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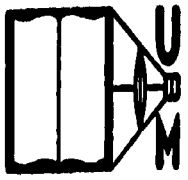
TITLE THE METHYL ALCOHOL MOLECULE AND ITS MICROWAVE SPECTRUM

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THE METHYL ALCOHOL MOLECULE
and
ITS MICROWAVE SPECTRUM

by

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of the requirements for the degree of
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CHAPTER I

INTRODUCTION

The methyl alcohol molecule, CH_3OH, has been the subject of numerous investigations, both experimental and theoretical. Among the important experimental researches are those by Borden and Barker[1] who examined the infra-red spectrum from 2.5μ to 26 μ, by Coles[2] and by Hughes, Good and Coles[3] who investigated the microwave spectrum from 17,000 to 38,000 m.c./sec., and by Edwards, Gilliam, and Gordy[4] who examined the microwave region from 36,000 to 50,000 m.c./sec.

The theoretical discussions which have been most used in this thesis are those of Koehler and Dennison[5], and of Burkhard and Dennison[6]. A brief description of these papers is given in the following paragraphs, reserving for later sections a more detailed discussion.

The paper of Koehler and Dennison[5] deals with what may be called the symmetrical model of methyl alcohol in which both the OH and CH_3 groups of the molecule are regarded as symmetrical rotators, the two groups rotating about a common axis of symmetry subject to a hindering potential $V = \frac{H}{2}(1 - \cos 3x)$. Here x is the angle of rotation of one rotator with respect to the other, and H is the so-called barrier height of the hindering potential. On this basis the theory of the hindered rotator

is developed, and the general appearance of various infra-red bands is obtained. Because of the limitation of the theory and because of lack of sufficient empirical data at the time, however, Koehler and Dennison were not able to obtain either the structural constants of the molecule or a good value for the height of the potential barrier H.

The extension of the theory to the case in which the OH group is considered to be an asymmetric rotator, and the system subject to the same type of potential as above, was accomplished by Burkhard and Dennison[6]. Using this model which describes more accurately the methanol molecule, and employing the experimental results of Coles[2] and of Edwards, Gilliam, and Gordy[4], they obtained values for the structural constants of the molecule, for the barrier height H, and for the component of the electric moment perpendicular to the symmetry axis. They were, however, forced to make assumptions concerning the dimensions of the CH_3 and OH groups, and limited their calculations to the normal isotopic form of methyl alcohol, $C^{12}\ H_3\ O^{16}\ H$. Further, also because of the lack of observational data, there were few checks on the results of their work.

Recent experimental results[3], both for the normal form and for the various isotopic modifications of the methyl alcohol

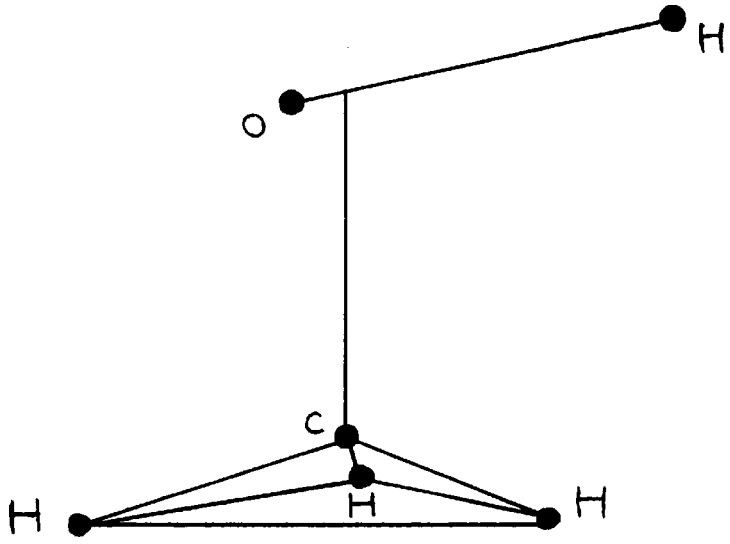
molecule, have enabled further extensions and application of the theory, and have made possible the calculation of new molecular constants, as well as more accurate and refined values of the old ones. This thesis presents an extensive correlation between the existing experimental data and the predictions of the theory, and, in addition, includes such various topics as the Stark effects, both first and second order, of a number of lines, the K-type doubling effect, and the interesting phenomenon of the so-called "mirror" lines.

THE METHYL ALCOHOL MOLECULE

The methyl alcohol molecule, CH_3 OH, is perhaps the simplest example of a wide class of molecules exhibiting the phenomenon of internal, or hindered rotation. This effect, in the case of methanol exerts a profound influence on the nature of the far infra-red and the microwave spectra. In fact, any reasonable interpretation of the micro-wave spectrum of methyl alcohol would be completely hopeless without taking hindered rotation into account.

The general structure of methyl alcohol is well known from chemical and spectroscopic studies, and is illustrated in the

following diagram:



The molecule may be described as consisting of a pyramidal CH_3, or methyl group, and an OH group, the two rotating relative to each other about the symmetry axis of the methyl group with the O atom near this axis. The fact that the O atom is not exactly on the symmetry axis, but is slightly displaced, has been shown by the work of Burkhard and Dennison[6], and is supported also by the results of the present investigation. Insofar as the problem of hindered rotation in methyl alcohol is concerned, these two groups may be considered to be rigid to a high degree of approximation. This fact may be seen by the following argument.

The hindering potential $V = \frac{H}{2}(1 - \cos 3x)$ may be expanded about $x = o$ to obtain the harmonic oscillator approximation $V = + \frac{9H}{4} x^2$. Therefore, the force constant for torsional oscillation, K, is given by $K = \frac{9H}{2g^2}$, where g is the perpendicular distance of the off-axis hydrogen atom to the symmetry axis. According to Burkhard and Dennison $H \sim 380$ cm^{-1}, $g \sim .8 \times 10^{-8}$ cm., and so $K \sim 2700$ $\frac{dynes}{cm.}$. If we now consider the OH deformation frequency, which at 1030 cm^{-1} is the lowest of all the remaining normal vibrations, one finds for its force constant $K' = 4\pi^2 f^2 m$ the value 62,500 $\frac{dynes}{cm.}$. The ratio of K' to K is about 20; consequently, the torsional forces are at least 20 times smaller than those causing the other fundamental vibrations, and, hence, relatively little distortion of the molecule is produced by the torsional motion.

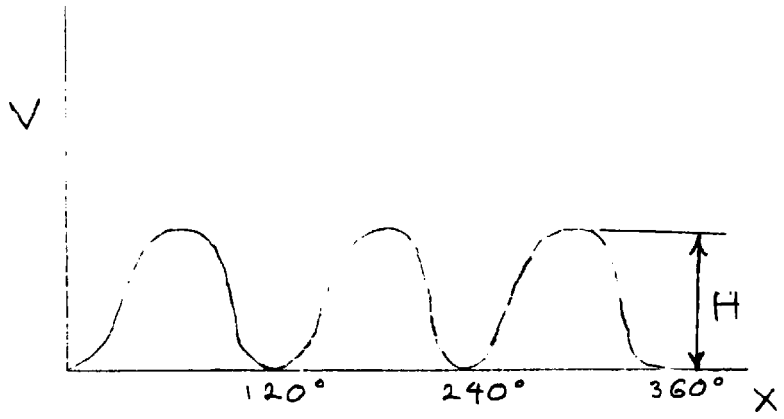
The relative motion of these two groups, as revealed by the spectrum, is not free, but is constrained by a hindering potential which, because of the three symmetrically placed hydrogen atoms of the methyl group, repeats itself every 120°. Since very little is known concerning the exact nature of such a potential, it seems reasonable at the outset to choose it of a sinusoidal form. Such a potential may reasonably be expected to approximate the actual situation, and moreover the most important features of the spectrum depend upon the general

properties of the potential such as its periodicity and the height of the barrier but not upon any finer details. A corresponding state of affairs exists for many ammonia-like molecules for which the positions of the energy levels of the inversion spectrum are found to be relatively insensitive to the precise form of the double minimum potential.

The hindering potential will be taken in the particular form

$$V = \frac{H}{2}(1 - \cos 3x),$$

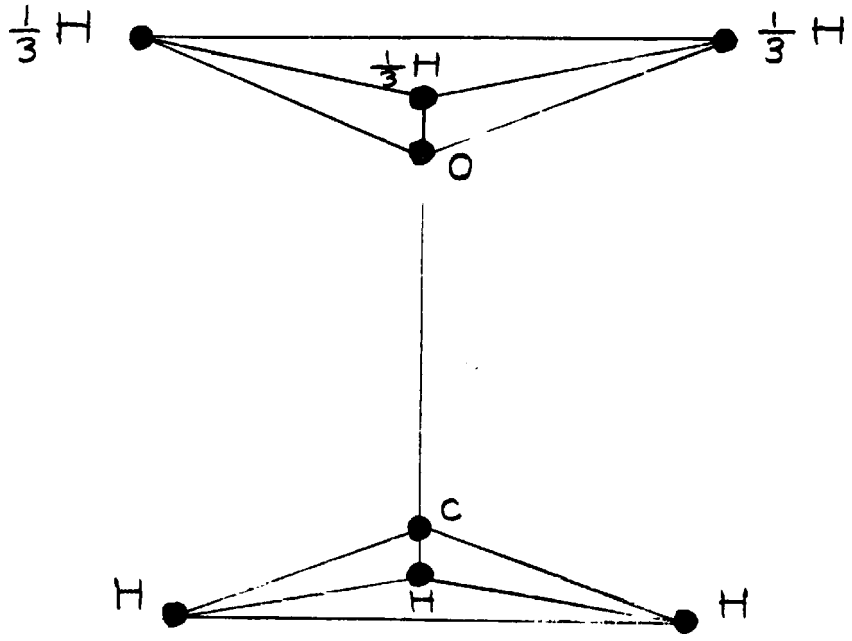
and is illustrated in the accompanying diagram.



H is the height of the potential barrier, and x is the angle measuring the relative rotation of the OH bar (about the symmetry axis) with respect to the CH_3 group. The symmetry axis is defined to be that line passing through the carbon nucleus

and the center of gravity of the three hydrogen atoms. This particular form for the potential agrees with that used by Koehler and Dennison and by Burkhard and Dennison.

As already mentioned, the molecule is almost, though not quite, a symmetrical rotator, and in a first approximation may be so regarded, as has been done by Koehler and Dennison. In effect, they assumed the following model:

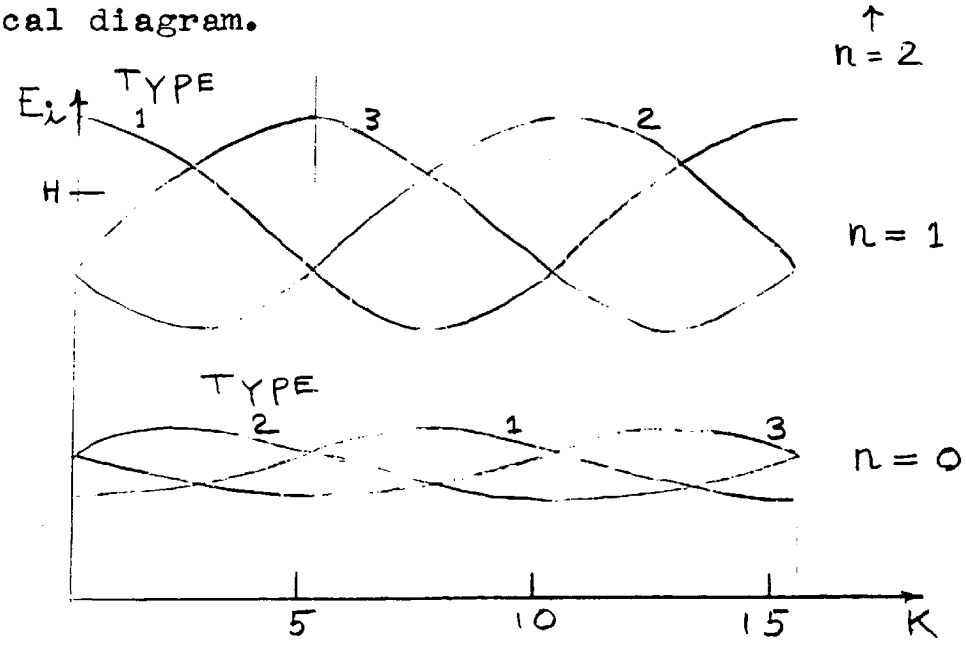


On the basis of this symmetrical model they obtained for the total rotational energy of the molecule the expression

$$E = \frac{\hbar^2}{2}\left[\frac{1}{A}(J^2 + J) + \left(\frac{1}{C} - \frac{1}{A}\right)K^2\right] + E_i,$$

where J and K are the usual quantum numbers, A is the large moment of inertia of the molecule about an axis perpendicular to the symmetry axis of the molecule and passing through the center of gravity, and C is the small moment of inertia of the entire molecule about the symmetry axis. E_i is the contribution of the hindered rotation motion to the energy, and is added to an energy expression which is just the usual one for a symmetric rigid rotator.

Qualitatively, the nature of E_i is illustrated in the following typical diagram.



For an infinitely large hindering potential H, the levels within a given n group merge, and become identical with the ordinary simple harmonic oscillator levels. The fact that for a finite H there are, in general, three such levels in a given n group

is due to the three-fold splitting produced by the three-fold nature of the hindering potential. n is referred to as the vibrational or torsional quantum number.

The splitting referred to is a function of the quantum number K, and is periodic in K with a period, however, in general, not equal to an integral number. This splitting, which increases with increasing energy or n, is a measure of the penetrability of the barrier. In the limiting case of very large energies, the levels become essentially those of the free rotator, for which the hindering potential vanishes.

The three levels in a given n group are distinguished by different type or τ numbers, which run from one through three, and which are connected with the different possible symmetry properties of the wave function. These type numbers are good quantum numbers in the symmetric rotor approximation, and together with K and n (note the absence of J) completely specify the internal energy levels. Only points on the above diagram that correspond to integral K's have, of course, any physical meaning.

In the next chapter the theory here so briefly and qualitatively sketched will be quantitatively extended (following Burkhard and Dennison) to include the general case of the asymmetric rotator. It will be found, however, that the

general features of the internal energy levels discussed above will change only slightly when the asymmetry is small.

That an approach more general than that afforded by the symmetrical model is needed is indicated by several items of evidence. One of these consists of what may be called the Coles series of lines, a group of lines in the microwave region which has been identified with the $J \rightarrow J$, $K = 1 \rightarrow 2$, type $= 2 \rightarrow 1$ transitions. It is only on the basis that a slight asymmetry in the molecule exists that the Coles series can be satisfactorily explained, since the symmetric model theory of Koehler and Dennison predicts a coincidence of all the frequencies corresponding to the various $J \rightarrow J$ transitions. Furthermore, the Stark effect of the Coles series of lines, as well as lines that exhibit only a second order Stark effect, and the "mirror" lines are examples of other phenomena which clearly indicate the shortcomings of the symmetric model.

A more general point of view is one in which the OH group is regarded not as a symmetric, but as an asymmetric rotator. It is evident that such a model of the methyl alcohol molecule is more natural than the symmetric one, allowing, in particular, for the possibility that the oxygen atom may not be exactly on the symmetry axis of the methyl group.

Let a coordinate system be introduced whose origin is at the center of gravity of the molecule with the z axis parallel to the symmetry axis of the CH_3 group, and with the y axis in the C O H plane. The following moments of inertia, which are of prime interest in this thesis, may then be defined:

$$A = \sum_i m_i \, (x_i^2 + z_i^2)$$

$$B = \sum_i m_i \, (y_i^2 + z_i^2)$$

$$C = \sum_i m_i \, (x_i^2 + y_i^2)$$

$$D = \sum_i m_i \, y_i \, z_i \, ,$$

where m_i is the mass of an atom at the position x_i, y_i, z_i, and the summation is over all the atoms in the molecule. The moment of inertia C_2 is defined as that of the CH_3 group about its symmetry axis, and C_1 is defined by $C_1 \equiv C\text{-}C_2 = A - B$.

Besides these molecular parameters there is also the total electric moment μ and its components $\mu_{//}$ and $\mu_{\perp}$, parallel and perpendicular to the CH_3 symmetry axis, respectively, and the previously defined barrier height H. The constants H, $\mu_{\perp}$, and $\mu_{//}$, together with the six dimensions necessary to specify the configuration of the methyl alcohol molecule constitute a total of nine independent parameters.

The most important emperical data available which can be used for determining these constants are the previously mentioned Coles series of lines for the $C^{12}H_3\ O^{16}H$, $C^{13}H_3\ O\ ^{16}H$, and $C^{12}H_3\ O^{18}H$ molecules, together with the Stark effects, and the positions of two $J = 3 \rightarrow 4$ lines and a $J = o \rightarrow 1$ line for the $C^{12}H_3\ O^{16}H$ molecule. A portion of this data serves as the primary basis for calculation, while the remainder, together with other measurements not here indicated, can be used as checks.

