave functions have been made with a particular value of the barrier height. These results are preliminary in the sense that the barrier height chosen is probably not the correct one for methyl alcohol. The predicted spectrum is therefore not in very good agreement with the observed spectrum. The qualitative features are very interesting however and will undoubtedly lead to a better evaluation of the barrier height.

A first set of computations was undertaken to determine the energy levels having $K=0$ for various barrier heights. The results are shown in Fig. 3. This figure is a correct plot of the levels which were drawn qualitatively in the lower portion of Fig. 2. The information thus obtained was used in the following way. The transition from the ground state ($n=0$) to the first excited state ($n=1$) will approximately correspond to the most intense region of the absorption spectrum. An examination of the spectrum as reported by Borden and Barker indicated that the absorption increased in intensity as the wave-length increased. An estimate indicated that it would reach a maximum intensity at about 350 cm^{-1}. This could be only a very rough estimate indeed since their observations did not extend beyond 380 cm^{-1}. A reference to Fig. 3 shows that the difference between the levels $n=0$ and $n=1$ will be equal to 350 cm^{-1} when the barrier height measured from the bottom of one of the minima is 770 cm^{-1}.

The rest of the calculations were made with a particular value of the barrier height. The constants employed were:

$$H=769.43 \text{ cm}^{-1},$$
$$\alpha=s/2=2\pi^2cC_1C_2H/hC=7.7699,$$
$$\sigma=-KC_1/C=-0.20766K,$$
$$W_\alpha=24.7568\{R+15.5398\} \text{ cm}^{-1}.$$

It will be remembered that the total energy of the system is equal to W_α plus the energy of the symmetrical rotator, namely $(\hbar^2/2A)(J^2+J-K^2)+\hbar^2K^2/2C$. The values of W_α for any K are to be found from the continued fractions (Eqs. (16), (17) and (18)) by the method of successive approximation. The continued fractions converge so rapidly that it was necessary to calculate only about five or six terms. The results for $n=0$, 1, 2 and 3 are shown in Fig. 4. It must be noted that only integral values of K have physical meaning.

The curves of Fig. 4, although calculated for a particular barrier and ratio of moments of inertia, are characteristic solutions of the problem and are worth considerable study. Thus the ground levels ($n=0$) are seen to be three in number. Initially when $K=0$, the two upper levels combine to form a degenerate level at 192.34 cm^{-1} (energy is measured from the bottom of one of the potential minima). The other level lies 1.4 cm^{-1} lower. As K increases the degeneracy disappears and the positions of the levels oscillate up and down over the comparatively narrow range of 1.9 cm^{-1}. The spread of this triplet state in frequency units represents the inverse of the time it would take the system in one potential minimum to leak through to one of the other minima. The three curves giving the levels are of course identical but are displaced laterally by the amount C/C_1.

The first excited levels ($n=1$), also three in number, lie about 538 cm^{-1} above the minima. The spread of the energy levels as K changes is larger than that of the ground state, being 33 cm^{-1}. This increase in the "width" of the level

