unexcited N^{13} nucleus has two protons in the $1S_{\frac{1}{2}}$ shell, four protons in the $1P_{\frac{3}{2}}$ shell, and one proton in the $1P_{\frac{1}{2}}$ shell. The excited levels available to the outer proton are: $1D_{\frac{5}{2}}$, $1D_{\frac{3}{2}}$, $2S_{\frac{1}{2}}$, $1F_{\frac{7}{2}}$, $1F_{\frac{5}{2}}$, $2P_{\frac{3}{2}}$, $2P_{\frac{1}{2}}$; etc. On the basis of the present analysis, the $D_{\frac{5}{2}}$ and $P_{\frac{3}{2}}$ levels appear at about 3.5 Mev while the $D_{\frac{3}{2}}$ and $P_{\frac{1}{2}}$ levels presumably lie above 5.6 Mev, since experiment shows no other scattering anomalies below this energy. So, it appears that these doublets are inverted and the splitting is large.[§]

§ *Note added in proof:* In the single particle approximation the reduced widths of the energy levels are approximately equal to $\hbar^2/\mu a$. (See reference 4.) On the basis of this analysis, the reduced widths of the $S_{\frac{1}{2}}$, $P_{\frac{3}{2}}$, and $D_{\frac{5}{2}}$ levels are 82 percent, 4.1 percent, and 24 percent of this value, respectively. The relatively small width of the $P_{\frac{3}{2}}$ level indicates that it is not a single particle level but

It is possible that one or more levels of high angular momentum or very small reduced width lie below 5.64 Mev, even though none was observed.[2] In the single-level approximation, the width of any level is inversely proportional to A_i^2 which increases rapidly with l. As the elastic scattering cross section was measured at 30-kev intervals away from the observed anomalies, such a level could have escaped detection.

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rather arises from the excitation of two or more nucleons. If such is the case, the above argument does not apply so far as the $P_{\frac{3}{2}}$ level is concerned.

The Molecular Structure of Methyl Alcohol

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A qualitative discussion of the near and far infrared spectrum of methyl alcohol shows that the rotational states, including the hindered rotation, may be well represented by a model consisting of a rigid hydroxyl and a rigid methyl group. These groups may perform a mutual rotation with respect to each other about the symmetry axis of the methyl group subject to a hindering potential which is assumed to have the form $V=\frac{1}{2}H(1-\cos3x)$ where x is the angle of mutual rotation. A series of lines in the microwave spectrum, discovered by Hershberger and Turkevich, have recently been measured with great accuracy by Coles who also determined their Stark splitting. The positive identification of these lines leads at once to an estimate of the barrier height H.

The wave equation for the rotation of methyl alcohol is obtained and the matrix elements of the hamiltonian are evaluated using the wave functions derived by Koehler and Dennison on the basis of a simplified model. Diagonalizing the hamiltonian yields the energy levels which are found to predict correctly the principal features of the microwave spectrum. A quantitative comparison serves to fix the moments and product of inertia to have the values, $A=34.28$, $C_1=1.236$ and $D=-0.107$ all times 10^{-40} g cm². The two components of the electric moment are determined, $\mu_{||}=0.893$ and $\mu_\perp=1.435\times10^{-18}$ esu. A relation is obtained between the barrier height H and the moment of inertia C_2 of the methyl group about its symmetry axis. Assuming C_2 to be equal to the methane moment of inertia, then $H=380$ cm⁻¹. If, in addition to taking a methane-like structure for the methyl group, it is assumed that the OH distance is the same as in water, namely 0.958A, one finds that (1) the CO distance is 1.421A, (2) the symmetry axis of the methyl group lies between the O and H atoms with the O displaced 0.084A from it and (3) the COH bond angle is 110° 15'. This latter angle is 5° 44' greater than the apex angle in water vapor.

INTRODUCTION

THE spectrum of methyl alcohol has been examined by a number of investigators. The region from 2.5μ to 26μ was mapped by Borden and Barker[1] and the principal fundamental vibration frequencies were identified. The spectrum from 20μ to 57μ was measured by Lawson and Randall[2] who found it to consist of an intense series of irregularly but closely spaced lines. These are undoubtedly connected with the torsional vibration or hindered rotation of the molecule. More recently the microwave spectrum has been explored. A series of lines around 25,000 Mc which, from the regularity of their spacing, must clearly have a common

origin, were discovered by Hershberger and Turkevich.[3] These lines were also observed by Dailey[4] and later were remeasured with high precison by Coles.[5] Coles not only found many more members of the series but also determined the number and spacing of the Stark components. Edwards, Gilliam, and Gordy[6] have measured a number of lines between 50,000 Mc and 35,000 Mc.

The general structure of methyl alcohol is fairly well known from chemical and spectroscopic evidence and is shown in Fig. 1. The methyl group is presumably very similar to the methyl group in methane or in the methyl

[1] A. Borden and E. F. Barker, J. Chem. Phys. 6, 553 (1938).
[2] J. R. Lawson, thesis, University of Michigan (1938).
[3] W. D. Hershberger and J. Turkevich, Phys. Rev. 71, 554 (1947).
[4] B. P. Dailey, Phys. Rev. 72, 84 (1947).
[5] D. K. Coles, Phys. Rev. 74, 1194 (1948).
[6] Edwards, Gilliam, and Gordy (to be published). We are very much indebted to Professor Gordy for sending us a preliminary account of their work.

halides where it is known that the CH distance is about 1.10A and the HCH angle is closely equal to the tetrahedral angle of 109° 28'. The distance between the carbon and oxygen has been estimated from electron diffraction measurements on similar molecules to be about 1.44A. There is little doubt but that the oxygen atom must lie close to the symmetry axis of the methyl group although not necessarily directly upon it. The symmetry axis may be defined as the line passing through the carbon atom and the center of gravity of the three hydrogen atoms. The OH distance is most probably of the same order as it is in the water molecule, namely, 0.958A and as a first approximation it is expected that the COH angle will be about equal to 105°, the apex angle in water.

The fundamental vibrations of methyl alcohol are 12 in number, of which one is to be associated with a torsional motion of the hydroxyl group with respect to the methyl group. This torsional motion has often been called a hindered rotation. Clearly, as the hydrogen of the hydroxyl group moves in a circle whose axis is the symmetry axis of the methyl group, it will encounter a potential with three identical minima. If the potential barriers separating the minima are sufficiently high, the hydrogen will oscillate with the torsional frequency. If the equal barriers are sufficiently low, the motion will approximate a free rotation of the hydroxyl group relative to the methyl group.