The general procedure to be used in these calculations will be the following: 1) D and $\mu_\perp$ are determined for $C^{12}H_3O^{16}H$ from the Stark coefficients of the Coles series. The value for μ must be assumed, and for this purpose the figure of $\mu = 1.69 \times 10^{-18}$ esu found by Kubo[8] is used. It can be shown that the values of D and $\mu_\perp$ so determined are quite insensitive within wide limits to the exact figures initially adopted for the other constants C_1, C_2, B and H, and that, therefore, the results obtained for D and $\mu_\perp$ will be very good even after only one cycle of calculations. 2) The quantities C_1, C_2, B and H for the normal, or $C^{12}\ H_3\ O^{16}\ H$ molecule, are calculated from four simultaneous equations, using the value found for D by the above method. These four equations are obtained by utilizing the frequency measurements of the two $J = 3 \rightarrow 4$ lines and

the $J = o \rightarrow 1$ line already mentioned, and the position of the origin of the Coles series. Conversely to 1), the values here obtained for C_1, C_2, B, and H are quite insensitive within wide limits to D. 3) The various inter-atomic distances are then obtained from the constants B, C_1, D, and C_2 for the normal molecule, together with the value for D for the $C^{12}H_3\ O^{18}\ H$ molecule found by the method in 1) from the Coles series data for the substance.

The cycle of calculation is repeated until self-consistency for the various constants is obtained. One may then proceed to a consideration of other empirical evidence in order to determine the reliability of these values, as well as to further test the validity of the asymmetric rotor theory. Among the data to be examined in this way are the position of the origin of the Coles series for the $C^{13}\ H_3\ O^{16}\ H$ and the $C^{12}\ H_3\ O^{18}\ H$ molecules, the value of the so-called $(J^2 + J)^2$ coefficient of the Coles series for all three isotopes, and the positions and Stark effects of a number of other measured lines in the microwave region.

CHAPTER II

THE THEORY OF HINDERED ROTATION IN METHYL ALCOHOL

In this chapter the theory of hindered rotation in methyl alcohol is discussed, first following the symmetric model approach of Koehler and Dennison[5], and then the asymmetric model theory of Burkhard and Dennison[6]. The treatment is then extended to include such topics as the theory of the K-type doubling of the energy levels and the associated Stark effect, and the generalized selection rules for a hindered asymmetric rotator. Finally, the interpretation of certain of the experimental features of the micro wave spectrum of methyl alcohol will be discussed in a general way (reserving until later a more detailed discussion) on the basis of the theory thus developed.

1. The Symmetric Model Theory

In the symmetric model theory of Koehler and Dennison, as previously mentioned, both the OH and CH_3 groups are regarded as symmetric rotors with moments of inertia C_1 and C_2 respectively, about the axis of symmetry of the molecule. The moment of inertia A is defined about an axis passing through the center of gravity of the molecule and perpendicular to the axis of symmetry.

Then, the kinetic energy is classically given by the expression:

$$T = \frac{A}{2}(\dot{\theta}^2 + \dot{\psi}^2 \sin^2\theta) + \frac{C_1}{2}(\dot{\psi}\cos\theta + \dot{\varphi}_1)^2 + \frac{C_2}{2}(\dot{\psi}\cos\theta + \dot{\varphi}_2)^2 ,$$

where θ, ψ, φ_1, and φ_2 are the usual Eulerian angles, the subscripts 1 and 2 referring to the OH and to the CH_3 groups, respectively.

The transition to quantum mechanics is made in the usual way, the resultant wave equation being

$$\frac{1}{A\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial u}{\partial\theta}\right] + \frac{1}{A\sin^2\theta}\frac{\partial^2 u}{\partial\psi^2} + \left[\frac{1}{C_1} + \frac{\cos^2\theta}{A\sin^2\theta}\right]\frac{\partial^2 u}{\partial\varphi_1^2} + \left[\frac{1}{C_2} + \frac{\cos^2\theta}{A\sin^2\theta}\right]\frac{\partial^2 u}{\partial\varphi_2^2}$$

$$- \frac{2\cos\theta}{A\sin^2\theta}\left[\frac{\partial^2 u}{\partial\psi\partial\varphi_1} + \frac{\partial^2 u}{\partial\psi\partial\varphi_2}\right] + \frac{2\cos^2\theta}{A\sin^2\theta}\frac{\partial^2 u}{\partial\varphi_1\partial\varphi_2} + \frac{2}{\hbar^2}\left[W - V\right]u = 0 .$$

The hindering potential V, as explained in Chapter I, is taken to be

$$V = \frac{H}{2}\left[1 - \cos 3(\varphi_1 - \varphi_2)\right] .$$

The coordinates

$$\varphi = \frac{C_1\varphi_1 + C_2\varphi_2}{C} \quad \text{and} \quad x = \varphi_1 - \varphi_2$$

are now introduced into the wave equation. The solution for u can be written in the form

$$u = \frac{1}{2\pi} e^{iK\varphi} e^{iM\psi} \Theta(\theta) m(x),$$

where Θ and m satisfy the equations:

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

$$\frac{d^2m}{dx^2} + [R + S\cos 3x]m = 0 ,$$

and

$$R = \frac{2}{\hbar^2}\frac{C_1C_2}{C}\left(W_i - \frac{H}{2}\right), \quad S = \frac{2}{\hbar^2}\frac{C_1C_2}{C}\frac{H}{2} .$$

m(x) is that portion of the wave function which depends upon the internal or the hindered rotation coordinates of the system.

The total energy W of the molecule is

$$W = \frac{\hbar^2}{2}\left[\frac{J^2 + J}{A} + K^2\left(\frac{1}{C} - \frac{1}{A}\right)\right] + W_i .$$

W_i represents the contribution of the hindered rotation motion to the energy, while the remainder of the expression on the right is the usual energy for a symmetric rigid rotator.

By invoking the appropriate boundary conditions, namely that the wave function be single valued and periodic in φ_1 and φ_2, it may be shown that

$$m(x) = e^{-\imath K\frac{C_1}{C}} P(x),$$

where p(x) is periodic with period 2π. By expanding P(x) in a Fourier series,

$$P(x) = \sum_{\tau=-\infty}^{\infty} a_\tau e^{\imath\tau x},$$

and substituting the resulting expression for m(x) into the differential equation for m(x) the following recursion formula for a_τ is obtained:

$$\frac{\delta}{R-(\sigma+\tau)^2}\, a_{\tau-3} + a_\tau + \frac{\delta}{R-(\sigma+\tau)^2}\, a_{\tau+3} = 0 ,$$

where

$$\sigma = -K\frac{c_1}{c}, \quad \text{and} \quad \delta = \frac{S}{2} = \frac{2\pi^2}{h^2}\,\frac{c_1 c_2}{c}\,H .$$

This equation shows that P(x) can be classified as belonging to one of the following three types of wave functions:

Type 1: $P(x) = \ldots\ a_{-3}e^{-i3x} + a_0 + a_3 e^{i3x} + \ldots$.

Type 2: $P(x) = \ldots\ a_{-4}e^{-i4x} + a_1 e^{-ix} + a_2 e^{2ix} + \ldots$.

Type 3: $P(x) = \ldots\ a_{-5}e^{-i5x} + a_{-2}e^{-2ix} + a_1 e^{ix} + \ldots$.

The a_τ can be eliminated from the recursion relation by the use of convergence requirements, resulting in continued fraction relations for the internal energy and for the value of the a_τ themselves. As an example, eigenvalues for type 1 solutions are given by

$$1 - \cfrac{\left[\frac{\delta^2}{(0)(3)}\right]}{1 - \cfrac{\left[\frac{\delta^2}{(3)(6)}\right]}{1 - \cfrac{\left[\frac{\delta^2}{(6)(9)}\right]}{1 - \text{etc.}}}} \quad = \quad \cfrac{\left[\frac{\delta^2}{(0)(-3)}\right]}{1 - \cfrac{\left[\frac{\delta^2}{(-3)(-6)}\right]}{1 - \cfrac{\left[\frac{\delta^2}{(-6)(-9)}\right]}{1 - \text{etc.}}}}$$

where $(\tau) = R-(\sigma+\tau)^2$. This equation thus determines R, and hence, W_1, for a given σ. The eigenvalues for type 2 and 3 solutions may be found from those for type 1 by the relations

$$W_1(\sigma)[\tau = 2] = W_1(\sigma-1)[\tau = 1], \quad W_1(\sigma)[\tau = 3] = W_1(\sigma+1)[\tau = 1].$$

For $\sigma = o$, n = 1, 3, 5, ... and type 1 eigenvalues it is more convenient to use the following expression, which may be shown to be equivalent to the earlier form:

$$\cfrac{\left[\frac{\lambda^2}{(3)(6)}\right]}{1-\cfrac{\left[\frac{\lambda^2}{(6)(9)}\right]}{1-\text{etc.}}} = 1$$

Having determined R for a given type and σ, the a_τ can be calculated from the equations:

$$a_\tau = \cfrac{-\left[\frac{\lambda}{\tau}\right] a_{\tau-3}}{1-\cfrac{\left[\frac{\lambda^2}{(\tau)(\tau+3)}\right]}{1-\cfrac{\left[\frac{\lambda^2}{(\tau+3)(\tau+6)}\right]}{1-\text{etc.}}}} \qquad \text{for } \tau > 0,$$

$$a_\tau = \cfrac{-\left[\frac{\delta}{(\tau)}\right] a_{\tau+3}}{1-\cfrac{\left[\frac{\delta^2}{(\tau)(\tau-3)}\right]}{1-\cfrac{\left[\frac{\delta^2}{(\tau-3)(\tau-6)}\right]}{1-\text{etc.}}}} \qquad \text{for } \tau < 0 .$$

It is convenient to normalize the a_τ using the condition

$$\sum_{\tau=-\infty}^{\tau=+\infty} a_\tau^2 = 1 .$$

The selection rules for the symmetric hindered rotator are the following:

For $\mu_{II} = 0$, $\mu_\perp \neq 0$,

$\Delta J = 0, \pm 1$, $\Delta M = 0, \pm 1$, $\Delta K = \pm 1$, Δn = anything.

$\tau = 1 \rightarrow 3$

$= 3 \rightarrow 2$ for $K \rightarrow K + 1$

$= 2 \rightarrow 1$

$\tau = 1 \rightarrow 2$

$= 2 \rightarrow 3$ for $K \rightarrow K - 1$

$= 3 \rightarrow 1$

For $\mu_\perp = 0$, $\mu_{II} \neq 0$

$\Delta J = 0, \pm 1$, $\Delta M = 0, \pm 1$, $\Delta K = 0$, $\Delta n = 0$, $\tau \rightarrow \tau$

For the methyl alcohol molecule, for which both $\mu_\perp$ and μ_{II} differ from zero, both of the above cases apply, the intensities being proportional to $\mu_\perp^2$ and to μ_{II}^2, respectively.

There are two special cases of particular interest in the symmetric hindered rotator theory: 1) the free rotator case, and 2) the bound case. The first is obtained when the hindered rotation energy is much greater than the hindering potential, or $W_i >> H$, and corresponds to free rotation of the OH bar about the symmetry axis. The bound case on the other hand applies when $W_i << H$, or when the internal energy is much less than the hindering potential, and these correspond classically to a vibratory motion of the OH bar in one of the potential minima.

Free Case

The differential equation for the internal motion for this case becomes

$$\frac{d^2m}{dx^2} + RM = o \ .$$

This leads to the formulas

$$m(x) = \frac{1}{\sqrt{2\pi}} e^{i(\sigma + m)x}$$

$$W_i = \frac{H}{2} + \frac{\hbar^2}{2} \frac{C}{C_1 C_2} (m - \frac{C_1}{C} K)^2$$

where $m = o, \pm 1, \pm 2, \ldots$. The selection rules are $\Delta J = o, \pm 1$, $\Delta m = \pm 1$, and $\Delta(K-m) = o$.

Bound Case

For this case the hindering potential can be expanded about the minimum at x = o, only terms through x^2 being retained. The differential equation for the internal motion then becomes

$$\frac{d^2 m}{d x^2} + (\lambda - \xi^2 x^2) m = 0 ,$$

where

$$\lambda = \frac{2}{\hbar^2} \frac{C_1 C_2}{C} W_i , \qquad \xi^2 = \frac{9 C_1 C_2 H}{2 \hbar^2 C} .$$

Solving this equation, one obtains

$$W_i = 3 \hbar \left(\frac{C H}{2 C_1 C_2} \right)^{1/2} \left(n + \tfrac{1}{2} \right) ,$$

$$m_n(x) = N_n e^{-\frac{1}{2} \xi x^2} H_n(\xi^{1/2} x) , \qquad -\tfrac{1}{3}\pi \le x \le \tfrac{1}{3}\pi ,$$

where n = o, 1, 2,..., Hn is the $n^{\underline{th}}$ Hermite polynormal, and Nn is the normalization factor. To obtain the correct o-order wave functions one must take suitable combinations of $m_n(x)$ centered at x = o, $\frac{2\pi}{3}$, and $\frac{4\pi}{3}$. The selection role is that for a simple harmonic oscillator: $\Delta n = \pm 1$.

2. The Asymmetric Model Theory

As noted in Chapter I, the asymmetric hindered rotator model used in the present work is taken to be that of a rigid OH bar rotating about the symmetry axis of the rigid CH_3 group, and subject to a hindering potential of the same form as for

the symmetric case, namely, $V = \frac{H}{2}(1-\cos 3x)$. The moments of inertia C_1 and C_2, the large moments of inertia A and B, and the cross product of inertia D for this model have been defined in Chapter I.

The wave equation for this asymmetric model was first obtained by Burkhard and Dennison[6], who also evaluated the matrix elements of the Hamiltonian, using as a basis the wave functions for the symmetrical hindered rotator model. This is a valid procedure since the number of variables involved is the same in both the symmetric and asymmetric cases, and the boundary conditions are identical.

The matrix elements found by Burkhard and Dennison, together with some additional elements having to do with the Stark energy, are given on this and the following page.

TABLE I

$$H^{J\,K\,\tau\,n}_{J\,K\,\tau\,n} = \frac{\hbar^2}{2}\left[\frac{1}{A}(J^2+J-K^2) + \frac{K^2}{C} + \frac{(A-B)C_1+D^2}{2A(BC_1-D^2)}(J^2+J-K^2)\right.$$

$$\left. - \frac{D^2}{(BC_1-D^2)C_1}\int_0^{2\pi} P^*_{K\tau n}\frac{d^2}{dx^2}P_{K\tau n}\,dx\right] + W^{\sim}_{K\tau n} + \frac{\mu_{11}EKM}{J^2+J}$$

$$H^{J\,K\,\tau\,n'}_{J\,K\,\tau\,n} = -\frac{\hbar^2}{2}\frac{D^2}{(BC_1-D^2)C_1}\int_0^{2\pi} P^*_{K\tau n}\frac{d^2}{dx^2}P_{K\tau n'}\,dx$$

$$H^{J\,K+1\,\tau'\,n'}_{J\,K\,\tau\,n} = \frac{\hbar^2}{2}\frac{D}{BC_1-D^2}\left[(J-K)(J+K+1)\right]^{\frac{1}{2}}\int_0^{2\pi} P^*_{K\tau n}e^{-\lambda x}\left(\frac{1}{i}\frac{d}{dx}-\frac{1}{2}\right)P_{K+1\,\tau'n'}\,dx$$

$$+\frac{\mu_\perp EM}{2}\frac{\left[(J+K+1)(J-K)\right]^{\frac{1}{2}}}{J^2+J}\int_0^{2\pi} P^*_{K\tau n}e^{-\lambda x}P_{K+1\,\tau'n'}\,dx$$

$$H^{J\,K+2\,\tau'\,n'}_{J\,K\,\tau\,n} = \frac{\hbar^2}{2}\frac{(A-B)C_1+D^2}{4A(BC_1-D^2)}\left[(J-K)(J-K-1)(J+K+1)(J+K+2)\right]^{\frac{1}{2}}\int_0^{2\pi} P^*_{K\tau n}e^{-2\lambda x}P_{K+2,\tau'n'}\,dx$$

$$H^{J+1\,K\,\tau\,n}_{J\,K\,\tau\,n} = \mu_{11}E\,\frac{\sqrt{(J+K+1)(J-K+1)(J+M+1)(J-M+1)}}{(J+1)\sqrt{(2J+1)(2J+3)}}$$

$$H^{J-1\,K\,\tau\,n}_{J\,K\,\tau\,n} = \mu_{11}E\,\frac{\sqrt{(J^2-K^2)(J^2-M^2)}}{J\sqrt{4J^2-1}}$$

$$H^{J+1\,K\pm1\,\tau'n'}_{J\,K\,\tau\,n} = \mp\frac{\mu_\perp E\sqrt{(J\pm K+1)(J\pm K+2)(J+M+1)(J-M+1)}}{2(J+1)\sqrt{(2J+1)(2J+3)}}$$

$$\times\int_0^{2\pi} P^*_{K\tau n}e^{\mp\lambda x}P_{K\pm1\,\tau'n'}\,dx$$

$$H^{J-1\,K\pm1\,\tau'n'}_{J\,K\,\tau\,n} = \frac{\pm\mu_\perp E\sqrt{(J\mp K)(J\mp K-1)(J^2-M^2)}}{2J\sqrt{4J^2-1}}\int_0^{2\pi} P^*_{K\tau n}e^{\mp\lambda x}P_{K\pm1\,\tau'n'}\,dx$$

E is the electric field strength, while the electric dipole moments of the molecule parallel and perpendicular to the symmetry axis are denoted by $\mu_{||}$ and $\mu_{\perp}$, respectively. The quantum numbers J, K, τ, n, and M, and the wave functions $P^{(x)}_{K\tau n}$ have already been specified in the preceding section dealing with the symmetric model.