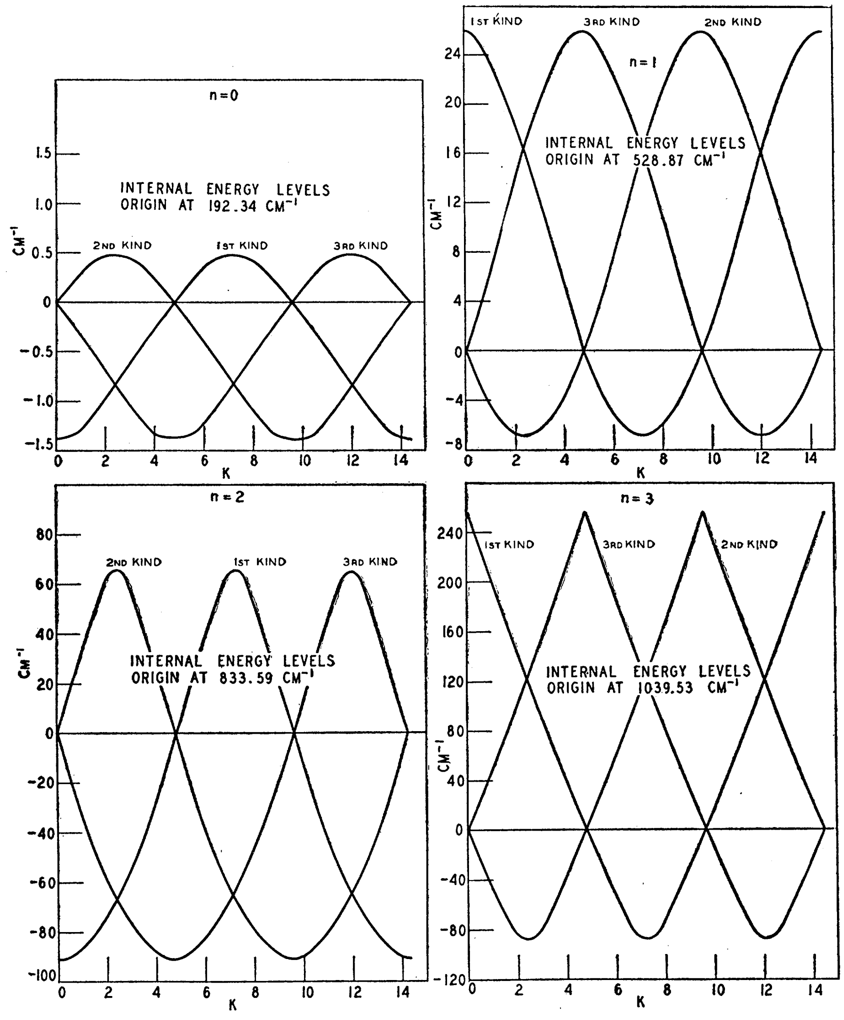

Fig. 4. Values of W_α for $n=0$, 1, 2, and 3 for various values of K.

indicates the greater ease with which the system may penetrate the barrier in this excited state. If we go to still higher values of n we will be dealing with states which lie above the potential barrier. The properties of these states must rapidly approach those of the free rotator as we go to larger values of n. Two points are to be noted. First, for the higher states the spread of the levels becomes so large that the upper levels of one state, say the nth state, nearly reach up to the lower levels of the $(n+1)$th state. In the second place the maxima and minima of the energy *versus* K curves become so sharp as to suggest discontinuities. These phenomena are immediately explicable when we consider the energy curves for the free rotator. As has been shown, in this case

$$W_\alpha=\left(m-K\frac{C_1}{C}\right)^2\frac{C\hbar^2}{2C_1C_2}.$$

The resulting parabolae are drawn in Fig. 5 in such a manner as to illustrate their relationship to the preceding curves where the barrier height is not zero.

The next step in the calculation is to obtain the wave functions describing the states. This has been accomplished by employing Eqs. (19) and (20) to compute the coefficients in the Fourier expansion (Eq. (8)) of the wave function. The results of this process are shown in Fig. 6 for the wave functions of the first kind. They are given in normalized form. The coefficients of the second and third kind are found by displacing the curves laterally by an amount C/C_1. It is interesting to observe that as we go to the higher states which must resemble the free rotator one of the Fourier coefficients becomes large compared with the others. For the completely free rotator we have seen that only one of the coefficients differs from zero. A series of the actual wave functions were plotted and it was found, in accordance with our expectations, that the wave functions in the ground state approximate quite accurately to linear combinations of the Hermitian orthogonal functions centered about the potential minima. On the other hand, the wave functions of the excited states above the barrier (already for states having $n=2$) closely resemble the sine and cosine functions of the free rotator.

The internal transition probabilities may now be evaluated (Eqs. (21) and (22)). These show oscillations of the same general character as those existing in the energy levels. However, the amplitude of the oscillation is small for a transition connecting two states which lie well below the potential barrier. Thus the maximum value of the internal transition probability for the transition $n=0$ to $n=1$ is 0.0480 while the minimum value is 0.0339. As we connect successively higher and higher states these fluctuations become more violent. The maximum and minimum values for the transitions $n=1$ to $n=2$ and $n=2$ to $n=3$ are 0.2706, 0.0225 and 0.8910, 0.0012, respectively. The fact that the maximum value increases as the internal rotation becomes more free is connected with the fact that the amplitude of oscillation becomes larger as the influence of the hindering potential decreases. From our definition of the internal transition probability it is clear that this quantity will equal 1 for the allowed free rotator transitions.