It was found by Borden and Barker[1] that, excluding the torsional frequency, the remaining fundamental frequencies are relatively high, the lowest being approximately 1000 cm^{-1}. The torsional frequency, as will appear from the present analysis, is only around 250 cm^{-1} and, consequently, the forces giving rise to the torsional oscillation are of the order of 16 times weaker than those producing the other fundamental vibrations. Thus, to a high degree of approximation in treating the problem of hindered rotation in methyl alcohol, one may consider that both the hydroxyl group and the methyl group are individually rigid and that their mutual motion consists only of a rotation of the one group relative to the other where the angle between the symmetry axis of the methyl group and the line of the hydroxyl group remains constant. The potential energy associated with this motion must be periodic and repeat itself upon a rotation through 120°. Since little is known concerning the detailed nature of such hindering potentials it is natural at the outset to assume the simple sinusoidal form, namely $V = \frac{1}{2}H(1 - \cos 3x)$ where x is the angle of mutual rotation. This form will be used throughout the present work and, while it is undoubtedly only approximately correct, it appears evident that the most important features of the spectrum can be well represented by it. A similar situation is encountered with the ammonia molecule, where the inversion levels are relatively independent of the precise form of the double minimum potential.

Among the early discussions of the theory of hindered

FIG. 1. The general structure of methyl alcohol.
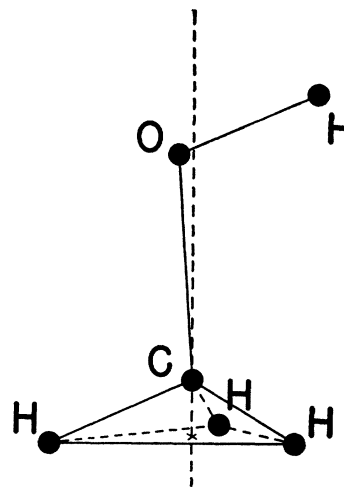
rotation are those by Nielsen,[7] and by Koehler and Dennison.[8] In the work of Koehler and Dennison the molecule was assumed for simplicity to consist of two symmetrical rotators having a common axis joining them. These rotators represented the hydroxyl and the methyl groups, and their moments of inertia along the symmetry axis were designated C_1 and C_2, respectively. In the present paper this simplifying assumption with regard to the hydroxyl group will not be employed but for a general understanding of the nature of the energy levels and for a qualitative estimate of the height of the barrier the Koehler-Dennison discussion will be sufficiently exact. They found that the rotational energy —including the hindered rotation—could be written as the sum of two terms $E = E_\alpha + E_\beta$, where

$$E_\beta = \hbar^2[(J^2 + J - K^2)/2A + K^2/2C],$$

and is thus equal to the usual rotational energy of a symmetrical top. A is defined as the moment of inertia about an axis which is perpendicular to the symmetry axis and which passes through the center of gravity of the molecule and $C = C_1 + C_2$. E_α represents the internal or hindered rotation contribution and consists of successive groups of levels, each group containing three levels identified by the quantum number $\tau = 1$, 2 or 3. The groups were denoted by the number $n = 0, 1, 2, \cdots$. The qualitative interpretation is that, when the barrier is relatively high, each group represents a vibrational energy level of the torsional oscillation. Thus their positions (for high barrier) are approximately given by $h\nu_t(n + \frac{1}{2})$, where ν_t is the torsional frequency. The fact that each group contains 3 levels is of course due to the threefold nature of the potential. The splitting of the levels in any group is a periodic function of the rotational quantum number, K, times the ratio of moments of inertia $C_1/(C_1 + C_2)$ but in order of magnitude it is equal to the exchange frequency between two minima. It is thus the analog of the inversion frequency in

[7] H. H. Nielsen, Phys. Rev. 40, 445 (1932).
[8] J. S. Koehler and D. M. Dennison, Phys. Rev. 57, 1006 (1940).

ammonia and consequently is a sensitive function of the barrier height.

The far infrared spectrum predicted by Koehler and Dennison was exceedingly complicated and to this extent only it agreed with the experimental results found by Lawson and Randall. It was so complex a function of the molecular constants, and the individual calculations were so tedious, that it did not seem practical to proceed further. The microwave spectrum has, however, furnished the means of evaluating the barrier height and the other molecular constants. The qualitative reasoning will be given before presenting the exact theory.

The lines observed by Hershberger and Turkevich,[3] Dailey,[4] and Coles,[5] belong to a series and their positions may be expressed as an analytic function of $J^2 + J$. An inspection of the structure of the energy levels of the molecule shows that there is only one type of transition which can give rise to a series of lines in this region. It is (expressed as an emission rather than as an absorption line) $J \to J$, $K \to K - 1$, $\tau \to \tau'$, $n = 0 \to 0$ and the series members correspond to $J = K$, $K+1$, $K+2$, etc. The Stark effect measurements of Coles show that the first line which lies at 24,934 Mc or 0.831 cm^{-1} has $J = 2$ and the series has been traced as high as $J = 30$. Since the series is analytic the position of a possible line with $J = 1$ can be predicted with great accuracy. No line is found at this point and one must conclude that the first member of the series corresponds to $J = 2 \to 2$. The K transition must therefore be $K = 2 \to 1$.

The frequency of the transition can be expressed as the sum of two terms $\nu = \nu_\alpha + \nu_\beta$, where ν_β is the contribution due to the usual rotational energy of a symmetrical top; namely, since $K = 2 \to 1$, $\nu_\beta = (3h/8\pi^2 c) \times (1/C - 1/A)$. The values of A and C, the moments of inertia for the entire molecule, may be estimated from the approximate dimensions given earlier and a substitution yields $\nu_\beta = 9.9$ cm^{-1} and therefore $\nu_\alpha = -9.1$ cm^{-1}. The situation is thus one in which the microwave lines result from a large positive term due to the usual rotation and on almost equally large negative term arising from the hindered rotation. An examination of the form of the hindered rotation levels shows that the selection rules (see reference 8) permit only one transition which results in a negative term. This is $\tau = 1 \to 2$.

The energy E_α, as is shown in reference 8, depends upon the quantum number K, upon the moments of inertia C_1 and C_2 and upon the barrier height, H. A rather crude initial estimate gives $C_1 = 1.43 \times 10^{-40}$ and $C_2 = 5.33 \times 10^{-40}$ and these lead to a barrier height $H = 325$ cm^{-1}. The value for barrier height just obtained is not an accurate one since a simplified theory and approximate moments of inertia have been used but it must be of the right order of magnitude. The crucial point in its derivation was the identification of the microwave lines. About this the Stark effect measurements leave little doubt. Further progress requires the development of a more exact theory. It will be shown that this theory predicts (1) the magnitude of the Stark

effect coefficients and (2) the spacing of the lines in the microwave series. Using the approximate values for C_1, C_2, and H it is found that both of these quantities agree qualitatively with the experimental results. It may be remarked that no agreement is obtained if the microwave lines are assumed to be due to a transition $K = 1 \to 2$ and $\tau = 2 \to 1$ with $\nu_\beta = -9.9$ and $\nu_\alpha = +10.7$ cm^{-1}; a possibility which up to now could not be excluded.