Ignoring for the moment the Stark energy term, it is to be noted that the matrix elements of the Hamiltonian are all diagonal in J, and can be divided into four groups. These consist of

1) Terms diagonal in all the quantum numbers J, K, τ, n. When these are compared with the energy expression for the symmetric model, it is seen that they are identical except for two differences: a) the quantity $\frac{1}{A}$ in the symmetric model energy formula is now replaced by

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

and, b) there is present an additional term

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

For methyl alcohol the coefficient of this integral is of the order of .01cm^{-1}. The integral for the state n = 0, τ = 1

itself varies from about -1.5 at K = o to about - 7 at K = 10.

2) A term diagonal in J, K, τ, but not in n, and proportional to

$$\frac{D^2}{C_1(BC_1-D^2)} \quad .$$

3) An element connecting the states K and K + 1, non-diagonal in τ, and proportional to $\frac{D}{BC_1-D^2}\sqrt{(J + K + 1)(J-K)}$. For methyl alcohol the numerical value of this term is much less than the difference of the diagonal terms of the states that it connects, provided the values of J involved are moderate. For n = o, K = o, τ = 3, for example, it is of the order of $.009cm^{-1}(J^2 + J)^{1/2}$.

4) A term non-diagonal in τ and n, and connecting the states K and K + 2. This element is proportional to

$$\frac{C_1^2 + D^2}{A(BC_2-D^2)} \sqrt{(J-K)(J-K-1)(J+K+1)(J+K+2)},$$

and, is also relatively small for moderate values of J. For n = o, K = o, τ = 1 it has the approximate value of $.006cm^{-1}\sqrt{J(J-1)(J+1)(J+2)}$ for methyl alcohol.

It is to be observed that when one sets D=A-B=0 in the above matrix elements, the off-diagonal terms vanish, and the diagonal term becomes exactly equal to the energy expression

for the symmetric model. Consequently, it can be expected that the effect of the off-diagonal elements will be fairly small for the methyl alcohol molecule, which has only a relatively slight asymmetry, at least for the case of moderate J's. It is only in connection with the finer details of the infra-red and microwave spectra that these terms become important, or even, in some cases, absolutely essential.

Returning now to a discussion of the Stark energy matrix elements, it is to be noted that these, unlike the ones for the energy proper discussed above, can be non-diagonal, as well as diagonal in J. Those terms that are diagonal in J have been derived by Burkhard and Dennison, who in their paper, however, have neglected to give the expressions non-diagonal in J since they were concerned with the theory of the first order Stark effect in which these terms do not enter. The matrix elements here given include the terms non-diagonal in J as well as those diagonal in J. For the former expressions, as well as the latter, non-vanishing connections can only occur between states in which $\Delta K = o, \pm 1$.

In these formulas there is no restriction on the value of n', but only those elements will be non-zero for which τ obeys the following rules: For elements in which $K \rightarrow K + 1$, the

possible τ connections are $1 \rightarrow 3$, $3 \rightarrow 2$, and $2 \rightarrow 1$, while for elements in which $K \rightarrow K + 2$, they are $1 \rightarrow 2$, $2 \rightarrow 3$, and $3 \rightarrow 1$.

The energy levels of the molecule are found as usual by solving the secular determinant

$$\left| H^{J'K'\tau'n'}_{JK\tau n} - W\,\delta^{J'K'\tau'n'}_{JK\tau n} \right| = 0 ,$$

which factors into three sub-determinants as a consequence of the above rules governing non-zero τ connections. These three determinants may be characterized by the K and τ values of their diagonal elements:

	K = ··· -3	-2	-1	0	1	2	3 ···
Determinant 1	τ = ··· 3	2	1	3	2	1	3 ···
" 2	τ = ··· 2	1	3	2	1	3	2 ···
" 3	τ = ··· 1	3	2	1	3	2	1 ··· .

Now, it can be shown that

$$P_{K1n}(x) = (-1)^n P^*_{-K1n}(x)$$

$$P_{K2n}(x) = (-1)^n P^*_{-K3n}(x) ,$$

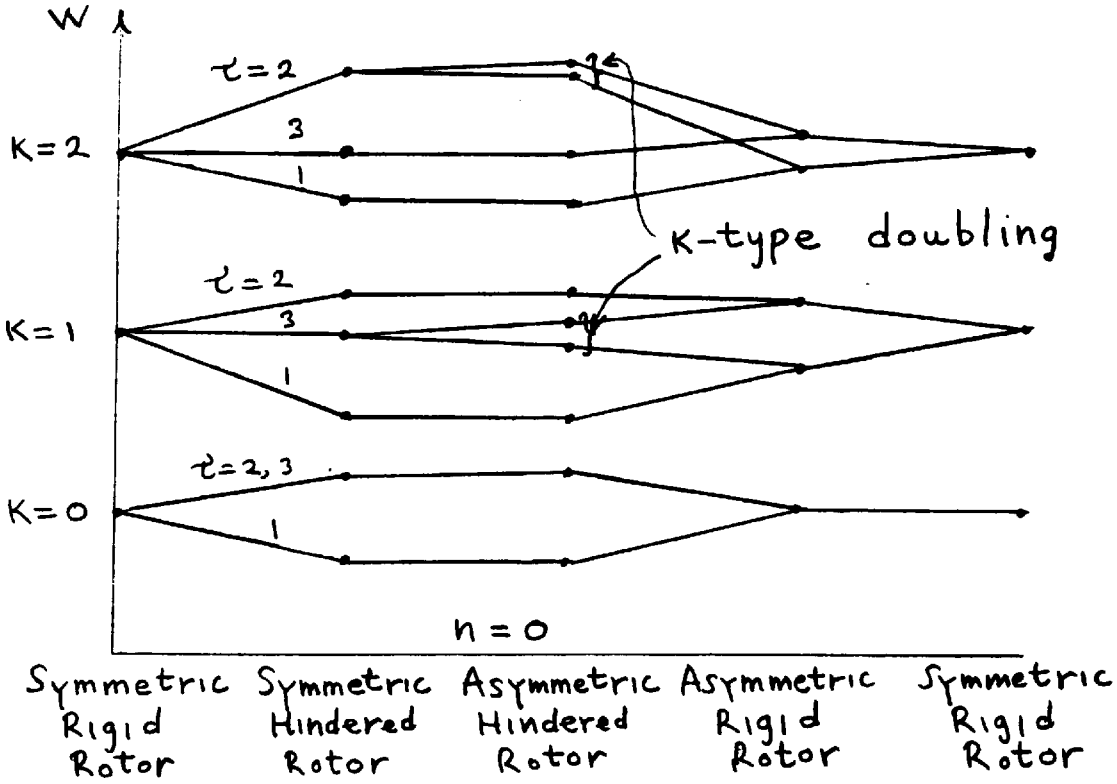
from which it follows that determinant 1 is the same as determinant 2, except for a possible change in sign, and that, therefore, the roots of the two determinants are identical.

There is then a double degeneracy for these particular levels, which a closer investigation shows to belong to the symmetry class E, and, consequently, not removable by any perturbation having a three-fold symmetry.

By virtue of these same equations, it may be seen that the diagonal elements of determinant 3 occur in pairs, being equal about K = o; that is, $H_{K=-1,\tau=2} = H_{13}$, $H_{-23} = H_{22}$, etc. Because of the non-diagonal terms, however, all levels with the exception of that corresponding to K = o, τ = 1 will be split into two components, the members of which may be shown to belong to the symmetry classes A_1 and A_2. This splitting, known as K-type doubling, decreases rapidly with increasing K, and increases with increasing J, but, in any case, for molecules such as those of methyl alcohol whose asymmetry is relatively slight, the splitting will usually be small.

These features of the energy levels are illustrated in the following diagram, which depicts the behavior of the levels for K = o, 1, and 2 (for a fixed J and n = o) in four limiting cases, together with the proper connections between them. These cases are those of a symmetric rigid rotator, a symmetric hindered rotator, an asymmetric hindered rotator, and an asymmetric rigid rotator. The diagram is intended to

be merely schematic, and not an accurate representation of the actual position of the energy levels.



It will be noted that the effect of hindered rotation for the symmetrical rotator is to split each K level into three levels with the exception of K = o, for which case a degeneracy exists between the type 2 and 3 levels. The magnitude of the splitting is a measure of the penetrability of the barrier.

When a slight asymmetry is introduced, the K = 1, type 3 and the K = 2, type 2 levels split slightly, the splitting increasing with the amount of asymmetry.

Beginning now from the right side of the diagram, a rigid symmetrical rotator becomes a rigid asymmetric rotator. As is well-known, the effect of the asymmetry is to split each K level into two components with the exception of that for which K = o which remains single. This splitting, the so-called K-type doubling, was first discussed by Wang[7], and is given by the expression

$$\Delta W_K = \frac{h^2}{\pi^2} c \left(\frac{b}{8}\right)^K \frac{(J+K)!}{(J-K)!\,(K-1)!^2} ,$$

where

$$c = \frac{1}{C} - \frac{1}{2}\left(\frac{1}{A} + \frac{1}{B}\right), \quad b = \frac{\frac{1}{B} - \frac{1}{A}}{\frac{2}{C} - \frac{1}{A} - \frac{1}{B}} ,$$

and A, B, C are the principal moments of inertia of a nearly symmetric rigid top with $B \cong A$, and $C<B<A$. The general form of this J dependence, $\frac{(J+K)!}{(J-K)!}$, is maintained for the hindered rotator case, though ΔW_K then becomes a more complex function of K, and is also dependent on the barrier height H.

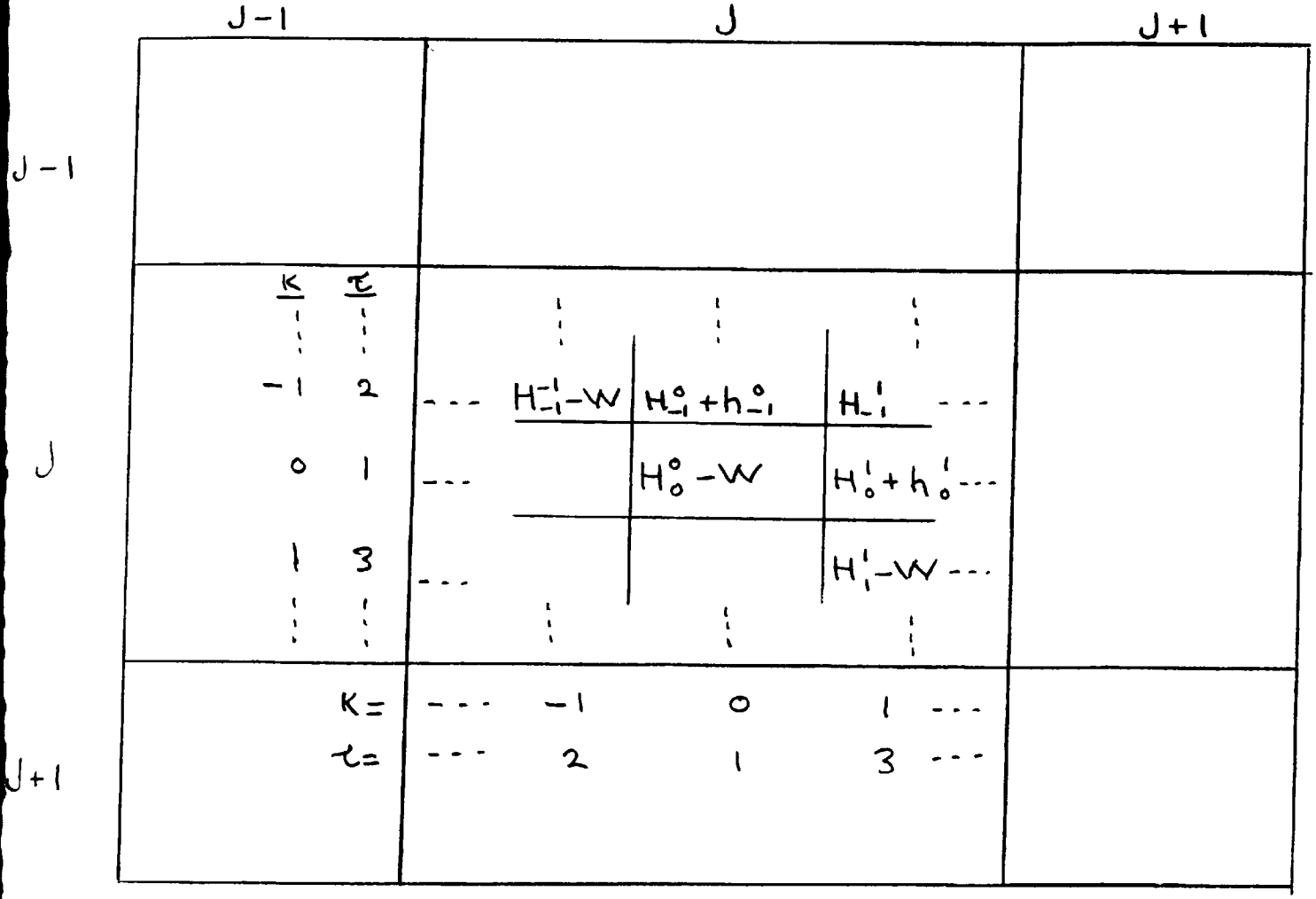
In the center of the diagram both sides merge to form the asymmetric rotator with hindered rotation. Here one sees both features discussed above occuring: 1) a splitting due to the

penetration of the hindering potential barrier, and 2) a splitting of one third of the levels caused by the asymmetry of the molecule.

3. Theory of the K-type Doubling

In this section the theory of K-type doubling for the asymmetric hindered rotator will be developed together with the associated Stark effect. The problem is similar to that for the rigid asymmetric rotator, though it differs from it in two respects. These dissimilarities are occasioned by the existence of the hindering potential, and by the presence of the cross product of inertia term D. When proper account is taken of these two factors it can be verified that the formulas developed for the hindered asymmetric rotator go over into those for the rigid asymmetric rotator. The results obtained in this section will later be utilized in an attempt to explain certain experimental features of the microwave spectrum.