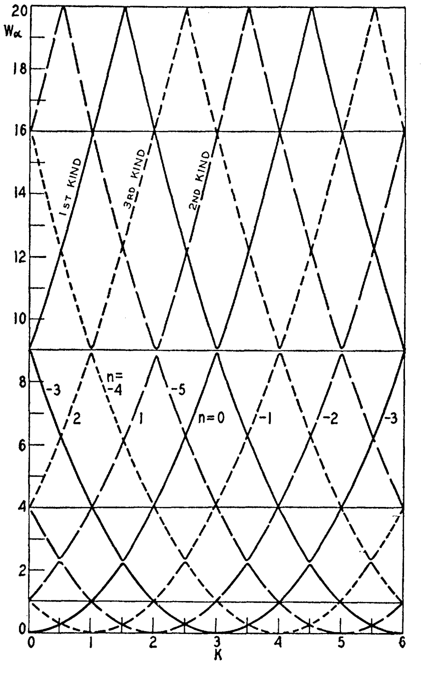

FIG. 5. Values of W_α as a function of K for the free rotator.

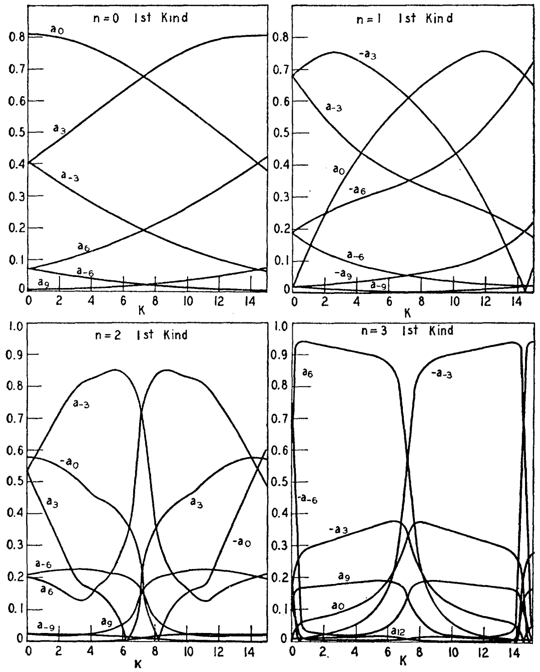

FIG. 6. Fourier coefficients.

The analysis will enable us to calculate any desired portion of the spectrum. We have applied it to what may be described as the fundamental band, that is, the transition $n=0$ to $n=1$. We have also applied it to the first upperstage band which corresponds to the transition from $n=1$ to $n=2$. The results are shown in Fig. 7. The lines in these figures represent zero branch lines and refer to transitions in which $\Delta J=0$. Each zero branch line will be the center for the positive and negative branches which will be composed of lines having a spacing of $h/4\pi^2cA=1.57$ cm^{-1}. The lines in the positive and negative branches result from transitions in which $\Delta J=\pm1$. These lines will generally merge together to form a fairly continuous background of absorption. In order to calculate the positions of the lines in Fig. 7 it was of course necessary to use the total energy of the system, that is W_α plus the symmetrical rotator energy referred to earlier. The total intensity of absorption also depends upon both the internal and the symmetric rotator transition probabilities. It can readily be shown that the intensity of a particular line is given by the expression,

$$\overset{JK}{I}_{J'K'} = \Gamma\nu(1-e^{-h\nu/kT})I^2(\overset{JK}{S}_{J'K'})^2 g_{JK}e^{-W/kT},$$

where Γ is a constant, I^2 is the internal transition probability for this particular transition, and

$$(\overset{JK}{S}_{J'K'})^2$$

is the square of the matrix element of the direction cosines using the symmetric rotator wave functions. Here g_{JK} is the statistical weight of the state and takes into account the affects caused by the nuclear spins of the hydrogen nuclei in the CH_3 group. The above formula is identical with the usual expression for the intensities of the lines of a symmetrical rotator except for the inclusion of the factor I^2 and the addition of W_α to the energy.

The Predicted Spectrum; Correlation with Experiment

We are now in a position to describe the general features of the spectrum of methyl alcohol as predicted by our model. Since the weaker lines arising from transitions in which $\Delta J = \pm 1$ will usually form a continuous background of absorption we will only consider the transitions in which $\Delta J = 0$. The positions and intensities of the lines associated with $\Delta J = \pm 1$ can be easily calculated if necessary.