The following procedure will be adopted:

1. The methyl alcohol will be represented by a model consisting of a rigid hydroxyl and a rigid methyl group. It is assumed that the hydroxyl group can rotate about the symmetry axis of the methyl group subject to the potential $V = \frac{1}{2}H(1 - \cos 3x)$, where x is the angle of mutual rotation.

2. The kinetic energy will be derived and from this the Schroedinger wave equation obtained.

3. Matrix elements of the hamiltonian will be found using the wave functions of the simplified model employed by Koehler and Dennison. The matrix elements are all diagonal in the quantum number J but, in addition to the elements diagonal in K, possess elements where $K \to K \pm 1$ and $K \to K \pm 2$. Diagonalizing the hamiltonian yields the energy levels.

4. The predicted microwave spectrum will be compared with the observed spectrum for the purpose of obtaining values for the molecular constants.

KINETIC AND POTENTIAL ENERGIES

The kinetic energy of the model which has been chosen to represent the methyl alcohol molecule—namely, a rigid methyl group and a rigid hydroxyl group which may rotate with respect to each other—may be derived in the following manner. Consider two vectors ϱ_1 and ϱ_2 drawn from the center of gravity of the molecule (which for simplicity is assumed to be stationary) to the respective centers of gravity of the hydroxyl and methyl groups. Let r_i be a vector drawn from the center of gravity of the hydroxyl group to the mass m_i of that group. Let R_i be the corresponding vector from the center of gravity of the methyl group to the mass M_i. Let x, y, z and X, Y, Z be two sets of axes moving rigidly with the hydroxyl and methyl groups respectively and with origins at the centers of gravity of those groups. The Z axis is taken to be the symmetry axis of the methyl group and z is chosen to be parallel to Z. The oxygen and hydrogen atoms comprising the hydroxyl group are assumed to lie in the yz plane.

The angular velocities of the hydroxyl and methyl groups will be denoted by the vectors ω and Ω, respectively, and their components along the moving axes will be ω_x, ω_y, ω_z and Ω_X, Ω_Y, Ω_Z.

With these definitions the vector velocities of the individual particles in each group are, respectively,

$$\mathbf{v}_i = d\varrho_1/dt + \boldsymbol{\omega} \times \mathbf{r}_i, \quad \mathbf{V}_i = d\varrho_2/dt + \boldsymbol{\Omega} \times \mathbf{R}_i.$$

Since, from their definitions $\Sigma m_i \mathbf{r}_i = \Sigma M_i \mathbf{R}_i = 0$, twice the kinetic energy becomes

$$2T = \Sigma m_i (d\varrho_1/dt)^2 + \Sigma M_i (d\varrho_2/dt)^2$$
$$+ \Sigma m_i (\boldsymbol{\omega} \times \mathbf{r}_i)^2 + \Sigma M_i (\boldsymbol{\Omega} \times \mathbf{R}_i)^2.$$

The vector ϱ_1 has a constant length and lies in the zy plane. The angle which it makes with the OH line is a constant. Thus, ϱ_1 moves as though it were rigidly connected to the hydroxyl group. The velocity of the center of gravity of the entire molecule as seen from the moving x, y, z coordinate system is $(\boldsymbol{\omega} \times \varrho_1)$. This is, however, the negative of the velocity of the x, y, z origin as viewed from the center of gravity of the molecule. Therefore,

$$d\varrho_1/dt = -(\boldsymbol{\omega} \times \varrho_1).$$

From the definitions of ϱ_1 and ϱ_2 one has

$$\Sigma m_i \varrho_1 + \Sigma M_i \varrho_2 = 0,$$

and a substitution yields

$$2T = \Sigma m_i (\boldsymbol{\omega} \times \varrho_1)^2 + \Sigma M_i (\boldsymbol{\omega} \times \varrho_2)^2$$
$$+ \Sigma m_i (\boldsymbol{\omega} \times \mathbf{r}_i)^2 + \Sigma M_i (\boldsymbol{\Omega} \times \mathbf{R}_i)^2.$$

Since the z and Z axes are always parallel, $\omega_x^2 + \omega_y^2$ is necessarily equal to $\Omega_X^2 + \Omega_Y^2$. Expanding the above expression one obtains

$$2T = A(\Omega_X^2 + \Omega_Y^2) - (A - B)\omega_y^2$$
$$- 2D\omega_y\omega_z + C_1\omega_z^2 + C_2\Omega_Z^2.$$

The meaning of these moments and products of inertia are most easily seen by constructing a coordinate system ξ, η, ζ whose origin lies at the center of gravity of the entire molecule and whose axes are parallel to the axes xyz. If μ_i denotes a mass of either of the two groups, $A = \Sigma\mu_i(\eta_i^2 + \zeta_i^2)$ and is the moment of inertia of the molecule about the ξ axis. $B = \Sigma\mu_i(\xi_i^2 + \zeta_i^2)$ is the moment of inertia about the η axis. One may define $C = \Sigma\mu_i(\xi_i^2 + \eta_i^2)$ as the moment about the ζ axis. $D = \Sigma\mu_i\eta_i\zeta_i$ is the product of inertia with respect to the $\eta\zeta$ axes. $C_2 = \Sigma M_i(X_i^2 + Y_i^2)$ and is the moment of inertia of the methyl group along the Z or symmetry axis and $C_1 = C - C_2 = A - B$.

The orientation of the x, y, z axes which determine the position of the hydroxyl group may be expressed by means of the eulerian angles θ, ϕ_1, ψ and, as usual, one one obtains

$$\omega_x = \dot\theta \cos\phi_1 + \dot\psi \sin\theta \sin\phi_1,$$
$$\omega_y = -\dot\theta \sin\phi_1 + \dot\psi \sin\theta \cos\phi_1,$$
$$\omega_z = \dot\phi_1 + \dot\psi \cos\theta.$$

The eulerian angles which fix the orientation of the methyl group are θ, ϕ_2, ψ and, since the z and Z axes are always parallel, only differ from the earlier ones in the angle ϕ_2 which measures the rotation of the methyl group about its symmetry axis. The expressions for Ω_X, Ω_Y, and Ω_Z may be obtained from ω_x, ω_y, ω_z by merely introducing ϕ_2 instead of ϕ_1. A substitution now yields the kinetic energy as a function of θ, ψ, ϕ_1, ϕ_2, and their time derivatives.