The problem involved is essentially that of solving for the roots of the secular determinant 3, whose diagonal elements, it will be recalled, are degenerate in pairs about K= o. When written out, this determinant has the form



$H_K^{K'}$ are the matrix elements of the Hamiltonian proper for the asymmetric hindered rotator, while $h_K^{K'}$ are the Stark energy matrix elements, depending linearly on the electric field strength E. Strictly speaking, these terms are a function of

the quantum number τ, but since τ is not correlated unambiguously with K, for convenience it is omitted in this section. Likewise, the various possible n connection must also be tacitly understood. The n = o $\rightarrow$ o connections are, however, the principal ones for the n = o levels, which will be the ones of primary interest in this dissertation, and though, strictly speaking, the n = o $\rightarrow$ 1, n = o $\rightarrow$ 2, etc. terms should also be taken into account, the effect of these is usually relatively small. The roots of the secular determinant are determined by a straightforward process, and the results for the energy levels corresponding to different K's are given by the following formulas:

<u>K = 1</u>

$$W = D_1 + aE^2 \pm \sqrt{E^2x^2 + (b + dE^2)^2}, \quad \text{where}$$

$$a = \sum_{J'K'} \frac{\left[h(E)_{J\,1}^{J'K'}\right]^2}{W_{J1}^{o} - W_{J'K'}^{o}}, \quad b = H_{J\,1}^{J-1}, \quad d = \sum_{J'} \frac{\left[h_{J\,1}^{J'\,o}\right]^2}{W_{J1}^{o} - W_{J'o}^{o}}, \quad x = \frac{\mu_{11} M}{J^2 + J}.$$

<u>K = 2</u>

$$W = D_2 + eE^2 \pm \sqrt{4E^2x^2 + f^2}, \quad \text{where}$$

$$e = \sum_{J'K'} \frac{\left[h_{J\,2}^{J'K'}\right]^2}{W_{J2}^{o} - W_{J'K'}^{o}}, \qquad f = \frac{\left[H_{J\,2}^{J\,o}\right]^2}{W_{J2}^{o} - W_{Jo}^{o}}$$

K = 3

$$W = D_3 + gE^2 \pm \sqrt{qE^2x^2 + \ell^2}, \quad \text{where}$$

$$g = \sum_{J'K'} \frac{\left[h^{J'K'}_{J\,3}\right]^2}{W^0_{J3} - W^0_{J'K'}}, \qquad \ell = \frac{H^{J-1}_{J\,1}\left[H^{J\,3}_{J\,1}\right]^2}{(W^0_{J1} - W^0_{J3})^2}$$

K = 4

$$W = D_4 + mE^2 \pm \sqrt{16E^2x^2 + p^2}, \quad \text{where}$$

$$m = \sum_{J'K'} \frac{\left[h^{J'K'}_{J\,4}\right]^2}{W^0_{J4} - W^0_{J'K'}}, \qquad P = \frac{\left[H^{J\,4}_{J\,2}\right]^2\left[H^{J\,2}_{J\,0}\right]^2}{(W^0_{J2} - W^0_{J4})^2(W^0_{J4} - W^0_{J0})}.$$

In these equations $W^0_{JK} = H^{JK}_{JK}$, and $D_K = W^0_{JK}$ + higher order terms. Since the purpose of developing the above formulas has been to obtain the splitting of the levels, and, consequently, these higher order terms are not of interest at this point, their precise form will not be given. If one includes n = o $\longrightarrow$ 1, 2, etc. terms, then

$$a = \sum_{J'K'n'}{}' \frac{\left[h^{J'K'n'}_{J\,1\,0}\right]^2}{W^0_{J10} - W^0_{J'K'n'}} \qquad d = \sum_{J'n'} \frac{\left[h^{J'0n'}_{J\,1\,0}\right]^2}{W^0_{J10} - W^0_{J'0n'}}$$

$$b = H^{J-10}_{J\,10} - \sum_{K'n'}{}' \frac{H^{J\,K'n'}_{J-1\,0} H^{J\,1\,0}_{J\,K'n'}}{W^0_{JK'n'} - W^0_{J-10}}$$

$$e = \sum_{J'K'n'}{}' \frac{\left[h^{J'K'n'}_{J\,2\,0}\right]^2}{W^0_{J'K'n'} - W^0_{J20}} \qquad f = \sum_{K'n'}{}' \frac{H^{J\,K'n'}_{J-2\,0} H^{J\,2\,0}_{J\,Kn}}{W^0_{JK'n'} - W^0_{J20}}$$

$$g = \sum_{J'K'n'}{}' \frac{\left[h_{J\,3\,0}^{J'K'n'}\right]^2}{W^0_{J'Kn'} - W^0_{J30}} \qquad l = \sum_{K'n'}{}' \frac{H^{J\,K'n'}_{J-3\,0} H^{J\,3\,0}_{J\,K'n'}}{W^0_{JK'n'} - W^0_{J30}}$$

$$m = \sum_{J'K'n'}{}' \frac{\left[h_{J\,4\,0}^{J'K'n'}\right]^2}{W^0_{J'K'n'} - W^0_{J40}} \qquad - \sum_{\substack{K,n \\ J'K'n'}}{}' \frac{H^{J\,Kn}_{J-3\,0} H^{J'K'n'}_{J\,Kn} H^{J\,3\,0}_{J'K'n'}}{(W^0_{JKn} - W^0_{J30})(W^0_{J'K'n'} - W^0_{J30})}$$

$$(K,n) \neq (K',n')$$

The primes over the summation marks signify that the running indices must be chosen in such a way that the energy denominators are not equal to zero.

From the above equation it follows that the splitting of the K= 1, 2, and 3 levels is 2b, 2f, and 2l, respectively. The general formula for the splitting of the $K^{\underline{th}}$ level is

$$\Delta W_K = 2 \frac{H^{J\ -K+2}_{J\ -K} H^{J\ -K+4}_{J\ -K+2} \cdots H^{J\ K}_{J\ K-2}}{(W^0_{J\,-K+2} - W^0_{J\,K})(W^0_{J\,-K+4} - W^0_{J\,K}) \cdots (W^0_{J\,K-2} - W^0_{J\,K})} ,$$

where the matrix elements and energies are explicitly given by

$$H^{J\ K+2}_{J\ K} = \frac{\hbar^2}{2} \frac{(A-B)C_1 + D^2}{4A(BC_1 - D^2)} \left[(J-K)(J-K-1)(J+K+1)(J+K+2)\right]^{\frac{1}{2}} \int_0^{2\pi} p^*_K \frac{d^2 p_K}{dx^2}\, dx ,$$

$$W^0_{JK} = \frac{\hbar^2}{2}\left[\frac{K^2}{C} + (J^2+J-K^2)\left(\frac{1}{A} + \frac{(A-B)C_1 + D^2}{2A(BC_1 - D^2)}\right) - \frac{D^2}{(BC_1 - D^2)C_1} \int_0^{2\pi} p^*_K \frac{d^2 p_K}{dx^2}\, dx\right] + W^i_K .$$

When substituted into the expression for W_K, the factor $\left[(J-K)(J-K-1)(J+K+1)(J+K+2)\right]^{\frac{1}{2}}$ gives rise to the quantity $\frac{(J+K)!}{(J-K)!}$ which, as has been seen, is one of the factors of the Wang expression and gives the J dependence of the splitting. The remaining factors of ΔW_K for the hindered rotator are not the same as the corresponding portions of the Wang expression, but for methyl alcohol an examination shows that the two formulas yield results which are of the same order of magnitude. Indeed, the formula for the asymmetric hindered rotator may be shown in the limit of $H = \infty$ to go over exactly into the usual Wang expression, provided a transformation to principal axis has been effected.

Utilizing future values for the molecular constants, calculations show that the K-type splittings for methyl alcohol are given by the following expressions:

$\underline{K = 1}$ $\quad \Delta W_1 = 400.3(J^2 + J) \ \frac{\text{m.c.}}{\text{sec.}}$

$\underline{K = 2}$ $\quad \Delta W_2 = .08596(J-1)(J)(J+1)(J+2) \ \frac{\text{m.c.}}{\text{sec.}}$

$\underline{K = 3}$ $\quad \Delta W_3 = 2.121 \times 10^{-5} \ (J-2)(J-1)(J)(J+1)(J+2)(J+3) \ \frac{\text{m.c.}}{\text{sec.}}$

$\underline{K = 4}$ $\quad \Delta W_4 = 1.91 \times 10^{-9} \ (J-3)(J-2)\cdots(J+4) \ \frac{\text{m.c.}}{\text{sec.}}$

An examination shows that the Stark effect of levels with K-type doubling is quadratic in the field strength E, provided the K-type splitting is much larger than the Stark splitting. As a matter of fact, it follows from the formulas already derived for the energy of K-type levels that for weak electric fields

$$\underline{K=1} \quad W = (D_1 \pm b) + E^2\left[a \pm \left(\frac{X^2}{2b} - d\right)\right] \quad \text{for } E\sqrt{X^2-2bd} \ll b$$

$$\underline{K=2} \quad W = (D_2 \pm f) + E^2\left[e \pm \frac{2X^2}{f}\right] \quad \text{for } 2EX \ll f$$

$$\underline{K=3} \quad W = (D_3 \pm \ell) + E^2\left[g \pm \frac{9X^2}{2\ell}\right] \quad \text{for } 3EX \ll \ell$$

$$\underline{K=4} \quad W = (D_4 \pm p) + E^2\left[m \pm \frac{8X^2}{p}\right] \quad \text{for } 4EX \ll p \ .$$

Just as the symmetric rigid rotator possesses a linear Stark effect due to the degeneracy of its energy levels, while a quadratic Stark effect exists for the asymmetric rotator because the degeneracy has been removed, so for the asymmetric hindered rotator, also, the removal of the degeneracy by the off-diagonal matrix elements produces a quadratic Stark effect. As the field strength E is increased, the above approximations begin to lose their validity, breaking down completely when

the Stark splittings are of the same order of magnitude as the K-type splitting. For field strength still higher the Stark effect becomes linear. The last situation is very likely to be the case for levels with high K's, for which the K-type splitting is usually very small. Experimental examples of precisely this behavior will indeed be encountered. Finally, it should be noted that just as for the equations governing the magnitude of the K-type doubling, these Stark formulas reduce, as one might expect, to the usual equations for the rigid asymmetric top when the appropriate degeneration is made.

4. Selection Rules for the Asymmetric Hindered Rotator

Selection rules for the symmetric hindered rotator have been already stated. The present section deals with an extension of the selection rules for the case of the asymmetric hindered rotator where, as for the symmetric hindered rotator, the electric moment may be resolved into two components, $\mu_{\parallel}$ lying along the symmetry axis of the methyl group, and $\mu_{\perp}$ which is normal to the symmetry axis and in the COH plane. The case for which there is no external field E will be first considered.

The wave function Ψ for the asymmetric hindered rotator can be expanded linearly in terms of the symmetric hindered rotator

wave functions $u_{JK\tau n}$. As a consequence of the three-fold factoring of the secular determinant already discussed, however, there are three different possible classes of Ψ, each class containing only those symmetric wave functions which are associated with a given determinant. Thus, the Ψ corresponding to an energy eigenvalue of determinant 1, 2, and 3 will have the form

$$\Psi_1 = \cdots a_{-2} u_{K=-2,\tau=2} + a_{-1} u_{-11} + a_0 u_{03} + a_1 u_{12} + a_2 u_{21} + \cdots$$

$$\Psi_2 = \cdots b_{-2} u_{-21} + b_{-1} u_{-13} + b_0 u_{02} + b_1 u_{11} + b_2 u_{23} + \cdots$$

$$\Psi_3 = \cdots c_{-2} u_{-23} + c_{-1} u_{-12} + c_0 u_{01} + c_1 u_{13} + c_2 u_{22} + \cdots ,$$

respectively, where the omitted quantum numbers J, n, and M must be understood. It is to be noted that, in general, these expansions will contain the wave functions $u_{JK\tau nM}$ corresponding to all K such that $|K| \leq J$.

To determine the selection rules one must calculate the matrix elements of the dipole moment along the space-fixed axis X, Y, Z between two states Ψ_a and Ψ_b. These will have the following form:

$$(\mu_F)_{ab} = \int \Psi_a^* \mu_F \Psi_b \, d\tau ,$$

where F is either X, Y, or Z, and μ_F is the quantum mechanical

operator of the dipole moment along F. By using the above-mentioned expansions of Ψ one can reduce this integral to a sum of integrals over the symmetric wave functions, and, hence, from a knowledge of the selection rules for the symmetric rotator, be able to deduce those for the asymmetric hindered rotator.

It may then readily be seen that no transitions are possible between energy levels belonging to different determinents. Also, since the matrix elements of the Hamiltonian are diagonal in J and M, i.e., J and M are good quantum numbers, the selection rules for J and M will be the same as for the symmetric hindered rotator. That is, $\Delta J = o, \pm 1$, and $\Delta M = o, \pm 1$. Δn can be anything.

Transitions between all levels of determinant 1 are, in general, possible, consistent, of course, with the requirement that $|K| \leq J$, while the same holds for levels of determinant 2. It should, however, be remembered that the two determinants are degenerate with respect to each other, and that the energy levels of the two are identical. Thus, the transition $K = 1$, $\tau = 1 \rightarrow K = -1$, $\tau = 3$, for example, is effectively also a transition to the state $K = 1$, $\tau = 2$, since the $K = 1, \tau = 3$ and the $K = -1, \tau = 3$ levels coincide. Since the methyl alcohol

molecule is only slightly asymmetric it may be expected that transitions that violate the selection rules for the symmetric rotator, though possible, will, in general, be weak.

The selection rules for transitions between energy states corresponding to determinant 3, because of the degeneracy existing between the diagonal elements of this determinant, must be considered seperately from those for determinants 1 and 2. It will be recalled, however, that for this particular determinant a K-type doubling or splitting of the energy levels occurs in higher order, thereby removing the degeneracy.

Let now a body-fixed coordinate system be introcued with the z axis parallel to the symmetry axis of the methyl group, the y axis in the COH plane, and the x axis perpendicular to this plane. Then

$$(\mu_F)_{ab} = \mu_\perp \int \Psi_a^* \cos(y,F) \Psi_b \, d\tau + \mu_{\parallel} \int \Psi_a^* \cos(z,F) \Psi_b \, d\tau ,$$

where cos(y,F) and cos(z,F) are the cosines of the anle between the F and the y and z axes, respectively. Consider the two transformations:

$$T_1 : \quad \theta \to \pi - \theta \quad \varphi \to \pi - \varphi \quad \psi \to \psi \quad x \to -x$$

$$T_2 : \quad \theta \to \theta \quad \varphi \to -\varphi \quad \psi \to -\psi \quad x \to -x$$

T_1 and T_2 leave the Hamiltonian for the asymmetric hindered rotator invarian. Since the levels of determinant 3 are non-degenerate and $T_1^2 = T_2^2 = 1$, it follows that the wave functions for the asymmetric hindered rotator must either remain unchanged in sign for these transformations, or change sign. These two different symmetry types will be denoted by + and − , respectively.

It can readily be verified that

$$T_1(\mu_x, \mu_y, \mu_z) = (\mu_x, \mu_y, -\mu_z)$$

$$T_2(\mu_x, \mu_y, \mu_z) = (-\mu_x, \mu_y, \mu_z)$$

From these one obtaines the rule that the transitions $++ \leftrightarrow --$ and $+- \leftrightarrow -+$ are forbidden, where the first sign refers to the behavior under T_1 and the second to that under T_2.

The symmetry properties of the levels may be obtained from the formulas

$$P^{(x)}_{K1n} = (-1)^n P^{+(x)}_{-K1n} \qquad P^{(x)}_{K2n} = (-1)^n P^{+(x)}_{-K3n}$$

from the properties of the symmetric wave functions under the above transformations, and from the fact that the wave function corresponding to the higher member of a K- type doublet has in the first order the form $u_{JK\tau n} + u_{J-K\tau' n}$, while the corresponding wave function for the lower level is $u_{JK\tau n} - u_{JK\tau' n}$. The most general selection rules will not be given here, however, since only transitions for which $\Delta M = 0$ are of interest

in this present thesis. For this special case the selection rules simplify, and become the following (for n → n transitions):

$\mu_\perp \neq 0, \mu_\parallel = 0$: For $\Delta J = 0$, $U \to U$, $L \to L$.
For $\Delta J = \pm 1$, $U \leftrightarrow L$.

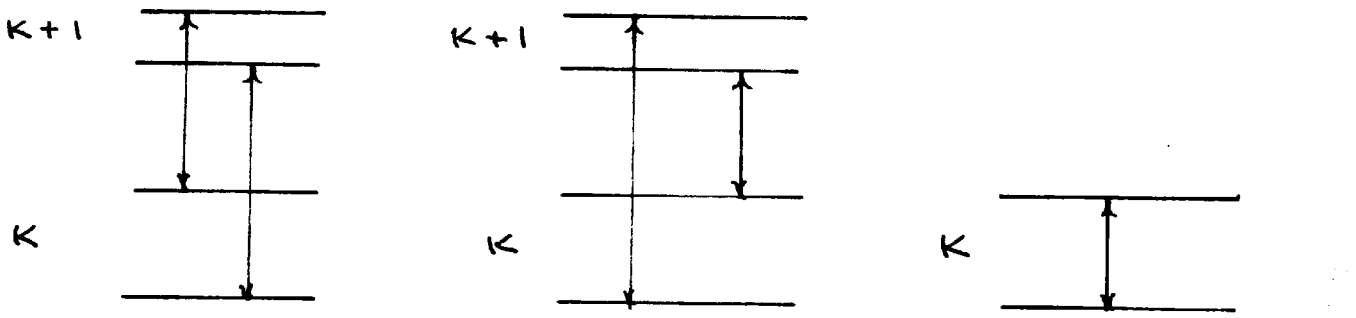
$\mu_\parallel \neq 0, \mu_\perp = 0$. $\Delta K = 0$.
For $\Delta J = 0$, $U \leftrightarrow L$.
For $\Delta J = \pm 1$, $U \to U$, $L \to L$.

U and L refer to the upper and lower states of the K-type doublet, respectively.

These selection rules are illustrated below.

Fig. 6

$\Delta M = 0$



$\Delta J = 0$ $\mu_\perp \neq 0$ $\mu_\parallel = 0$

$\Delta J = \pm 1$ $\mu_\perp \neq 0$ $\mu_\parallel = 0$

$\Delta J = \Delta K = 0$ $\mu_\parallel \neq 0$ $\mu_\perp = 0$

between levels of different classes would still hold, however.

Until now it has been assumed that no external field E is present. If E is not zero then the matrix elements of the Hamiltonian have $J \rightarrow J \pm 1$ connections, and this results in the possibility of transitions with $\Delta J = \pm 2$. The rule $\Delta M = 0, \pm 1$ is still valid, however, and intercombinations between levels of different classes as before are forbidden. Since, however, because of the presence of the Stark term, the Hamiltonian is no longer invariant under the transformations both T_1 and T_2 the wave functions for levels with K-type doubling no longer is either symmetric or antisymmetric. Consequently, all transitions between these levels are then permitted, so that previously forbidden lines become allowed, their intensities increasing with E. Such lines have actually been observed, and will later be discussed more in detail in connection with the so-called "mirror" lines.