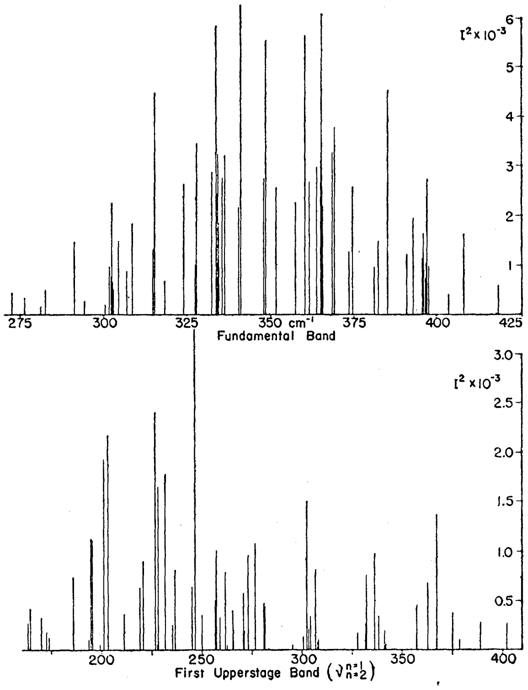

Fig. 7. Fundamental band and first upperstage band in methyl alcohol.

Starting in the far infra-red there will be a series of groups of lines corresponding to transitions in which $\Delta n = 0$ and $\Delta K = +1$. Let us consider only the lines resulting from transitions between states having a certain definite value of n. Then each group is a multiplet having three members since in absorbtion as $K \rightarrow K+1$, the allowed transitions are from a state of the first kind to one of the third kind, from one of the second kind to one of the first kind, and from a state of the third kind to one of the second kind. The average spacing between the multiplets is $(1/C-1/A)h/4\pi^2c = 6.6$ cm^{-1}. The positions of the lines within any given multiplet depends upon the value of K and upon the spread of the three levels for the particular n chosen. This spread is of course a sensitive function of the barrier height. In our calculations the three states with $n=0$ have a maximum separation of 1.9 cm^{-1}; this leads to a maximum spread of the multiplet lines of 2.4 cm^{-1}. The pattern of the lines within a multiplet varies rapidly as we go from one multiplet to another, that is, as we consider different values of K. Measurements of these lines, which should be strong in the region around 200μ have not as yet been made. A knowledge of them would lead at once to a reliable estimate of the barrier height. In addition to the transitions just described there will be transitions between the states $n=1$. Since this is an excited state the lines resulting will be weaker by the Boltzmann factor, which in the present case is about 0.18. The maximum spread of a multiplet of this series is around 44 cm^{-1}; thus in general the spread of each multiplet of this series is much greater than the mean spacing between multiplets.

The lines corresponding to the transitions $\Delta n=0$ will grow weaker as one proceeds to shorter wave-lengths but they will soon be augmented by the absorption resulting from transitions in which $\Delta n=1$. Thus there probably exists no very transparent region in the spectrum. A typical transition of the type $\Delta n=1$ is the fundamental ($n=0$ to 1) which has been illustrated in Fig. 6a. It consists of three superimposed bands for the same reason that the multiplets of the far infra-red consist of three members. Any one of the three bands resembles a normal perpendicular band only in the fact that the average spacing of the zero branch lines within it is $(1/C-1/A)h/4\pi^2c=6.6$ cm^{-1}. However neither the line spacing nor the line intensity is uniform. In each of the three bands the lines exhibit the phenomena of bunching together at intervals of $6.6(3C/C_1)=95$ cm^{-1}. The positions of bunching of one band are separated from those of another band of the triplet by one-third of this amount. This phenomena will probably only be evident in the fundamental band.

High upper stage transitions will eventually take place between levels which are so far above the barrier that they have all the properties of the free rotator levels. These transitions will give rise to groups of lines having a spacing between groups of $h/4\pi^2cC_1=39$ cm^{-1}. These groups are undoubtedly the series of absorption maxima with this spacing found by Borden and Barker in the region around 20μ.

Recently Lawson and Randall[2] have undertaken an investigation of the spectrum of methyl alcohol in which they were able to make measurements in the interval between 20 and 57μ. Their results show many points of similarity with the predicted spectrum. They find an intense absorption consisting of irregularly spaced strong lines which exhibit the tendency to bunch together at intervals. There is everywhere a strong background of absorption in which fine lines may often be discerned with the expected spacing $h/4\pi^2cA=1.57$ cm^{-1}. The most intense region of absorption occurs at 270 cm^{-1}. If we identify this with the position of the fundamental ($n=0$ to $n=1$) we would conclude upon referring to Fig. 3 that the appropriate barrier height should be 470 cm^{-1}, with an estimated uncertainty of 40 cm^{-1}. This is of course the value of the barrier height when measured from the bottom of one of the potential minima. We believe that the analysis of hindered rotation which we have given contains the essential qualitative features which will enable it to explain the spectrum of methyl alcohol. In order to obtain a quantitative fit between theory and experiment it will be necessary to evaluate the barrier height with greater precision. Further observations, particularly in the far infra-red, would furnish the necessary information.