The potential energy must be a periodic function of the relative rotation of the methyl and hydroxyl groups, that is, of $\phi_1 - \phi_2$ and must have a period of $2\pi/3$. As explained earlier, it is expected that the principal features of the spectrum will depend upon the periodic nature of the potential function and upon its general properties (such as the height of the barrier) but will be largely independent of any finer details. For this reason it is natural to choose the simple sinusoidal form,

$$V = \tfrac{1}{2}H[1 - \cos 3(\phi_1 - \phi_2)].$$

The wave equation may be obtained in the usual manner by expressing the laplacian in the curvilinear coordinates for which the metric is given by $2T$. After writing out the laplacian, making the substitutions,

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

and inserting the hindering potential, the wave equation takes the following form:

$$\mathrm{I}\left\{
\begin{aligned}
&\frac{(A+B)C_1 - D^2}{2A(BC_1 - D^2)}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial u}{\partial\theta}\right) + \cot^2\theta\frac{\partial^2 u}{\partial\phi^2}\right.\\
&\left. - \frac{2\cot\theta}{\sin\theta}\frac{\partial^2 u}{\partial\phi\partial\psi} + \frac{1}{\sin^2\theta}\frac{\partial^2 u}{\partial\psi^2}\right] + \frac{1}{C}\frac{\partial^2 u}{\partial\phi^2} + \frac{C}{C_1 C_2}\frac{\partial^2 u}{\partial x^2}\\
&+ \frac{2}{\hbar^2}\left[E - \frac{H}{2}(1 - \cos 3x)\right]u,
\end{aligned}
\right.$$

$$\mathrm{II}\left\{ + \frac{D^2}{C_1(BC_1 - D^2)}\left[\frac{C_1^2}{C^2}\frac{\partial^2 u}{\partial\phi^2} + \frac{2C_1}{C}\frac{\partial^2 u}{\partial\phi\partial x} + \frac{\partial^2 u}{\partial x^2}\right],\right.$$

$$\mathrm{III}\left\{
\begin{aligned}
&+ \frac{2D}{BC_1 - D^2}\left[\left(\frac{\partial^2 u}{\partial\psi\partial x} + \frac{C_1}{C}\frac{\partial^2 u}{\partial\phi\partial\psi} - \cos\theta\frac{\partial^2 u}{\partial\phi\partial x}\right.\right.\\
&\left.- \frac{C_1}{C}\cos\theta\frac{\partial^2 u}{\partial\phi^2} - \frac{1}{2}\sin\theta\frac{\partial u}{\partial\theta}\right)\frac{\cos(\phi + (C_2/C)x)}{\sin\theta}\\
&- \left(\frac{\partial^2 u}{\partial\theta\partial x} + \frac{C_1}{C}\frac{\partial^2 u}{\partial\theta\partial\phi} + \frac{1}{2\sin\theta}\frac{\partial u}{\partial\psi} - \frac{\cos\theta}{2\sin\theta}\frac{\partial u}{\partial\phi}\right)\\
&\left.\times\sin\left(\phi + \frac{C_2}{C}x\right)\right],
\end{aligned}
\right.$$

$$\mathrm{IV}\left\{
\begin{aligned}
&+ \frac{(A-B)C_1 + D^2}{2A(BC_1 - D^2)}\left[\left(\frac{1}{\sin^2\theta}\frac{\partial^2 u}{\partial\psi^2} - \frac{\partial^2 u}{\partial\theta^2} + \cot^2\theta\frac{\partial^2 u}{\partial\phi^2}\right.\right.\\
&\left.- \frac{2\cot\theta}{\sin\theta}\frac{\partial^2 u}{\partial\phi\partial\psi} + \cot\theta\frac{\partial u}{\partial\theta}\right)\cos 2\left(\phi + \frac{C_2}{C}x\right)\\
&+ \left(2\cot\theta\frac{\partial^2 u}{\partial\theta\partial\phi} - \frac{2}{\sin\theta}\frac{\partial^2 u}{\partial\theta\partial\psi} + \frac{2\cot\theta}{\sin\theta}\frac{\partial u}{\partial\psi}\right.\\
&\left.\left.- (1 + 2\cot^2\theta)\frac{\partial u}{\partial\phi}\right)\sin 2\left(\phi + \frac{C_2}{C}x\right)\right] = 0.
\end{aligned}
\right.$$

The boundary conditions governing the solutions of the wave equation are the same as those which were applicable to the simpler model studied by Koehler and Dennison[8] and are that the functions must remain finite at the poles $\theta=0$ or π and that they must be periodic with period 2π in the angles ψ, ϕ_1, and ϕ_2.

It will be noted that the wave equation has been divided into four groups of terms. Group I when set equal to zero is identical with the wave equation discussed by Koehler and Dennison providing their moment of inertia A is replaced by

$$2A(BC_1-D^2)/(AC_1+BC_1-D^2).$$

Its solutions, subject to the above boundary conditions, may be written,

$$u=\frac{1}{2\pi}e^{iK\phi}e^{iM\psi}\Theta_{JKM}\exp(-iC_1Kx/C)P_{(x)}{}^{K\tau n}.$$

The quantity $e^{iK\phi}e^{iM\psi}\Theta_{JKM}$ is the usual symmetric top wave function. $M_{(x)}=\exp(-iC_1Kx/C)P_{(x)}{}^{K\tau n}$ satisfies the equation

$$d^2M/dx^2+(R+S\cos3x)M=0,$$

where

$$R=(2C_1C_2/C\hbar^2)(E^{K\tau n}-H/2),\quad S=C_1C_2H/C\hbar^2.$$

The total energy is equal to the sum of $E^{K\tau n}$ and E^{JK} where the latter is the symmetrical top energy,

$$E^{JK}=[\hbar^2(AC_1+BC_1-D^2)/4A(BC_1-D^2)]$$
$$\times(J^2+J-K^2)+\hbar^2K^2/2C.$$

The boundary conditions require $P_{(x)}{}^{K\tau n}$ to be periodic in x with period 2π and it is customary to express it as

$$P_{(x)}{}^{K\tau\eta}=\sum_{-\infty}^{+\infty}a_me^{imx},$$

where m is an integer that may be shown to increase in steps of 3. The first kind where $\tau=1$ has a series where m takes on the values $\cdots-6,\ -3,\ 0,\ 3,\ 6,\ \cdots$. When $\tau=2$, m may be $\cdots-4,\ -1,\ 2,\ 5,\ \cdots$ and when $\tau=3$, $m=\cdots-5,\ -2,\ 1,\ 4,\ \cdots$. Both $E^{K\tau n}$ and the a_m are determined through finding the roots of continued fractions.[9]

The matrix elements of the hamiltonian corresponding to the complete wave equation will now be evaluated using the wave functions which are the solutions of the Group I terms. Since we shall be interested in the Stark effect it will be convenient to add these terms to the hamiltonian. They are

$$\mu_{\parallel}\mathscr{E}\cos\theta+\mu_{\perp}\mathscr{E}\sin\theta\cos\phi_1,$$

where

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

$\mathscr{E}$ is the electric field intensity and $\mu_{\parallel}$ and $\mu_{\perp}$ are the respective components of the permanent electric moment of the molecule, parallel and perpendicular to the symmetry axis of the methyl group. $\mu_{\parallel}\mathscr{E}\cos\theta$ belongs with the Group I terms and $\mu_{\perp}\mathscr{E}\sin\theta\cos\phi_1$ with Group III.