The following is a summary of the preceding results, for the selection rules for a molecule of the methyl alcohol type:

TABLE 2

E = 0

$\Delta J = 0, \pm 1, \quad \Delta M = 0, \pm 1, \quad \Delta n =$ anything.

Transitions between levels of different classes are forbidden.

All transitions between the levels of determinant 1 are allowed, and also between those of determinant 2, where the levels are characterized by the quantum number

K =	···	-2	-1	0	1	2 ···
τ =	···	2	1	3	2	1 ···

for determinant 1, and by

K =	···	-2	-1	0	1	2 ···
τ =	···	1	3	2	1	3 ···

for determinant 2.

Only certain transitions are allowed (the rules have been stated for $\Delta M = 0$) for levels belonging to determinant 3, for which

K =	···	-2	-1	0	1	2 ···
τ =	···	3	2	1	3	2 ··· .

It may again be pointed out that for methyl alcohol, where the asymmetry is slight, the transitions which violate the selection rules for the symmetric rotator will, in general, be weak.

The Interpretation of Experimental Results

A correlation between the predictions of the theory which has been outlined and the experimental microwave data may be made, and in many ways leads to a convincing identification of the observed lines. It will prove convenient to divide the observed data into a number of categories.

a. The Coles Series of Lines

This series, as has already been mentioned, consists of a group of lines in the microwave region which have been accurately measured by Coles[2]. The members of the series have been identified by Burkhard and Dennison[6] as due to the $J \rightarrow J$, $K = 1 \rightarrow 2$, $\tau = 2 \rightarrow 1$, $n = 0 \rightarrow 0$ transitions. The series for the $C^{12}H_3O^{16}H$, for the $C^{13}H_3O^{16}H$, and for the $C^{12}H_3O^{18}H$ isotopic forms of methyl alcohol has been observed, and the frequencies of the constituent lines measured by Hughes, Good and Coles[3].

The positions of the Coles lines may be represented by a power series in $(J^2 + J)$:

$$\nu = \nu_0 + a(J^2+J) + b(J^2+J)^2 + \cdots$$

If terms only through $e(J^2+J)^5$ are retained, the coefficients appearing in this equation may be determined from the observed frequencies for the $J = 2, 3, 4, 5, 6, 7$ lines. For the $C^{12}H_3O^{16}H$ molecule these coefficients are (in $\frac{\text{m.c.}}{\text{sec.}}$)

$$\nu_0 = 24948.05 \qquad a = -2.9453 \qquad b = .11147$$

$$c = -3.065 \times 10^{-5} \qquad d = 7.3 \times 10^{-9} \qquad e = -4.5 \times 10^{-9}$$

These values differ slightly from those of Burkhard and Dennison obtained by keeping terms only through $d(J^2 + J)^4$ and based upon a different set of observed lines, thus showing

that the value of b, the coefficient of the $(J^2 + J)^2$ term and of considerable interest in this thesis, is probably no more reliable than about 1%.

The value of the coefficient for the other two isotopes, $C^{13}H_3\ O^{16}H$ and $C^{12}H_3\ O^{18}H$ obtained in a similar manner, but retaining terms only through $d(J^2 + J)^4$, are (in $\frac{\text{m.c.}}{\text{sec.}}$)

$C^{13}H_3\ O^{16}H$

$\nu_o = 27,065.58 \quad a = -2.6536 \quad b = .09008 \quad c = 3.361 \times 10^{-4}$

$d = -4.88 \times 10^{-6}$

$C^{12}H_3O^{18}H$

$\nu_o = 33918.57 \quad a = -.4448 \quad b = .08550 \quad c = -2.971 \times 10^{-5}$

$d = -3.01 \times 10^{-8}$

The theoretical expression for the Coles series may be readily obtained by the usual perturbation theory methods. An inspection of the Hamiltonian off-diagonal terms shows that they yield contributions to the energy arrangeable in powers of $(J^2 + J)$, in agreement with Coles assumption. The resultant expression obtained in this way for the quantity ν_o is

$$\nu_o = \frac{\hbar^2}{2}\left[-\frac{3}{A} - \frac{3}{2}\frac{C_1^2+D^2}{A(BC_1-D^2)} + \frac{3}{C}\right] + \mathcal{E}_{210} - \mathcal{E}_{120} + \sum_{K'\tau'n'} \frac{\left[H^{2\,K'\tau'n'}_{2\,2\,1\,0}\right]^2}{W^0_{2210} - W^0_{2K'\tau'n'}} - \sum_{K'\tau'n'} \frac{\left[H^{2K'\tau'n'}_{2\,1\,2\,0}\right]^2}{W^0_{2120} - W^0_{2K'\tau'n'}}, \text{ where}$$

$$\mathcal{E}_{K\tau n} = W^{\wedge}_{K\tau n} - \frac{\hbar^2}{2}\frac{D^2}{(BC_1-D^2)C_1}\int_0^{2\pi} P^*_{K\tau n}\frac{d^2 P_{K\tau n}}{dx^2}\,dx .$$

The last two terms in the equation for ν_o are due to off-diagonal elements and will, in general, be fairly small. This formula will be utilized in future applications.

ν_o and the other coefficients a, b, c, ... are seen to be functions of H and of the moments of inertia, and yield relations which can be used to help determine the molecular constants. Only ν_o and b are suitable for this purpose, however, because of certain effects to be discussed.

The Gordy Lines

Edwards, Gilliam, and Gordy[4] have investigated lines due to the transitions $J = 0 \rightarrow 1$, $K = 0 \rightarrow 0$, $\tau \rightarrow \tau$, $n \rightarrow n$. The theoretical expression for these frequencies of the Gordy type - as they will be referred to in this thesis - is given by

$$\nu_g^{n,\tau} = \frac{h^2}{2}\left[\frac{1}{A} + \frac{C_1^2 + D^2}{2A(BC_1 - D^2)}\right] + \sum_{K'n'\tau'} \frac{\left[H_{1\,0\,n\tau}^{1\,K'n'\tau'}\right]^2}{W_{1\,0\,n\tau}^{0} - W_{1\,K'n'\tau'}^{0}} .$$

The effect of the last term for the normal methyl alcohol molecule $C^{12}H_3O^{16}H$ is small. For $\tau = 1$, $n = 0$, for example, it is about $-6 \frac{m.c.}{sec.}$. The splitting between various lines corresponding to different n's and τ's is even smaller, being of the order of a few tenths of a megacycle/sec. or less. Lines separated by such slight frequency differences probably would not be resolved, and, therefore, on the basis of the

above formula, only one component should be observed.

Edwards, Gilliam, and Gordy have attempted to locate such a line for the isotopes $C^{12}H_3O^{16}H$, $C^{13}H_3O^{16}H$, $C^{12}H_3O^{16}D$, and $C^{12}D_3O^{16}D$ by taking measurements in regions where the Gordy frequencies might be expected to occur. According to their results, the following lines are to be ascribed to the $J = 0 \rightarrow 1$, $K = 0 \rightarrow 0$ transitions:

$C^{12}H_3O^{16}H$	$C^{13}H_3O^{16}H$	$C^{12}H_3O^{16}D$	$C^{12}D_3O^{16}D$
49867.2 $\frac{m.c.}{sec.}$	48529.6 $\frac{m.c.}{sec.}$	47359.7 $\frac{m.c.}{sec.}$	38530 $\frac{m.c.}{sec.}$ or 38967.0 $\frac{m.c.}{sec.}$

Unfortunately, at the time these measurements were taken, no Stark effect observations were attempted, and, therefore, the above identifications remain in doubt. A recent private communication from Gordy states, however, that the line at 49867.2 $\frac{m.c.}{sec.}$ for the normal molecule appears to have only one Stark component, as would be expected if it were due to a $J = 0 \rightarrow 1$, $K = 0 \rightarrow 0$ transition.

On the other hand, evidence has accumulated that a doublet at 48372 $\frac{m.c.}{sec.}$ and 48376 $\frac{m.c.}{sec.}$ is also caused by a transition of the Gordy type. According to a private communication from Coles, a single Stark component was also observed for this doublet. If both these experimental observations

are correct*, then, apparently, different values of the torsional number n are involved in the transitions for the doublet and for the line at 49867.2 $\frac{m.c.}{sec.}$, the most likely ones being 0 and 1. The problem then arises as to the reason for the large separation of 1490 $\frac{m.c.}{sec.}$ between the doublet and the single line, since, as mentioned above, the contribution of the off-diagonal terms are far too small to account for this great splitting. A calculation shows the effect of centrifugal stretching, which should also cause a splitting, to be only of the order of 100 $\frac{m.c.}{sec.}$.

Knowing which frequency is the correct one for the basic $n = 0 \rightarrow 0$ transition is important because from it the large moment of inertia A is essentially determined. The value of A, in turn, affects all the other molecular constants. Whether the $n = 0 \rightarrow 0$ transition is to be associated with the line at 49867 $\frac{m.c.}{sec.}$, and the $n = 1 \rightarrow 1$ transition with the doublet at 48374 $\frac{m.c.}{sec.}$, or the converse, or whether some other possibility may exist, remains to be established experimentally.

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* As the above was being written, an announcement by Swan[9] appeared stating that the line at 49867.2 $\frac{m.c.}{sec.}$ has a first order Stark effect (a second order Stark effect is predicted by theory for lines of the Gordy type), and, thus, appears to be improperly identified by Gordy.

At present the weight of theoretical arguments seem to favor the doublet as the likely choice, but there is also evidence for choosing the line at 49867 $\frac{m.c.}{sec.}$ as due to the basic $n = 0 \rightarrow 0$ transition. This is the following: 1) Only one strong line for $C^{12}H_3O^{16}D$ was observed by Edwards, Gilliam, and Gordy in the expected region. This line, located at 47359.7 $\frac{m.c.}{sec.}$, presumably is due to the basic Gordy transition. However, if this is actually the case, then calculations based upon any molecular model of reasonable dimensions for the methyl alcohol molecule lead to results which clearly favor the line at 49867 $\frac{m.c.}{sec.}$ as the corresponding one for the normal molecule. 2) One would expect the $n = 0 \rightarrow 0$ frequency to be higher than the $n = 1 \rightarrow 1$ frequency, as is the case in methyl silane, CH_3SiH_3. The observed splitting for this molecule is, however, only of the order of several hundred megacycles/sec.

The evidence favoring the doublet at 48374 $\frac{m.c.}{sec.}$ appears to be stronger than that for the line at 49867 $\frac{m.c.}{sec.}$, and is the following: 1) A line observed at 28316 $\frac{m.c.}{sec.}$ by Hughes, Good, and Coles[3], and one at 19967 $\frac{m.c.}{sec.}$ measured by Hughes (private communication) have been identified as due to the $J = 3 \rightarrow 4$, $K = 1 \rightarrow 0$, $\tau = 2 \rightarrow 3$, $n = 0 \rightarrow 0$, and $J = 3 \rightarrow 2$, $K = 0 \rightarrow 1$, $K = 3 \rightarrow 2$, $n = 0 \rightarrow 0$ transitions, respectively.

Now it is readily shown that, except for slight correction terms, the sum of these two frequencies should be equal to the frequency of the basic Gordy line. This sum is 48283 $\frac{m.c.}{sec.}$, while, if the corrections are included, the figure of 48370 $\frac{m.c.}{sec.}$ is obtained, very nearly equal to the frequency of the doublet at 483.74 $\frac{m.c.}{sec.}$.* 2) According to Borden and Barker[1], they obtained from the fine structure of the vibration band at 1034 cm^{-1} the quadratic equation

$$\nu = 1034.18 + 1.5975m - .0088m^2 \ cm^{-1}$$

for the normal methyl alcohol molecule. If m is identified with the quantum number J, then a simple calculation shows that the basic Gordy frequency is 48160 $\frac{m.c.}{sec.}$, provided the assumption is made, as seems plausible, that the general appearance of the fine structure of the band is due primarily to a $n = 0 \rightarrow 0$ transition. Recent work by C. W. Peters at the University of Michigan on the same band of $C^{12}H_3O^{16}H$ and the corresponding band of $C^{12}H_3O^{16}D$, using a high resolution grating spectrometer, also confirms this choice.

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* It may be remarked in passing that both choices for the basic Gordy line yield predicted values for the frequencies of certain observed lines that seem to be about equally good.

3) More reasonable values for C_2 and the inter-atomic distances is obtained. C_2, for example, turns out to be 5.34×10^{-40} gm cm^2, a value almost equal to the corresponding moment of inertia for CH_4, while on the basis of the other possibility for the basic Gordy line, C_2 is 5.16×10^{-40} gm cm^2. This latter value, though perhaps not impossible, yet is rather extreme. Similarly, the calculated OH distance is also more plausible.

The evidence presented above seems to favor the doublet at 48374 $\frac{\text{m.c.}}{\text{sec.}}$ as the proper choice corresponding to the $n=0 \rightarrow 0$ transition. Consequently, this value will be the one used in the present work.

Other Identified Lines

Besides the members of the Coles series and the Gordy lines, there are a number of other lines in the microwave region of methyl alcohol which have been identified, and which are important in this thesis. The following table, based upon the measurements of Hughes, Good, and Coles[3], summarizes the data pertinent to these lines.

See table next page.

TABLE 3

Frequency $\left(\frac{m.c.}{sec.}\right)$	Stark Coeff. B.	Transition Involved			
ν_f 19967	——	J= 3→2	K=0→1	=3→2	n=0→0
ν_a = 28316.03	~11 $\frac{m.c.}{sec.esu}$	3→4	1→0	2→3	0→0
ν_b = 36169.24	6.52	3→4	0→1	2→1	0→0
ν_e = 37703.72	3.09	8→7	1→2	1→3	0→0
ν_d' = 38293.5	13.0	5→6	3→2	1→2	0→0
ν_d'' = 38452.69	13.0				

Many other lines have been measured by Hughes, Good and Coles, but these are mostly due to transitions involving higher J values, and will not be listed here. The Stark effect has been measured for all these lines except for the one at 19967 $\frac{m.c.}{sec.}$, and is found to be linear. The following formula was found to apply to the observed Stark pattern:

$$\Delta\nu_M = B\,M\,E \qquad M = \text{magnetic quantum number}$$

The coefficient B is given in the above table. From the Stark effect can also be predicted the J values involved in the transitions. The remaining quantum numbers K, τ, n have been inferred from the Stark coefficients and from the approximate frequencies to be expected for various transitions.

It is found that the calculated values for the frequencies corresponding to various transitions vary only by the

order of several thousand megacycles/sec. for different sets of reasonable parameters. Since the frequencies for these transitions may vary from zero to several hundred megacycles/sec., or more, the quantum numbers K, τ, and n can be generally uniquely determined. The observed values for the Stark coefficients can then be used to furnish a final confirmation.

Since the lines listed in the above table will be utilized in future calculations, it will prove convenient to give at this point the theoretical expression for their frequencies. These are

$$\nu_a = \frac{9}{2}\nu_g^0 - \frac{\hbar^2}{2}\frac{1}{C} + \varepsilon_{030} - \varepsilon_{120}$$

$$\nu_b = \frac{7}{2}\nu_g^0 + \frac{\hbar^2}{2}\frac{1}{C} + \varepsilon_{110} - \varepsilon_{020}$$

$$\nu_f = -\frac{7}{2}\nu_g^0 + \frac{\hbar^2}{2}\frac{1}{C} + \varepsilon_{120} - \varepsilon_{030} ,$$

$$\nu'_d = \frac{17}{2}\nu_g^0 - \frac{\hbar^2}{2}\frac{5}{C} + \varepsilon_{220} - \varepsilon_{310}$$

$$\nu''_d - \nu'_d = \frac{\left(H^{6\,0\,1\,0}_{6\,2\,2\,0}\right)^2}{W^0_{010} - W^0_{220}}$$

$$\nu_e = -\frac{19}{2}\nu_g^0 + \frac{\hbar^2}{2}\frac{3}{C} + \varepsilon_{230} - \varepsilon_{110}$$

where

$$\nu_g^0 = \frac{\hbar^2}{2}\left[\frac{2}{A} + \frac{C_1^2 + D^2}{A(BC_1 - D^2)}\right], \text{ and}$$

$$\varepsilon_{K\tau n} = W^2_{K\tau n} - \frac{\hbar^2}{2}\frac{D}{(BC_1 - D^2)}\int_0^{2\pi} p^*_{K\tau n}\frac{d^2 p_{K\tau n}}{dx^2}\,dx .$$

CHAPTER III

THE CALCULATION OF THE MOLECULAR CONSTANTS

This chapter deals with the calculation of the molecular structure of the methyl alcohol molecule from the microwave data. The particular constants to be determined are the moments and products of inertia, both for the normal form of the molecule and for various isotopic modifications, the inter-atomic distances, and the hindered potential barrier height.