The Group I terms yield elements of the hamiltonian which are diagonal in all four quantum numbers. Since the Group II terms do not contain θ, ϕ or x, explicitly, they are diagonal in JK and τ but need not be diagonal in n. Each term of Group III contains either the sine or cosine of $\phi+C_2x/C$ and will therefore connect states where $K\rightarrow K\pm1$. Similarly Group IV terms connect states where $K\rightarrow K\pm2$. The actual evaluation of the matrix elements may be performed through the known properties of the symmetric top wave functions (see for example Reiche and Rademaker).[10] Assembling these results one obtains

$$H_{JK\tau n}^{JK\tau n}=\hbar^2\Big[\{(AC_1+BC_1-D^2)(J^2+J-K^2)/4A(BC_1-D^2)\}+K^2/2C$$

$$-(D^2/2C_1(BC_1-D^2))\int_0^{2\pi}(P^{K\tau n})^*\frac{d^2}{dx^2}P^{K\tau n}dx\Big]+E^{K\tau n}+\mu_{\parallel}\mathscr{E}KM/(J^2+J),$$

$$H_{JK\tau n'}^{JK\tau n}=-[\hbar^2D^2/2C_1(BC_1-D^2)]\int_0^{2\pi}(P^{K\tau n})^*\frac{d^2}{dx^2}P^{K\tau n'}dx,$$

where $n'\neq n$

$$H_{JK+1\tau'n'}^{J\ K\ \tau\ n}=\Big\{[\hbar^2D/2(BC_1-D^2)]\int_0^{2\pi}\Big[\frac{e^{-ix}}{i}(P^{K\tau n})^*\frac{d}{dx}P^{K+1\tau'n'}-\frac{1}{2}e^{-ix}(P^{K\tau n})^*P^{K+1\tau'n'}\Big]dx$$

$$+[\mu_{\perp}\mathscr{E}M/2(J^2+J)]\int_0^{2\pi}e^{-ix}(P^{K\tau n})^*P^{K+1\tau'n'}dx\Big\}[(J+K+1)(J-K)]^{\frac{1}{2}},$$

$$H_{JK+2\tau'n'}^{J\ K\ \tau\ n}=[\hbar^2(AC_1-BC_1+D^2)/8A(BC_1-D^2)][(J-K)(J-K-1)(J+K+1)(J+K+2)]^{\frac{1}{2}}$$

$$\times\int_0^{2\pi}(P^{K\tau n})^*e^{-2ix}P^{K+2\tau'n'}dx.$$

[9] In the formulas (16), (17), and (18) given by Koehler and Dennison (see reference 8), the right-hand side of the equations should have a positive and not a negative sign.

[10] F. Reiche and H. Rademaker, Z. Physik. 41, 453 (1927).

In these formulas there is no restriction on the values of n' but the only nonvanishing elements will be those for which τ' obeys the following rules. For the elements where $K \rightarrow K+1$ the possible τ connections are $1 \rightarrow 3$, $3 \rightarrow 2$ and $2 \rightarrow 1$. For the elements where $K \rightarrow K+2$ the nonvanishing elements are those where τ goes from $1 \rightarrow 2$, $2 \rightarrow 3$, or $3 \rightarrow 1$.

The energy levels of the system are found as usual by calculating the roots of the determinant

$$|H_{JK'\tau'n'}^{JK\tau n} - E\delta_{K'}{}^{K}\delta_{\tau'}{}^{\tau}\delta_{n'}{}^{n}| = 0.$$

The τ connections given above have as their consequence that the energy determinant factors into three determinants. These may be designated by listing the possible K and τ values which characterize their diagonal terms.

$$
\begin{array}{llllllllllll}
K= & \cdots & -4 & -3 & -2 & -1 & 0 & 1 & 2 & 3 & 4 \cdots, \\
\text{Determinant 1: } \tau= & \cdots & 1 & 3 & 2 & 1 & 3 & 2 & 1 & 3 & 2 \cdots, \\
\text{Determinant 2: } \tau= & \cdots & 3 & 2 & 1 & 3 & 2 & 1 & 3 & 2 & 1 \cdots, \\
\text{Determinant 3: } \tau= & \cdots & 2 & 1 & 3 & 2 & 1 & 3 & 2 & 1 & 3 \cdots.
\end{array}
$$

From the definition of the quantum number τ (see reference 8) the states K, $\tau = 1, 2, 3$, are, respectively, identical with the states $-K$, $\tau = 1, 3, 2$. For this reason the roots of determinant 1 are identical with those of determinant 2 and the levels so found are therefore all doubly degenerate. An examination of the symmetry properties of the molecule shows that they belong to the class E and that consequently their degeneracy cannot be removed by any perturbation having threefold symmetry.

The roots of determinant 3, with the exception of the root corresponding to $K=0$, $\tau = 1$ which is single, all occur in pairs the members of which may be shown to belong to the symmetry classes A_1 and A_2. If the asymmetry of the molecule is small, the separation of the levels belonging to a pair becomes very small and decreases rapidly as K increases.

The solution which has been obtained for the model consisting of a rigid hydroxyl and a rigid methyl group which are coupled through a hindered rotation may be compared with the results found by Koehler and Dennison for the model in which both groups were rigid symmetric rotators. There are five principal differences all of which, in the case of methyl alcohol, where $(A-B)$ and D are small compared with A, have only minor effects upon the infrared spectrum but which assume importance in considering the details of the microwave spectrum. They are:

1. In that part of the energy which was described as the rotational energy of a symmetrical top $1/A$ has been replaced by

$$\frac{AC_1 + BC_1 - D^2}{2A(BC_1 - D^2)} = \frac{1}{A} + \frac{C_1^2 + D^2}{A(BC_1 - D^2)}.$$

2. The diagonal element has been augmented by the term

$$-[\hbar^2 D^2 / 2C_1(BC_1 - D^2)] \int_0^{2\pi} (P^{K\tau n})^* \frac{d^2}{dx^2} P^{K\tau n} dx.$$

For methyl alcohol the coefficient, when divided by hc, is of the order of 0.01 cm^{-1}. The integral for the state $K=0$, $\tau = 1$, $n=0$ is of the order of -1.5 and its absolute value increases with K so that at $K=10$ it is approximately -7.

3. There now exists an off-diagonal term connecting the states K and $K \pm 1$. For moderate values of J (10 or less) the numerical value of this term is much less than the difference between the diagonal elements of the states it connects. The usual approximation methods show that these off-diagonal elements contribute a term to the energy which is mainly proportional to $J^2 + J$ and which depends upon the quantum numbers K, τ and n.