The results obtained are believed to be more reliable than those found by Burkhard and Dennison[6] because of new data available, and because of the greater number of consistency checks possible. The additional data allows the evaluation of a larger number of new molecular constants, such as the value for the moment of inertia of the methyl group, C_2, the moments of inertia for various isotopic molecules and self-consistent values for the inter-atomic dimensions.

The present chapter is divided into two main sections, the first dealing with the normal molecule $C^{12}H_3O^{16}H$, and the second with the other isotopic forms. The general procedure to be followed in the calculations has already been

outlined in the first chapter, and for the normal molecule consists first of finding the product of inertia, D, from those data most sensitively dependent upon it, namely the Stark coefficients of the Coles microwave series, and, second, of obtaining the moments of inertia B, C_1 and C_2, and the barrier height H from the positions of four of the most suitable microwave lines.

In calculating the product of inertia D for the other isotopic molecules the Stark coefficients are again employed together with the computed changes in the other moments of inertia. These latter are based upon estimates of the interatomic distances but are relatively insensitive to their precise values. With the aid of the isotopic products of inertia the interatomic distances may now be determined with considerable accuracy. The molecular constants have, at this point, all been evaluated, but the experimental data have not been exhausted and there thus remains a number of self consistancy checks possible.

THE NORMAL MOLECULE

The Calculation of D, $\mu_{||}$, and $\mu_{\perp}$

D, the cross product of inertia, and $\mu_{||}$, the component of the electric dipole moment parallel to the symmetry axis of the methanol molecule may best be evaluated from the Stark

data for the Coles series. The perpendicular component of the electric dipole moment $\mu_\perp$ is then obtained from the formula

$$\mu_\perp = \sqrt{(\mu_{tot})^2 - (\mu_{11})^2},$$

where μ_{tot} is the total electric moment of the molecule, which has been measured[8] from the temperature dependence of the dielectric constant and found to have the value of 1.69×10^{-18} esu.

The results obtained will depend to some extent upon the values assumed for the other molecular constants B, C_1, C_2 and H. This dependence, however, is quite insensitive, and accurate results are obtained after one or at the most two cycles of calculations.

The expression for the linear Stark effect for members of the Coles series is readily found from the matrix elements of the Hamiltonian for the asymmetric hindered rotator, and is given by the formula

$$\Delta\nu = ME\left(B' + \frac{A'}{J^2 + J}\right),$$

where

$$B = \frac{h^2 D \mu_\perp}{2 B C_1 - D^2} \sum_{n=0}^{\infty} \left[\frac{H^{1}_{K=2,\tau=1,n=0}\, h^{12n}_{210}}{W^0_{210} - W^0_{12n}} + \frac{H^{33n}_{210}\, h^{33n}_{210}}{W^0_{210} - W^0_{33n}} - \frac{H^{03n}_{120}\, h^{03n}_{120}}{W^0_{120} - W^0_{03n}} - \frac{H^{21n}_{120}\, h^{21n}_{120}}{W^0_{120} - W^0_{21n}} \right],$$

$$A = \mu_{11} + \frac{h^2 D \mu_\perp}{2 BC_1 - D^2} \sum_{n=0}^{\infty} \left[-2 \frac{H^{12n}_{210} h^{12n}_{210}}{W^0_{210} - W^0_{12n}} - 6 \frac{H^{33n}_{210} h^{33n}_{210}}{W^0_{210} - W^0_{33n}} + 2 \frac{H^{21n}_{120} h^{21n}_{120}}{W^0_{120} - W^0_{21n}} \right],$$

$$H^{k+1\,\tau'n'}_{k\tau n} = \sqrt{(J-K)(J+K+1)} \int P^*_{k\tau n} e^{-\lambda x} \left(\frac{1}{2} \frac{d}{dx} - \frac{1}{2} \right) P_{k+1\,\tau'n'}\, dx, \quad h^{k+1\,\tau'n'}_{k\tau n} = \frac{\sqrt{(J-K)(J+K+1)}}{J^2+J} \int_0^{2\pi} P^*_{k\tau n} e^{-\lambda x} P_{k+1,\tau'n'}\, dx$$

There is also a small quadratic term in E, but for the experimental fields usually employed it is usually negligible.

Hughes, Good, and Coles[3] have measured the values of A and B and found

$$A' = 131.1 \ \frac{\text{m.c.}}{\text{sec. esu}} \quad , \quad B' = 1.710 \ \frac{\text{m.c.}}{\text{sec. esu}} \ .$$

Using these values and the above equations, one obtains

$$A' = 131.1 = \mu_{11} - .1640 \ \frac{\mu_\perp D}{BC_1 - D^2} \ \frac{\text{m.c.}}{\text{sec. esu}} \ ,$$

$$B' = 1.710 = .11154 \ \frac{\mu_\perp D}{BC_1 - D^2} \ \frac{\text{m.c.}}{\text{sec. esu}} \ ,$$

and, finally,

$$D = -.1070 \times 10^{-40} \text{ gm cm}^2$$

$$\mu_{11} = -.885 \times 10^{-18} \text{ esu}$$

$$\mu_\perp = 1.440 \times 10^{-18} \text{ esu}$$

In calculating these figures values for C_1, C_2, B, and H were used that are determined in the next section. As already

mentioned, this is permissible because the results of the two sections are to a large degree independent of each other.

$\mu_{||}$ is chosen negative in conformity with the requirement of atomic electronegativity which demands that the parallel component of the moment be directed along the negative z axis. Similarly $\mu_{\perp}$ must be along the positive y axis, and is then positive. For these reasons the sign of D must be negative. This conclusion is also supported by the Stark data of the Coles series for various isotopic molecules. From the fact that D is negative it follows for plausible values of the COH angle that the symmetry axis cuts the line connecting the osygen and hydrogen nuclei between the center of gravity of the OH system and the hydrogen nucleus.

2. <u>The Calculation of C_1, C_2, B, and H</u>

The constants C_1, C_2, B and H are determined from the measured values for the frequencies of ν_a, ν_b, ν_c^0, and ν_g. These frequencies are given by the formulas

$$\nu_a = \frac{9}{2}\nu_g^0 - \frac{h^2}{2}\frac{1}{C} + \varepsilon_{030} - \varepsilon_{120} + \epsilon_a ,$$

$$\nu_b = \frac{7}{2}\nu_g^0 + \frac{h^2}{2}\frac{1}{C} + \varepsilon_{110} - \varepsilon_{020} + \epsilon_b ,$$

$$\nu_c^0 = -\frac{3}{2}\nu_g^0 + \frac{h^2}{2}\frac{3}{C} + \varepsilon_{210} - \varepsilon_{120} + \epsilon_c ,$$

$$\nu_g = \nu_g^0 + \epsilon_g ,$$

which differ from the previously derived expressions only by the presence of the correction terms ϵa, ϵb, ϵc, and ϵg. In these equations

$$\nu_g^\circ = \frac{h^2}{2}\left[\frac{1}{A} + \frac{C_1}{BC_1 - D^2}\right] .$$

ν_c° is the value of ν_c for $J = 0$. The correction terms are due to the following causes: 1) the $K \longrightarrow K \pm 1$ off-diagonal terms, 2) the $K \rightarrow K \pm 2$ off-diagonal terms, and the centrifugal stretching terms, caused both by the barrier height and by the moment of inertia effects. The magnitude of 1) and 2) may be readily calculated, while that part of 3) caused by the barrier height effect may be estimated from the $(J^2 + J)$ coefficient of the Coles series. The moment of inertia correction for methyl alcohol is, unfortunately, not known exactly, though it has been determined for the methyl halides by Slawsky and Dennison[10]. Using their values as order of magnitude estimates for methyl alcohol it is found that the moment of inertia effect is relatively slight for a given energy level provided the quantum numbers involved are small, and as this is the case for the present calculation, will consequently be neglected.

In this way the total corrections are found to be

$$\epsilon_a = -193 \frac{m.c.}{sec.}, \quad \epsilon_b = -136 \frac{m.c.}{sec.}, \quad \epsilon_c = 8 \frac{m.c.}{sec.}, \quad \epsilon_g = -6 \frac{m.c.}{sec.}$$

The diagonal terms $-\frac{\hbar^2}{2}\frac{D^2}{(BC_1-D^2)C_1}\int_0^{2\pi} p^*_{k\nu n}\frac{d^2 p_{k\nu n}}{dx^2}\,dx$ are also involved in the energy expression, and for the value of D obtained in the last section may be estimated to give the correction $\delta\nu_a = 30 \frac{m.c.}{sec.}$, $\delta\nu_b = 131 \frac{m.c.}{sec.}$, $\delta\nu_c = 139 \frac{m.c.}{sec.}$, $\delta\nu_g = 0$. Substituting these values together with the other correction terms into the frequency expression, and adopting the value of 48374 $\frac{m.c.}{sec.}$ for νg (the average of the doublet frequencies at 48372 $\frac{m.c.}{sec.}$ and 48376 $\frac{m.c.}{sec.}$, $\nu_a = 28316 \frac{m.c.}{sec.}$,

$\nu_b = 36169 \frac{m.c.}{sec.}$, and $\nu_c^0 = 24948 \frac{m.c.}{sec.}$, the equations for

ν_a, ν_b, and ν_c^0 become:

$$W^{\sim}_{120} - W^{\sim}_{030} + \frac{\hbar^2}{2}\frac{1}{C} = 189234 \frac{m.c.}{sec}$$

$$W^{\sim}_{020} - W^{\sim}_{110} - \frac{\hbar^2}{2}\frac{1}{C} = 133158 \frac{m.c.}{sec}$$

$$W^{\sim}_{120} - W^{\sim}_{210} - \frac{\hbar^2}{2}\frac{3}{C} = -97372 \frac{m.c.}{sec}$$

These three equations depend upon the three paramaters C_1, C_2, and H, and determine their values uniquely. The internal energy expressions appearing in these equations are complicated functions of the parameters, but approximate formulas have been found for the internal energy terms that are quite

accurate for paramaters in the neighborhood of the solution.

These are

$$W^{1}_{120} - W^{1}_{210} = \frac{C \times 10^{-40}}{C_1 C_2}\left[290164 - 19630\beta - 244\rho\right] \frac{m.c.}{sec.}$$

$$W^{1}_{120} - W^{1}_{020} = \frac{C \times 10^{-40}}{C_1 C_2}\left[63062 - 4823\beta + 262\rho\right] \frac{m.c.}{sec.}$$

$$W^{1}_{020} - W^{1}_{110} = \frac{C \times 10^{-40}}{C_1 C_2}\left[265157 - 17190\beta - 14\rho\right] \frac{m.c.}{sec.}$$

where $\beta = \left[\frac{2\pi^2 c}{h}\ \frac{C_1 C_2 H}{C}\right]^2 - 11.3$, $\rho = 1000\left(\frac{C_1}{C} - .19\right)$, and C_1, C_2, and C are in $gm\,cm^2$.

Using these equations the solutions for the molecular paramaters may readily be found. An exact calculation then confirms that the approximate formulas for the internal energy levels are in fact accurate to one or two $\frac{m.c.}{sec.}$. The values of the paramaters $\frac{C_1}{C}$, C and H determined in this manner are

$$\frac{C_1}{C} = .189275,\ C_2 = 5.33265 \times 10^{-40} gm\ cm^2,\ H = 374.821\ cm^{-1}$$

These lead to the values:

$$\rho = \frac{2\pi^2 C}{h}\ \frac{C_1 C_2 H}{C} = 3.37997,\quad C_1 = 1.24498 \times 10^{-40} gm\ cm^2,$$

$$\frac{\pi^2}{2}\ \frac{1}{C} = 127537\ \frac{m.c.}{sec.}\ .$$

B is determined by the equation for ν_J^0, and is found to be

$$B = 34.096 \times 10^{-40} \text{gm cm}^2 \quad ,$$

and, consequently,

$$A = B + C_1 = 35.341 \times 10^{-40} \text{ gm cm}^2 \ .$$

The appendix contains values for the energy levels and for the Fourier coefficients a_τ corresponding to the above constants.

That the equations used in determining the molecular paramaters are good ones can be seen by varying the frequencies ν_a, ν_b, ν_c in turn by 100 $\frac{\text{m.c.}}{\text{sec.}}$, and calculating the new set of molecular constants. If this is done it is found that the maximum changes in the constants are

$\Delta C_1 = .003 \times 10^{-40} \text{gm cm}^2$, $\Delta C_2 = .02 \times 10^{-40} \text{gm cm}^2$, $\Delta H = .3 \text{ cm}^{-1}$.

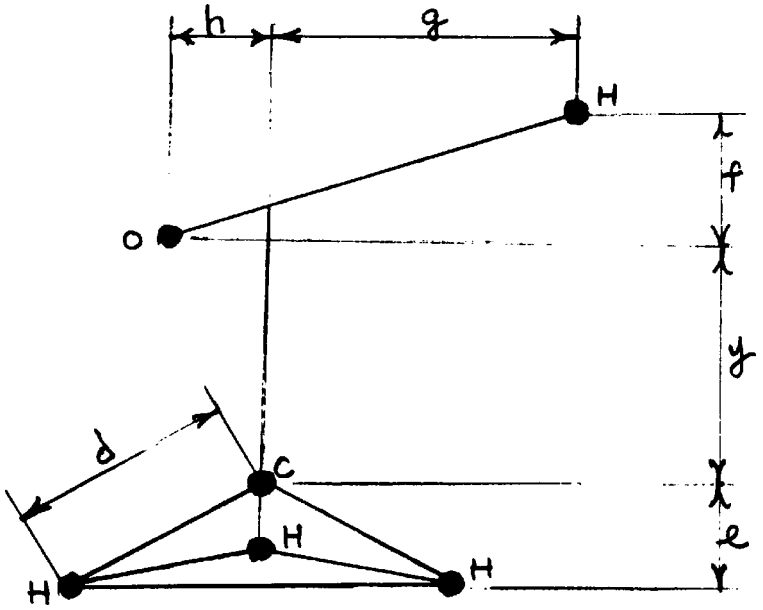
Thus, the results obtained for C_1, C_2, and H will still be quite good provided that the magnitude of the effect not taken into account does not exceed 100 $\frac{\text{m.c.}}{\text{sec.}}$.

It is interesting to note that the value of 5.333×10^{-40} gm cm^2 for the C_2 of methyl alcohol is quite close to the corresponding moment of inertia of the methyl group for methane, CH_4, which is $5.33^7 \times 10^{-40}$ gm cm^2. This near equality of the

two moments of inertia makes it plausible though not certain, the CH distance and the HCH angle of methyl alcohol do not differ much from those of methane.

3. The Isotopic Molecules $C^{13}H_3O^{16}H$, $C^{12}H_3O^{18}H$.

The molecular constants determined for the normal molecule in the preceding section are insufficient to determine the inter-atomic distances of the molecules. These can be specified by the following six paramaters which were found to be particularly convenient, and are illustrated in the following diagram:



To determine these distances it is necessary to find the moments of inertia not only for the normal molecule (which

are only four in number: C_1, C_2, D, and B) but also for other isotopic forms of the molecule. Fortunately, data are available for the two molecules $C^{13}H_3OH$ and $C^{12}H_3O^{18}H$ giving the positions of the Coles series of lines, together with the Stark effects, and these are sufficient to determine a number of other molecular constants. Unfortunately, however, it turns out in the course of the calculation that the distance d is not determined too accurately, and so a complete determination of all six distances has been found to be impossible. For this reason it has been thought best to adopt the methane value of 1.093A for the CH distance, the values determined for the other molecular distances being for the most part quite insensitive to the precise figure chosen.

Using the Stark data, one may determine the values of D, $\mu_{||}$, and $\mu_{\perp}$ for the $C^{13}H_3O^{16}H$ and $C^{12}H_3O^{18}H$ molecules, following exactly the same procedure as for the normal molecule, and again adopting the value of 1.69×10^{-18}esu for μ_{tot}. Since the value of C_1 for $C^{13}H_3O^{16}H$ is almost exactly equal to that for the normal molecule, the matrix elements and the internal energy levels may be taken to be identical for the two isotopic forms. Only $B(C^{13})$ will be different from the corresponding normal value, resulting in a slight change in the energy denominators of the Stark energy expression. $B(C^{13})$

must initially be obtained by assuming particular values for the distances f, j, and ℓ subject to the condition that $B(N) = 34.096 \times 10^{-40}$ gm cm^2, but it may readily be seen that $B(C^{13})$ is very little dependent upon the exact values adopted for the dimensions.

The situation is similar for the $C^{12}H_3O^{18}H$ molecule, subject, however, to the complication that $C_1(O^{18})$ is sufficiently different from $C_1(N)$ to necessitate a recalculation of the internal energy levels and the matrix elements of the Hamiltonian. The values of B and C_1 must here also be obtained initially on the basis of assumed dimension, but, as for the normal molecule, the results obtained are quite insensitive to B and C_1.