4. The off-diagonal elements connecting the states K and $K \pm 2$ have much the same properties as those just discussed and they will yield a term in the energy that is mainly proportional to $(J^2 + J)^2$.

Qualitatively, effects 3 and 4 are just what are necessary to explain the series of lines observed by Coles[5] since their members may be expressed as a power series in which the terms involving $(J^2 + J)$ and $(J^2 + J)^2$ are of dominant importance.

5. The energy levels $K=1$, $\tau = 3$; $K=2$, $\tau = 2$; $K=3$, $\tau = 1$; $K=4$, $\tau = 3$; etc., have become doublets with a spacing which decreases rapidly for large K values but which increases with J. This particular effect is the exact analog of the fact that the energy levels of the symmetrical top with the exception of $K=0$, become double if the top becomes asymmetric. Since neither of the levels $K=2$, $\tau = 1$ or $K=1$, $\tau = 2$ belong to the above class, the lines of the microwave series measured by Coles would not be expected to be double and are not observed to be.

It should be remarked that the matrix elements of the hamiltonian do degenerate properly to the elements of the hamiltonian for a rigid rotator when the barrier height goes to infinity. This degeneration is not immediately self-evident since the former elements contain C_1 while the latter contain only the total moment of inertia C. The point is that the diagonal elements (as the barrier becomes very high) contain the large term $h\nu_t(n+\frac{1}{2})$, where ν_t is the torsional frequency. The integrals occurring in the off-diagonal elements connecting n to $n \pm 1$ are proportional to $\nu_t^{\frac{1}{2}}$. The diagonalization process involves dividing the squares of the off diagonal elements by the difference of the diagonal elements they connect and thereby a number of finite terms are introduced which bring about the desired degeneration.

INTERPRETATION OF THE MICROWAVE SPECTRUM AND EVALUATION OF MOLECULAR CONSTANTS

It is expected that the first line of the normal rotation series, namely $J=1\rightarrow0$, $K=0\rightarrow0$, $\tau=1\rightarrow1$, $2\rightarrow2$ or $3\rightarrow3$, should fall in the region of 48,000 to 50,000 Mc. Edwards, Gilliam, and Gordy[6] have measured several lines in this neighborhood. A study of the corresponding lines due to isotopic molecules of methyl alcohol (to be reported later) appears to show that the strong line found at 49,867.2 Mc can be uniquely assigned to this transition. The only off-diagonal terms which might contribute to this transition are small and to a high order of approximation,

$$(h/8\pi^2)[(AC_1+BC_1-D^2)/A(BC_1-D^2)]=49,867.2\times10^6.$$

The small off-diagonal terms referred to predict that this line should be a doublet corresponding to the transitions $\tau=1\rightarrow1$ and to the two coincident transitions $\tau=2\rightarrow2$ and $3\rightarrow3$. An estimate of the doublet separation yields a value of only a fraction of a megacycle and consequently it might well have escaped observation.

It is convenient to consider next the Stark effect to which the diagonal elements furnish the term $\mu_{||}\mathscr{E}KM/(J^2+J)$. The process of diagonalizing the hamiltonian will involve squaring the off-diagonal elements and the cross product from $|H^{J\;K\;\tau\;n}_{JK\pm1\tau'n'}|^2$, gives rise to a first-order Stark energy which may be shown to have the form

$$[\tfrac{1}{2}\hbar^2D/(BC_1-D^2)][\mu_\perp\mathscr{E}M/(J^2+J)][f_1+(J^2+J)f_2].$$

The coefficients f_1 and f_2 are functions of K, τ and n and depend upon the indicated integrals containing $P_{(x)}^{K\tau n}$ and upon the resonance denominators.

The problem of evaluating the molecular constants for methyl alcohol is one of successive approximation and after one or two attempts the following trial values were selected,[11] $C_1=1.24\times10^{-40}$, $C_2=5.34\times10^{-40}$ and $H=368$ cm^{-1}. The integrals entering f_1 and f_2 are found to be quite insensitive to small changes in the constants and the most important of the resonance denominators is determined by the microwave lines themselves and, consequently, is independent of C_1, C_2 and H.

The microwave lines in question correspond to the transitions $J\rightarrow J$, $M\rightarrow M$ and K, τ, $n=2$, 1, $0\rightarrow1$, 2, 0. The first-order Stark frequencies for these transitions have been calculated using the trial values of the constants and are given by the formula,

$$\mu_{||}\mathscr{E}M/h(J^2+J)+[D/\{8\pi^2c(BC_1-D^2)\}]$$
$$\times[\mu_\perp\mathscr{E}M/(J^2+J)][0.105(J^2+J)-0.152].$$

The Stark frequencies measured by Coles may be ex-

pressed in cycles per second and are well represented by,[12]

$$[0.0111+0.877/(J^2+J)]M\mathscr{E}\times10^{-18}/h.$$

Identifying the corresponding terms one obtains,

$$\mu_{||}=0.893\times10^{-18}\text{ esu},$$

$$\mu_\perp hD/8\pi^2c\mu_{||}(BC_1-D^2)=0.1184\text{ cm}^{-1}.$$

The total electric moment of methyl alcohol has been meaxured by Kubo[13] and found to have the value 1.69 $\times10^{-18}$ esu and consequently, the absolute value of $\mu_\perp$ should be 1.435×10^{-18}. Further,

$$hD/8\pi^2c(BC_1-D^2)=-0.07368\text{ cm}^{-1}.$$

The table of atomic electronegativities shows that the component of the electric moment perpendicular to the axis lies along the positive y axis while the parallel component lies along the negative z axis and therefore $\mu_\perp/\mu_{||}$ in our notation, is negative. For this reason the Stark effect measurements demand that the product of inertia D must be negative.

It is interesting to calculate the components of the electric moment from the table of bond moments given by Pauling.[14] Assuming that the bond angle COH is 105° as in water vapor these yield $\mu_\perp=1.46$, and $\mu_{||}=-0.81\times10^{-18}$ esu. The total moment would then be 1.67×10^{-18} esu. The agreement between these approximate values and the Stark effects results is remarkably good.

The positions of the lines observed by Coles may be expressed by means of a power series in (J^2+J). The lines up through $J=8$ are accurately represented by

$$\nu=\nu_0+a(J^2+J)+b(J^2+J)^2+c(J^2+J)^3+d(J^2+J)^4$$

where, in megacycles, $\nu_0=24,948.13$, $c=-0.4094\times10^{-4}$, $a=-2.9656$, $d=-0.3168\times10^{-6}$, and $b=0.11258$.

The diagonalization of the hamiltonian gives rise, as mentioned earlier to two sets of terms, one proportional to J^2+J and the other to $(J^2+J)^2$. These results are correct for values of J where the magnitude of the off-diagonal elements is much smaller than the difference between the diagonal terms they connect. This condition obtains for J less than 10, and the dominant terms expressing the positions of the lines are indeed seen to be those proportional to (J^2+J) and to $(J^2+J)^2$.