The final results of the calculations are

	$C^{13}H_3O^{16}H$	$C^{12}H_3O^{18}H$	$C^{12}H_3O^{16}H$
D	$-.1259 \times 10^{-40}$ gm cm^2	$-.2498 \times 10^{-40}$ gm cm^2	$-.1070 \times 10^{-40}$ gm cm^2
$\mu_{\|\|}$	$-.886 \times 10^{-18}$ esu	$-.890 \times 10^{-18}$ esu	$-.885 \times 10^{-18}$ esu
$\mu_\perp$	1.439×10^{-18} esu	1.437×10^{-18} esu	1.440×10^{-18} esu

The normal molecule $C^{12}H_3O^{16}H$ figures are repeated for the purpose of comparisons. The values of $\mu_{\|\|}$ and $\mu_\perp$ should be the same for all molecules to a high degree of approximation. The deviations found in the above table are, however, within experimental error.

3. The Calculation of Inter-atomic Distances

The following method, although not unique, appears to be the most satisfactory.

As already discussed, six distances are required in order to completely specify the methyl alcohol molecule. Since, however, the CH distance turns out to be poorly determined by the data, necessitating an adoption of the methane value of 1.093A for the CH bond length, only five undetermined distances remain. In order to solve for these, the values for the five moments of inertia $C_1(N)$, $B(N)$, $D(N)$, C_2, and $D(O^{18})$ previously determined have been selected as the basis for the calculation.

The problem now is one of expressing these moments of inertia in terms of the distances h, g, f, j, and ℓ, and solving the five resulting equations for the five unknowns. The procedure is straight forward, though lengthy, since the equations are quadratic and must be treated by methods of successive approximation. The final values are:

$h = .0790$ A $\qquad j = 1.4319$ A

$g = .8070$ A $\qquad \ell = .3639$ A

$f = .3061$ A

From these values one can immediately calculate other distances and moments of inertia. These are listed in the following table where, for the sake of completeness, the constants pre-

viously obtained are also included.

TABLE 4

	$C^{12}H_3O^{16}H$	$C^{13}H_3O^{16}H$	$C^{12}H_3O^{18}H$
C_1	1.2500×10^{-40} gm cm^2	1.2453gm cm^2	1.2582gm cm^2
B	34.096	34.948	35.593
D	-.1070	-.1237	-.2498
$\frac{C_1}{C}$	.189275	.189313	.190900

h = .0790 A

g = .8070 A

f = .3061 A

$\overline{OH}$ = .9374 A

g + h = .8860 A

$\overline{CO}$ = 1.4340 A

$\angle HCH = 109^0 30'$

$\angle COH = 105^0 56'$

j = 1.4319 A

ℓ = .3639 A

d = 1.093 A(assumed)

angle of OH with symmetry axis = $70^0 55'$

distance of each H of CH_3 group to symmetry axis = 1.0307 A

The following points should be noted: 1) The oxygen atom is located .0790A away from the symmetry axis on the opposite side from that of the hydrogen atom, which in turn is .8070A from the symmetry axis. The center of gravity of the OH system for the normal molecule lies between the oxygen atom and the symmetry axis at a distance of .014A from the

latter. Thus, neither the oxygen atom nor the center of gravity of the OH bar is situated precisely along the axis of symmetry. 2) Because of the similarity between the COH portion of the CH_3 OH molecule and the H_2O molecule, the OH distance and the COH angle of the former can be expected to be fairly close to the OH distance and the HOH angle of the latter. Actually, for the water molecule the average OH distance is .9568 A , while the average HOH angle is $105^0 3'$. These differ slightly from the equilibrium values of .9584 A and $104^0 27'$, but either set compares favorably with the methyl alcohol values .9374A and $105^0 56'$. 3) The calculated CO distance is 1.4340 A , which is close to the figure 1.44 A found by election diffraction methods. The actual value obtained, however, depends strongly upon the dimensions assumed for the CH distance. In particular, a change of .01 A from the adopted value of 1.093 A for the CH distance will cause a change in the CO dimension of .008 A . 4) The calculated value of $109^0 30'$ for the HCH angle is very close to the figure of $109^0 28'$ for the corresponding angle in methane. This likeness is, however, also dependent upon the exact value assumed for the CH distance.

The dimensions given in the above table are merely a self-consistent set, and not intended to be regarded as accurate to the number of decimal places listed. The errors involved come from two sources: a) the experimental errors, which in many but not all instances are small because of the accuracy of the microwave measurements, and b) the limitation of the present theory in which, for example, the molecule is taken to be rigid, and a simple sinusoidal dependence is assumed for the hindering potential. The higher order terms introduced by these and other causes may very well influence the results, past experience generally showing an effect of one or two percent. An example of such errors is the discrepancy between the value of $-.1237 \times 10^{-40}$ gm cm^2 for the D of the $C^{13}H_3O^{16}H$ molecule based upon the above inter-atomic distances, and that of $-.1259 \times 10^{-40}$ gm cm^2 calculated from the Stark data. The difference of about $.002 \times 10^{-40}$ gm cm^2 between the two figures is seen to be within the expected deviation.

An examination of the calculational procedure used in determining the inter-atomic distances shows that most of the error in the dimensions comes from the uncertainties in D and in the assumed CH distance. If the possible variation in D is taken to be $.002 \times 10^{-40}$ gm cm^2 - a not unreason-

able value as seen above - then the following changes result in the molecular dimensions:

$\Delta j = .002A \quad \Delta f = .03A \quad \Delta g = .003A \quad \Delta h = .003A$.

Likewise if the CH distance is altered by .01A from the assumed value, the following changes occur:

$\Delta j = .008A \quad \Delta f = .015A \quad \Delta g = .001A \quad \Delta h = .001A.$

If both effects of the above magnitude occur together, then, approximately,

$\Delta(CO) = .008A \quad \Delta(OH) = .01A \quad \Delta \angle COH = 2^{\circ}$.

The change in f is seen to be the largest, corresponding to the fact that the moments of inertia are least dependent on this particular constant.

CHAPTER IV.

DISCUSSION OF ADDITIONAL EXPERIMENTAL DATA

In this chapter possible applications of the asymmetric hindered rotator theory will be discussed, and certain experimental aspects of the methyl alcohol microwave spectrum examined in an attempt to obtain a number of self-consistency checks on the values found for the molecular constants in the preceding sections. In particular such experimental features will be investigated as the positions of a number of lines, the $(J^2 + J)^2$ coefficients of the Coles series for a variety of isotopic molecules, the "mirror" lines, and the first and second order Stark effects. It will be seen that, in general, the results here obtained furnish good confirmation for the values already found for the molecular constants.

1. The Frequencies ν'_d, ν''_d, ν_e, and ν_f.

The lines designated as ν'_d, ν''_d, ν_e, and ν_f have been measured by Hughes, Good, and Coles[3], and are listed below, together with the corresponding transitions involved.

	Frequency $\left(\frac{\text{m.c.}}{\text{sec.}}\right)$	Transition Involved			
ν'_d	38293.5	$J = 5 \rightarrow 6$	$K = 3 \rightarrow 2$	$\tau = 1 \rightarrow 2$	$n = 0 \rightarrow 0$
ν''_d	38452.69				
ν_e	37703.72	$8 \rightarrow 7$	$1 \rightarrow 2$	$1 \rightarrow 3$	$0 \rightarrow 0$
ν_f	19967	$3 \rightarrow 2$	$0 \rightarrow 1$	$3 \rightarrow 2$	$0 \rightarrow 0$

The identification of these lines has been accomplished in the following manner. The J values of the transitions have been determined experimentally by use of the Stark effect, while the other quantum numbers have been found by a process of elimination, no other choice for them yielding reasonable results for the observed frequencies. The formulas for the frequencies have already been given, and will not be repeated here. In addition to the main terms involving the rotational and the hindered rotational energies, there are also the various corrections which are here of the order of several hundred megacycles/sec. because of the high values of the quantum numbers involved. As already noted, these corrections are due essentially to 1) the off-diagonal terms, and 2) the centrifugal stretching terms, including both the effect upon the barrier height and the moments of inertia. Since the moment of inertia effect for methyl alcohol is not known, it will here be neglected. The final values thus obtained for the four frequencies using the molecular constants of the preceding chapter are

	CALCULATED	OBSERVED
ν'_d	38605 $\frac{m.c.}{sec.}$	38294 $\frac{m.c.}{sec.}$
ν''_d	38749	38453
ν_e	37799	37704
ν_f	19978	19967

TABLE 5

The agreement of the observed and calculated values is very satisfactory, - the maximum difference being about 300 $\frac{m.c.}{sec.}$, - in view of the fact that the final values contain differences between terms involving hundreds of thousands of megacycles/sec. The calculated frequency for ν_f is particularly gratifying since the deviation from the experimental value is only 11 $\frac{m.c.}{sec.}$; furthermore, because of the fact that ν_f is connected with ν_a and ν_g by a sum rule involving very small correction terms, one might expect the most satisfactory results for just this particular line. Indeed, it is readily seen from the formulas for ν_a and ν_f that

$$\nu_f = \nu_g^o - \nu_a + \epsilon_a + \epsilon_f ,$$

where ϵ_a and ϵ_f are correction terms which are found to have the values (again neglecting the moment of inertia effects, which, anyway, should very nearly cancel)

$$\epsilon_a = -193 \frac{m.c.}{sec.} , \quad \epsilon_f = 89 \frac{m.c.}{sec.} .$$

It is this excellent agreement between the calculated and observed values of ν_f that is one of the strongest arguments for adopting $\nu_g = 48374 \frac{m.c.}{sec.}$, rather than the other possibility discussed earlier located at 49867 $\frac{m.c.}{sec.}$. If the latter frequency were instead chosen, a discrepancy of about 1500 $\frac{m.c.}{sec.}$ would exist between the calculated and the observed

values for ν_f that would be difficult to explain. The lines ν_d' and ν_d'' may be regarded as a single line which has been split into two components by the K-type doubling discussed earlier, which results from the asymmetry of the molecule. The calculated value of the splitting is found to be 144 $\frac{m.c.}{sec.}$, as against an observed value of 159 $\frac{m.c.}{sec.}$.

2. The $(J^2 + J)^2$ Coefficient

The $(J^2 + J)^2$ coefficient b of the Coles series of lines is defined through the series

$$\nu = \nu_0 + a(J^2+J) + b(J^2+J)^2 + \cdots$$

for the positions of the lines. Because of the centrifugal stretching effect which cannot be accurately calculated, the coefficient a of the $(J^2 + J)$ term is unsuitable as a check for the reliability of the molecular constants. The $(J^2 + J)^2$ term, however, may be shown to be relatively uncontaminated by their effect, and, therefore, may be properly used for a self-consistency check.

It may be mentioned in passing that provisional calculations attempting to account for the value of a for the three isotopic molecules listed below indicate that the centrifugal stretching term as given by Burkhard and Dennison must probably be modified. Tentative results indicate that the centrifugal

stretching term is about $-3.4(J^2 + J)\ \frac{m.c.}{sec.}$.

According to the results of Chapter II, b has the following values for the three molecules $C^{12}H_3O^{16}H$, $C^{13}H_3O^{16}H$, and $C^{16}H_3O^{18}H$:

$C^{12}H_3OH$	$C^{13}H_3O^{16}H$	$C^{12}H_3O^{18}H$
$.1115\ \frac{m.c.}{sec.}$	$.0901\ \frac{m.c.}{sec.}$	$.0855\ \frac{m.c.}{sec.}$

The theoretical expression for b is readily obtained by the usual perturbation theory and is

$$b = \left[\frac{\hbar^2}{2}\,\frac{C_1^2 + D^2}{4A(BC_1 - D^2)}\right]^2 \sum_n \left\{\frac{(H^{03n}_{210})^2}{W^0_{210} - W^0_{03n}} + \frac{(H^{42n}_{210})^2}{W^0_{210} - W^0_{42n}} - \frac{(H^{-11n}_{120})^2}{W^0_{120} - W^0_{-11n}} - \frac{(H^{33n}_{120})^2}{W^0_{120} - W^0_{33n}}\right\}$$

where

$$H^{\kappa'\tau'n'}_{\kappa\tau n} = \int_0^{2\pi} P^*_{\kappa\tau n} e^{-2i\kappa x} P_{\kappa'\tau'n'}\, dx .$$

On the basis of previous results for the moments of inertia,

$$\frac{\hbar^2}{2}\,\frac{C_1^2 + D^2}{4A(BC_1 - D^2)} = 218.23\ \frac{m.c.}{sec.}$$

for the normal molecule.

Evaluation of the matrix elements and the energy denominators is straightforward. The calculated values for b are then found to be

$C^{12}H_3O^{16}H$	$C^{13}H_3O^{16}H$	$C^{12}H_3O^{18}H$
$.1025\ \frac{m.c.}{sec.}$	$.0913\ \frac{m.c.}{sec.}$	$.0842\ \frac{m.c.}{sec.}$

It is expected that these calculated results should be correct only to within a few percent, since higher order ef-

fects such as the possible dependence of the moments of inertia upon the internal coordinates can give rise to deviation of this size. It is seen that the values for $C^{13}H_3O^{16}H$ and $C^{12}H_3O^{18}H$ are quite good, but that b for $C^{12}H_3O^{16}H$ is about 8% less than the empirical result. Since the experimental coefficients are believed to be accurate to better than one percent this anomaly is somewhat puzzling, particularly since the calculated values for the other two molecules are quite reasonable. The situation is not greatly changed by inclusion of the third order perturbation terms, since they modify the results by less than one percent.

3. The Origin of the Coles Series

The origin of the Coles series of lines, ν_0, is given by the expression

$$\nu_0 = -\frac{3}{2}\nu_g^0 + \frac{\hbar^2}{2}\frac{3}{C} + \mathcal{E}_{210} - \mathcal{E}_{120} + \epsilon_c .$$

This equation has already been applied for the case of the normal molecule, where it has been utilized to obtain one of the conditions determining the molecular constants. It is of interest, however, to calculate ν_0 for the other two isotopes $C^{13}H_3O^{16}H$ and $C^{12}H_3O^{18}H$ for which the Coles series data are also available. It is clear that, because of the changes in the moments of inertia, the Coles origins of these two

molecules will be displaced relative to the origin of the normal molecule. Utilizing the values found in the last chapter for the molecular paramaters of the isotopic molecules, and also making use of the expression for $W^{i}_{210} - W^{i}_{120}$ there developed, the following results are readily obtained:

TABLE 6

	ν_0(calc.)	ν_0(obs)
$C^{13}H_3O^{16}H$	26940 $\frac{m.c.}{sec.}$	27066 $\frac{m.c.}{sec.}$
$C^{12}H_3O^{18}H$	34492	33919
$C^{12}H_3O^{16}H$	24948	24948

The frequency shifts of the $C^{13}H_3O^{16}H$ and the $C^{12}H_3O^{18}H$ molecules relative to the normal molecules are then

	$\nu_0 - \nu_0$(N)(calc.)	$\nu_0 - \nu_0$(N)(obs)
$C^{13}H_3O^{16}H$ shift	9532 $\frac{m.c.}{sec.}$	8971 $\frac{m.c.}{sec.}$
$C^{12}H_3O^{18}H$ shift	1980	2118

The agreement between the calculated and observed shifts is moderately satisfactory. It was found that it would not be improved by any reasonable change in the molecular dimensions adopted earlier, and it was, therefore, concluded that the discrepancies must arise from the fact that the theory ignores effects to be associated from the non-rigidity of the methyl and hydroxyl groups.

4. The "Mirror" Lines

Hughes, Good, and Coles have measured a set of four lines in the $C^{13}H_3O^{16}H$ microwave spectrum which they term a "mirror image pattern" because two of the lines bear a mirror-like resemblance to the other two. The observed pattern is illustrated in the following diagram:



The lines at 26980.40 $\frac{m.c.}{sec.}$ and at 27104.80 $\frac{m.c.}{sec.}$ are forbidden in the absence of a field, appearing only when a Stark voltage is applied, and becoming stronger as the voltage is increased. The allowed lines at 26979.03 $\frac{m.c.}{sec.}$ and 27105.93 $\frac{m.c.}{sec.}$, which exhibit a second order Stark effect at low field strengths, merge with the forbidden lines at a field of several volts/cm, the mixture yielding a first order Stark effect at slightly higher voltages corresponding to a value of about 3.5 $\frac{m.c.}{sec.esu}$ for the coefficient of ME. The linear Stark patterns are slightly asymmetrical with frequency displacements on the low frequency side being ten percent greater than those on the high frequency side. From the Stark patterns it may be concluded that $\Delta J = \pm 1$, and that the J of the lowest state is at least 12.

As Hughes, Good, and Coles point out, such a "mirror image" set of lines may be interpreted as due to a transition between two K-type doublets. The transition in question appears to be one in which J = 13 → 12, K = 3 → 4, τ = 1 → 3, n = 0 → 0. The frequency is then given in the first order by the equation

$$\nu = -\frac{33}{2}\nu_g^\circ + \frac{\hbar^2}{2}\frac{\gamma}{C} + \varepsilon_{430} - \varepsilon_{310}.$$

From the calculated values for the moments of inertia for the $C^{13}H_3O^{16}H$ molecule one obtains

$$\nu_g^\circ = 47212 \ \frac{m.c.}{sec.} \qquad \frac{\hbar^2}{2}\frac{1}{C} = 127531.$$

Utilizing these figures, ν is found to be 27300 $\frac{m.c.}{sec.}$, in good agreement with the observed value of 27140 $\frac{m.c.}{sec.}$ for the center of the pattern.