It will prove convenient to examine first the contribution from the off diagonal terms for which $K\rightarrow K$ ±2. Their evaluation requires the calculation of the various integrals

$$\int_0^{2\pi}(P^{K\tau n})^*e^{-2ix}P^{K+2\tau'n'}dx$$

---

[11] The values $h=6.624\times10^{-27}$ and $C=2.99776\times10^{10}$ were used in the calculations.

[12] The figures shown here differ by about 2 percent from those given in reference 5 and represent Coles' latest values. We wish to thank Dr. Coles and his associates for many helpful discussions and for keeping us fully informed on the progress of their work.

[13] M. Kubo, Sci. Papers, Inst. Phys. Chem. Research Tokyo 26, 242 (1935).

[14] L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York 1939), p. 68.

as well as the diagonal elements in order to obtain the resonance denominators. All of these quantities depend upon the molecular constants C_1, C_2, and H but fortunately again they are not sensitively dependent. Using the trial values given earlier the energy levels and fourier coefficients of $P^{K\tau n}$ were calculated and the contribution from the off-diagonal elements $K \rightarrow K \pm 2$ were obtained. The final result for the transition in question, namely $K\tau n = 210 \rightarrow 120$ was, in cm^{-1},

$$\Delta \nu = \left[\frac{h(C_1{}^2 + D^2)}{32\pi^2 cA(BC_1 - D^2)} \right]^2 [0.0635(J^2 + J)^2$$

$$- 0.241(J^2 + J) - 0.662].$$

The coefficient b may be expressed in cm^{-1} and upon equating this to the first term in the above formula, one finds

$$\frac{h(C_1{}^2 + D^2)}{32\pi^2 cA(BC_1 - D^2)} = 7.691 \times 10^{-3} \text{ cm}^{-1}.$$

The experimental data have now been made to yield three relations involving the three constants A, $C_1 = A - B$ and D. The numerical solution for these quantities gives,

$$A = 34.281 \times 10^{-40}, \quad C_1 = 1.236 \times 10^{-40},$$

$$D = -0.107 \times 10^{-40} \text{ g cm}^2.$$

The accuracy of the determination will be discussed later.

The coefficient of the $J^2 + J$ term in the series observed by Coles cannot be utilized directly for the evaluation of the moments of inertia. The reason for this is that it depends upon three effects, only two of which can be calculated with any exactness. These are (1) the $J^2 + J$ contribution coming from the off-diagonal elements $K \rightarrow K \pm 2$. From the above formula, this has the numerical value -0.43 Mc, (2) The off-diagonal elements of the hamiltonian $K \rightarrow K \pm 1$ can be calculated using the trial values of $C_1 C_2$ and H. These result in an addition to the frequency of (in cm^{-1}),

$$[hD/8\pi^2 c(BC_1 - D^2)]^2[-0.0052(J^2 + J) + 0.055].$$

Using the values for the moments of inertia this becomes, in megacycles,

$$-0.85(J^2 + J) + 8.9.$$

The sum of these two contributions falls short of the experimental constant a by 1.70 Mc and is due to (3) the centrifugal stretching. This effect is best understood by considering a rotation of the molecule essentially about the A or B axes, that is $K \ll J$. A centrifugal force proportional to $J^2 + J$ will attempt, among other things, to increase the HOC angle. An increase of this angle will presumably lower the potential barrier slightly since for values of the angle around 180° the barrier goes to zero. A decrease in the barrier height

increases the distance between the hindered rotation levels E^{210} and E^{120}. Since this is a negative contribution to the microwave lines in question the effect will be to displace the lines towards smaller frequencies and since the change in the angle and hence in the barrier height is very small it will be proportional to $J^2 + J$. An order of magnitude estimate can be made in the following manner. From the frequency of the vibration resulting from the change in the HOC bond angle the bond angle force constant may be obtained. Balancing this against the centrifugal force the distortion of the angle $\delta\alpha$ is found. Making the rather crude assumption that the proportional change in the hindered rotation levels is equal to the proportional change in the angle, that is, to $\delta\alpha/(180° - \alpha_0)$ one obtains that the lines will be displaced by the amount $-2(J^2 + J)$ Mc; a result which is consistent with the $-1.70(J^2 + J)$ Mc cited above.

The last and most important step in the cycle of calculations will be to use the origin of the microwave series, ν_0 to provide a relation between the moments of inertia and the barrier height. The difference between the diagonal elements for which $JK\tau n = J210$ and $J120$ is equal to ν_0 minus the small constant terms 8.93 and -1.18 Mc arising from the respective off-diagonal elements $K \rightarrow K \pm 1$ and $K \rightarrow K \pm 2$. This quantity is 24,940.38 Mc which, for uniformity with the previous expressions, will be expressed in cm^{-1}:

$$0.83197 = (h/8\pi^2 c)\left[3/C - \frac{3(AC_1 + BC_1 - D^2)}{2A(BC_1 - D^2)} \right.$$

$$- (D^2/(BC_1 - D^2)C_1)\left(\int_0^{2\pi} (P^{210})^* \frac{d^2}{dx^2} P^{210} dx \right.$$

$$\left. - \int_0^{2\pi} (P^{120})^* \frac{d^2}{dx^2} P^{120} dx \right) \Bigg] + (E^{210} - E^{120})/hc.$$

The two integrals in the above expression have been calculated using the trial values for C_1, C_2, and H mentioned earlier and are equal to -1.662 and -2.444, respectively. They are not critically dependent upon the constants and in any case the magnitude of the whole term is small being only -0.00501 cm^{-1}. Substituting for the moments of inertia A, C_1, and D one obtains

$$3h/8\pi^2 cC + (E^{210} - E^{120})/hc = 3.33220 \text{ cm}^{-1}.$$

There are still two unknown constants, the barrier height H and the moment of inertia of the methyl group about its symmetry axis, C_2. The latter quantity has the value 5.328×10^{-40} g cm^2 in methane and this has been chosen as the point about which to make an expansion. The energy difference $E^{120} - E^{210}$ was calculated for a number of values of its variables, namely C_1/C and $\alpha = 2\pi^2 cC_1 C_2 H/hC$ and in the region of interest,

$$(E^{120} - E^{210})/hc = 9.7386 \text{ cm}^{-1} - (0.671)(\alpha^2 - 11.2)$$

$$+ 4.12(C_1/C - 0.19).$$

TABLE I. Barrier height H for several values of moment of inertia C_2.

$C_2 \times 10^{40}$	H, cm^{-1}
5.428	383.3
5.328	380.2
5.228	377.0

Using now the relation imposed by the origin of the microwave series, Table I has been constructed.

There is no reason to suppose that C_2 is precisely equal to the methane moment of inertia, and in fact measurements on other molecules containing methyl groups (such as the methyl halides) have revealed variations in C_2 of as much as 0.17×10^{-40}. It is however evident that H is not unduly sensitive to C_2, and in the remainder of this paper for purposes of discussion C_2 will be arbitrarily taken to be 5.328×10^{-40}.

DISCUSSION OF THE MOLECULAR CONSTANTS

The methyl alcohol constants as determined from the microwave spectrum are $A = 34.28 \times 10^{-40}$, $H = 380$ cm^{-1}, $C_1 = 1.236$, $\mu_{11} = 0.893 \times 10^{-18}$ esu, $D = -0.107$, $\mu_\perp = 1.435 \times 10^{-18}$, $C_2 = 5.328$ (assumed).

Since the microwave line at 49,867.2 Mc is, in the main, determined by A only, it is estimated that the value given above is probably not in error by more than a few tenths of a percent, provided of course that the microwave line has been properly identified. C_1 and D, on the other hand, depend more intimately upon the hindered rotation energies and matrix elements which are less well known since among other things the use of a sinusoidal potential function is only an assumption, although a plausible one. It is probable that C_1 and D are correct to within a few percent. It should be remarked that the moments and products of inertia given here are the effective ones for the normal vibrational state and not the equilibrium moments and products which would require many additional data for their determination.

The three quantities A, C_1, and D are, of course, quite insufficient for a determination of the six structural parameters of the molecule. If, however, the dimensions of the methyl group and of the hydroxyl group are assumed to be known, it is possible from the moments and product of inertia to fix the relative position of one group with respect to the other. In conformity with the somewhat arbitrary choice that has been made for C_2, the methyl group will be taken to have a methane like structure, that is, the CH distance will be set equal to 1.093A and the HCH angle will be 109° 28'.

Some information on the hydroxyl dimension may be obtained from a consideration of the vibration frequencies. The OH stretching frequency in methyl alcohol has been identified by Borden and Barker[1] and observed to lie at 3683 cm^{-1}. From the known force constants of the water molecule[15] one may calculate the vibration frequency to be associated with OH. After making an appropriate compensation for the effect of the anharmonic terms in the potential one obtains 3660 cm^{-1}. From Badger's rule this close equality of the frequencies would indicate that the OH equilibrium distance in methyl alcohol should not differ appreciably from its value in water, namely 0.958A. Assuming this to be the case, the quantities A, C_1, and D lead to the following results.

1. The symmetry axis of the methyl group, which was defined as the line determined by the carbon atom and the center of gravity of the three hydrogens, falls between the oxygen and the hydrogen of the hydroxyl group. The distance of the oxygen from the symmetry axis is 0.084A. This result depends principally upon the product of inertia D and in fact to a large extent upon the fact that D is small and negative. It is therefore considered to be quite reliable.

2. The COH angle has the value 110° 15' and is, in the main determined by C_1, D, and the assumption regarding the OH distance. It is appreciably, but perhaps not unreasonably, larger than the apex angle in water vapor[15] of 104° 31'. One might speculate that the large COH angle may be connected with the fact that the hindering potential barrier is somewhat lower than was originally anticipated.

3. The CO distance is found to be 1.421A. This figure depends upon the moments and products of inertia, upon the OH distance and the dimensions of the methyl group, and consequently is not as certain as one would wish.

The machinery that has been developed for obtaining the rotational energy levels of the methyl alcohol molecule is unfortunately very cumbersome. In an effort to gain an over-all picture of the levels it may be pointed out that by far the largest part of the energy comes from the diagonal terms of the hamiltonian and, of these, the expression

$$-[\hbar^2 D^2 / 2C_1(BC_1 - D^2)] \int_0^{2\pi} (P^{K\tau n})* \frac{d^2}{dx^2} P^{K\tau n} dx$$

is very small and may often be neglected. The remaining terms may be divided into the rotational energy of a symmetrical top and an internal rotation $E^{K\tau n}$. Using the numerical constants for the moments and products of inertia, the former may be expressed in wave numbers and becomes

$$0.83174(J^2 + J - K^2) + 4.2638K^2.$$

The internal rotation energy is a periodic function of $2\pi C_1 K / 3C$ and hence may be expanded as a fourier series in the angle γ which has here the numerical value $\gamma = (22.589)°K$. For the levels where $\tau = 1$ and $n = 0$, the internal energy in wave numbers has been calculated

[15] B. T. Darling and D. M. Dennison, Phys. Rev. 57, 128 (1940).

to be

$$E^{K10} = 136.3958 - 6.2785 \cos\gamma$$

$$+ 0.2507 \cos2\gamma - 0.0190 \cos3\gamma.$$

The remaining levels of this group, namely those for which $\tau = 2$ and 3 and $n = 0$, may be found by increasing γ by 120° and by 240°, respectively.

The higher internal energy levels cannot be determined with great accuracy at present, since these levels are near or above the top of the potential barrier and will depend to a larger extent upon the exact form of the hindering potential. The following formulas, which have been calculated for a sinusoidal potential, can only be considered as a guide to the true positions of the levels.

$$E^{K11} = 368.9 + 48.6 \cos\gamma + 9.1 \cos2\gamma + 2.7 \cos3\gamma,$$

$$E^{K12} = 608 - 124 \cos\gamma + 17 \cos2\gamma - 12 \cos3\gamma.$$

It must be emphasized that the values just given for the symmetrical top and the hindered rotation energies, as well as the figures for the molecular dimensions and barrier height, are dependent upon the moment of inertia C_2 and therefore must be viewed as provisional. Since it is unlikely that C_2 could differ from the methane moment of inertia by more than a few percent, it is believed that they are, at any rate, qualitatively correct.

The theory of the rotation of the methyl alcohol molecule as developed in the present paper appears to be successful in that it correctly predicts the principal features of the microwave spectrum and of the Stark splitting of the lines. The structural constants which have been derived from the experimental data are all reasonable. It would, however, be desirable to make further comparisons of the predictions of the theory with experimental observations in the hope of obtaining better values for the constants, of investigating the exact form of the hindering potential, and of finding a number of self-consistency checks. Two series of researches are being currently pursued with these purposes in mind. (1) The far infrared spectrum of methyl alcohol has been mapped from 22μ to 200μ. The entire region is found to be filled with intense lines whose spacing, while irregular, is of the order of from 1 to 1.5 cm^{-1}. It is believed that, by making use of the theory, most of these lines can be identified and the energy levels determined. Since the energy levels for $n = 0, 1, 2$, and probably 3 are well populated at room temperature, the complete rotation spectrum must involve many transitions and is understandably complex. (2) Recently the microwave spectra of the isotopic methyl alcohol molecules with C^{13}, O^{18}, and deuterium have been measured. These data together with the correct identification of some of the other microwave lines which have been observed and which do not belong to the series considered hitherto, should provide many checks on the validity of the theory.