From the formulas developed in Chapter II the splitting of the K = 3 level is given by

$$\Delta W_3 = \frac{2\, H^{13\ -1\ 2}_{13\ 1\ 3}\left(H^{13\ 3\ 1}_{13\ 1\ 3}\right)^2}{(W^\circ_{13} - W^\circ_{31})^2},$$

while the K = 4 level splitting is

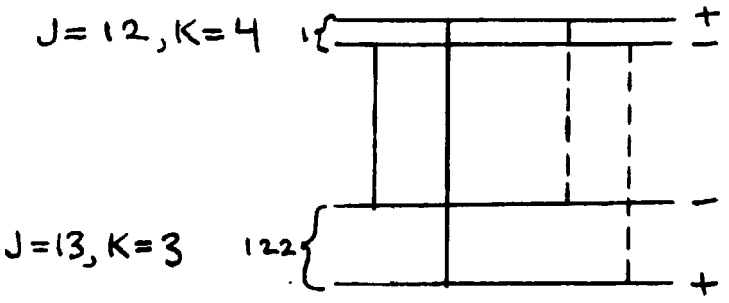
$$\Delta W_4 = \frac{2\left(H^{12\ 4\ 3}_{12\ 2\ 2}\right)^2\left(H^{12\ 2\ 2}_{12\ 0\ 1}\right)^2}{(W^\circ_{22} - W^\circ_{43})^2(W^\circ_{43} - W^\circ_{01})}.$$

Using the values for the molecular constants previously calculated one obtains

$$\Delta W_3 = 122 \frac{m.c.}{sec.}$$

$$\Delta W_4 = 1.0 \frac{m.c.}{sec.}$$

The energy level diagram for the transitions involved is shown below.



The + and - signs refer to the symmetry types of the levels as discussed in Chapter II. In the absence of a field only + → +, - → - transitions are allowed. With a field applied the other transitions + → -, - → + are also possible, the probability increasing with the strength of the field. On the basis of this scheme a separation between the allowed lines of 123 $\frac{m.c.}{sec.}$, and a forbidden-allowed splitting of 1.0 $\frac{m.c.}{sec.}$ are predicted. These values may be compared with the observed ones of 127 $\frac{m.c.}{sec.}$ and about 1.2 $\frac{m.c.}{sec.}$.

According to results previously obtained, a quadratic Stark effect is observed for low electric fields for levels with K-type doubling. As the field strength is increased to the point where the Stark splitting is larger than the K-type splitting, the Stark effect becomes predominantly linear. For the particular case of the "mirror" lines it is clear that the linear Stark effect will result from the K = 4 levels, since their splitting is very much less than that of the K = 3 levels. The linear Stark coefficient for the K = 4 state may be shown from the results of Chapter II to be $\frac{4\mu_{11}}{J^2+J}$, resulting in a calculated value of 3.4 $\frac{\text{m.c./sec.}}{\text{esu}}$ as compared with the observed value of 3.5 $\frac{\text{m.c./sec.}}{\text{esu}}$. The fact that the Stark pattern is slightly asymmetrical may be ascribed to the presence of energy terms in the K-type doubling expressions other than those linear in E.

It is seen that the general agreement between theory and experiment for the "mirror" lines is quite good. Not only are the positions of the lines well given by the theory, but many of the features of the Stark pattern also are explained.

5. The First Order Stark Effect

As discussed in Chapter II, Hughes, Good, and Coles have observed a number of lines in the microwave spectrum of the normal alcohol molecule which exhibit a linear Stark effect given by the formula

$$\Delta\nu_M = B\,M\,E \quad .$$

Inasmuch as coefficient B determining the magnitude of the Stark splitting has been measured by them for these lines it becomes possible to compare the experimental values for B with the theoretical ones predicted on the basis of the asymmetric rotor theory.

For those particular frequencies for which the transitions have been determined, it is a simple matter to write down the expressions for the linear Stark coefficients. The diagonal elements of the Hamiltonian, which depend upon $\mu_{\parallel}$, yield the main contributions, while the $K \rightarrow K \pm 1$ terms, which are a function of $\mu_{\perp}$, give small corrections. The calculated results for B obtained in this way are listed in the following table, together with the observed values.

TABLE 7

Frequency ($\frac{m.c.}{sec.}$)	Transition	B(Obs.) ($\frac{m.c./sec.}{esu}$)	B(Calc.)
28316.03	J= 3→4 K= 1→0 τ= 2→3	~ 11 *	11.7
36169.24	3→4 0→1 2→1	6.52	6.6
37703.72	8→7 1→2 1→3	3.09	2.9
38293.32	5→6 3→2 1→2	13.0	13.4
38452.69		13.0	13.4

* The value of 3.4 $\frac{m.c./sec.}{esu}$ listed by Hughes, Good and Coles[3] has subsequently been corrected by them (private communication).

It is seen that there is agreement between the two sets of values to within several percent. This is particularly gratifying for the two lines at 38293 $\frac{m.c.}{sec.}$ and 38453 $\frac{m.c.}{sec.}$, which are members of a K-type doublet, and for which the special formula previously developed for transitions of this type must be used.

6. The Second Order Stark Effect

The second order or quadratic Stark effect has been measured by Hughes, Good, and Coles for a number of lines in the microwave spectrum of methyl alcohol. The present section is devoted to the theory of the quadratic effect, and the interpretation of these experimental results.

The observed lines may be grouped in two classes: those for which the Stark effect is predominantly linear with a relatively slight quadratic admixture (for fields of the order of 1 esu.), and those for which the effect is purely quadratic. An example of the former category is given by members of the Coles series, and, indeed, by any first order lines, while the latter is represented by lines of the Gordy type and by a number of other components found in the microwave spectrum by Hughes, Good, and Coles.

a. Coles Lines

Besides possessing a linear Stark effect, the members of the Coles series have also a quadratic dependence which may

be represented by the equation

$$\Delta\nu = (C + DM^2) E^2 .$$

The coefficients of E^2 for some of the components of lines of the normal molecule have been determined by Hughes, Good, and Coles, and the M^2 dependence for a fixed voltage has been also studied for the J = 7 and J = 9 lines. The results obtained by them are summarized in the following table:

J	M	Coefficient of E^2 ($\frac{\text{m.c.}}{\text{sec. esu}^2}$)	Calculated Values
2	average of 2 and -2	.37	.31
3	-3	.38	.52

TABLE 8

J	Field in esu	Coefficient of M^2 (m.c./sec.)	
7	1.345	.024	.024
9	1.345	.0165	.0155

The values for the coefficient of E^2, and for the coefficients of M^2 are believed to be accurate to within 15% and 10%, respectively.

To determine the appropriate theoretical expression for the quadratic Stark effect for this case, it is necessary to utilize the matrix elements of the Stark energy expression

$$W = \mu_{\parallel} E \cos\theta + \mu_{\perp} E \sin\theta \cos\varphi_1 ,$$

which have already been listed in Chapter II.

For the particular case of the Coles series of lines in which $J \rightarrow J$, $K = 1 \rightarrow 2$, $\tau = 2 \rightarrow 1$ one then obtains, using the usual methods of perturbation theory, and the values for the molecular parameters previously found, the following results (in $\frac{m.c.}{sec.}$):

For $J = 2 \rightarrow 2$

$$\Delta\nu = E^2 \left[.0889M^2 - .0413\right] = .314E^2 \text{ for } M = 2.$$

For $J = 3 \rightarrow 3$

$$\Delta\nu = E^2 \left[.0483M^2 + .0881\right] = .523E^2 \text{ for } M = 3.$$

For $J = 7 \rightarrow 7$

M^2 coefficient $= .0132E^2 = .0239$ for $E = 1.345$ esu.

For $J = 9 \rightarrow 9$

M^2 coefficient $= .0086M^2 = .0155$ for $E = 1.345$ esu.

The agreement, except for the $J = 3 \rightarrow 3$ line, is within experimental error.

b. Second Order Lines

A number of lines have been observed by Hughes, Good and Coles which exhibit a pure quadratic effect, and which, as for the preceding case, can be represented by the equation

$$\Delta\nu = (C + DM^2)\, E^2 \quad .$$

The results obtained by these workers have been summarized

in the following table, which is adapted from their paper:

TABLE 9

Approximate Stark Effect Coefficients of Second Order Lines

Frequency $\left(\frac{m.c.}{sec.}\right)$	C $\left(\frac{m.c.}{sec. esu^2}\right)$	D $\left(\frac{m.c.}{sec. esu^2}\right)$	Lowest possible value of the smaller J
20971	+	+	10
21550	.33	.0174	10
23121	+	+	8
23348	+	+	
23445	.16	.011	8
26121	.32	-.038	9
27700	+	-	
28970	.16	-.034	8
35162	+	+	

The following second order transitions, which are of the K-type variety, have been found which yield calculated values for the frequencies in the region from 18000 $\frac{m.c.}{sec.}$ to 44000 $\frac{m.c.}{sec.}$:

TABLE 10

J =	K =	τ =	Calculated Frequency
9 → 8	1 → 2	3 → 2	29028 $\frac{m.c.}{sec.}$
9 → 10	2 → 1	2 → 3	23360
			-21350
10 → 11	2 → 1	2 → 3	22470
6 → 7	1 → 0	3 → 1	27110
			43920
6 → 5	0 → 1	1 → 3	18890
13 → 14	4 → 3	3 → 1	40525
			40715

Only one line of the K-type doublet has been listed if the other member falls outside the region of interest above indicated. It is to be noted that the number of observed lines is greater than the number of the calculated ones here given, a fact which may, perhaps, be explained by the possibility of transitions involving vibrational numbers greater than 0. A provisional calculation shows, for example, that the transitions $n = 1 \rightarrow 1$, $J = 10$ or $11 \rightarrow 11$ or 12, $K = 1 \rightarrow 2$, $\tau = 3 \rightarrow 2$ may possibly account for some of the measured lines.

Comparing the calculated values with the observed frequencies one sees that only two identifications may be made with fair certainty. These are

			$\nu_{calc.}$		$\nu_{obs.}$
$J = 9 \rightarrow 8$	$K = 1 \rightarrow 2$	$\tau = 3 \rightarrow 2$	29030	$\frac{m.c.}{sec.}$	28970
$6 \rightarrow 7$	$1 \rightarrow 0$	$3 \rightarrow 1$	27110		27700

Other identifications cannot safely be made, either because any one of several lines might reasonable be chosen to correspond to a given transition, or because the lowest possible value of the smaller J as given experimentally for the frequency does not correspond with the theoretical figure. Of these two tentatively identified lines only the first, unfortunately, has been measured for its second order Stark coefficients. Because of this fact, the following calculations will deal

only with the line at the calculated frequency of 29030 $\frac{m.c.}{sec.}$, corresponding to the transition $J = 9 \rightarrow 8$, $K = 1 \rightarrow 2$, $\tau = 3 \rightarrow 2$.

Referring back to the results of Chapter II, and making use of the expressions for the Stark energy matrix elements there given, one obtains after a lengthy, but straightforward calculation, the equations for the Stark energy shifts of the levels involved:

$$\Delta W_{913} = \begin{cases} (.0003\ M^2 - .0404)\ E^2\ \frac{m.c.}{sec.} & \text{for the upper level} \\ (.0012\ M^2 - .0600)\ E^2 & \text{for the lower level} \end{cases}$$

$$W_{822} = \begin{cases} (.0308\ M^2 + .0460)\ E^2 & \text{for the upper level} \\ (-.0326\ M^2 + .0460)\ E^2 & \text{for the lower level.} \end{cases}$$

Making use of the K-type selection rules one finds for the line at 29030 $\frac{m.c.}{sec.}$ that the quadratic effect for it is then given by

$$\Delta\nu = (-.0329\ M^2 + .0864)\ E^2\ \frac{m.c.}{sec.}$$

Comparing this equation with the experimental result

$$\Delta\nu = (-.034\ M^2 + .16)\ E^2\ \frac{m.c.}{sec.},$$

one sees that the agreement is fair for the coefficients of M^2, but quite poor for the E^2 coefficients. It is, however, quite possible that other effects exist which may contribute to the quadratic Stark effect. The phenomenon of polarization of the molecule, for example, would give such a second

order contribution, although, as has been estimated[11], the effect would be very small, $\Delta\nu$ being only of the order of only .1 $\frac{m.c.}{sec.}$ for a field of 10,000 $\frac{volts}{cm}$. More work, both theoretical and experimental, seems necessary before a satisfactory interpretation of the quadratic Stark effect is obtained.

c. The Gordy Lines

Although no experimental results for the Stark effect for lines of the Gordy type $J = 0 \rightarrow 1$, $K = 0 \rightarrow 0$, $\tau \rightarrow \tau$, $n \rightarrow n$ have been as yet published, it may be of interest to give here the theoretical treatment for this important case. Since the M transition is one in which $M = 0 \rightarrow 0$, it is clear that the Stark pattern will consist of only one line. A glance at the Stark matrix elements at once shows that for $M = 0$ the $J \rightarrow J$ terms vanish and that, therefore, the Stark effect will be purely quadratic. Indeed it is readily seen that for this special case the calculations are especially simple. A straightforward application of the usual perturbation theory yields the following expressions for the Stark energy of the two levels involved in the transition:

See next page.

$$\Delta W_{0\,0\tau n} = \frac{1}{3}\frac{\mu_{\parallel}^2 E^2}{W^0_{0\,0\tau n} - W^0_{1\,0\tau n}} + \frac{\mu_{\perp}^2 E^2}{6}\sum_{\tau' n'}\left\{\frac{\left[(e^{-iX})^{1}_{0\tau n}\right]^2}{W^0_{0\,0\tau n} - W^0_{1\,1\tau' n'}} + \frac{\left[(e^{iX})^{-1}_{0\tau n}\right]^2}{W^0_{0\,0\tau n} - W^0_{1\,1\tau' n'}}\right\}$$

$$\Delta W_{1\,0\tau n} = \frac{1}{4}\frac{\mu_{\parallel}^2 E^2}{W^0_{1\,0\tau n} - W^0_{0\,0\tau n}} + \frac{4}{15}\frac{\mu_{\parallel}^2 E^2}{W^0_{1\,0\tau n} - W^0_{2\,0\tau n}}$$
$$+ \frac{\mu_{\perp}^2 E^2}{10}\sum_{\tau' n'}\left\{\frac{\left[(e^{-iX})^{1}_{0\tau n}\right]^2}{W^0_{1\,0\tau n} - W^0_{2\,1\tau' n'}} + \frac{\left[(e^{iX})^{-1}_{0\tau n}\right]^2}{W^0_{1\,0\tau n} - W^0_{2\,-1\tau' n'}}\right\}, \text{ where}$$

$$(e^{\mp iX})^{K\pm 1\,\tau' n'}_{K\,\tau n} = \int_0^{2\pi} \rho^*_{K\tau n}\, e^{\mp iX}\, \rho_{K\pm 1\,\tau' n'}\, dx .$$

The Stark effect for the Gordy line is then given by

$$\Delta\nu_g = \Delta W_{1\,0\tau n} - \Delta W_{0\,0\tau n} .$$

As an example, consider the particular Gordy-type transition $J = 0 \to 1$, $K = 0 \to 0$, $\tau = 1 \to 1$, $n = 0 \to 0$. The above equations then become especially simple, and the result for $\Delta\nu$ is

$$\Delta\nu = \frac{7}{12}\frac{\mu_{\parallel}^2 E^2}{W^0_{1\,0\,1} - W^0_{0\,0\,1}} + \frac{4}{15}\frac{\mu_{\parallel}^2 E^2}{W^0_{1\,0\,1} - W^0_{2\,0\,1}} + \frac{1}{5}\frac{\mu_{\perp}^2 E^2 A^2}{W^0_{1\,0\,1} - W^0_{2\,1\,3}} - \frac{1}{3}\frac{\mu_{\perp}^2 E^2 A^2}{W^0_{0\,0\,1} - W^0_{1\,1\,3}},$$

where

$$A = (e^{-iX})^{1\,3\,0}_{0\,1\,0} .$$

The terms corresponding to the n = 1, 2, ··· states have been neglected, since their effect for this case is very slight. Using the values for the molecular parameters previously obtained, one finds that

$$\Delta\nu = .101\, E^2\, \frac{\text{m.c.}}{\text{sec.}} \quad , \quad (E \text{ in esu}).$$

The above theoretical expressions were derived, of course, on the assumption that the various Gordy-type lines are completely resolved from one another. If overlapping should occur, the Stark effect will then naturally be altered.

The theory thus developed affords in principle a method of identifying the various Gordy-type lines by means of their Stark effects. Since at the present time empirical data is not available, it has not, however, been deemed advisable to make further calculations.

APPENDIX 1

INTERNAL ENERGY LEVELS

The following tables for the internal energy levels $W_{K\tau_0}$ and for the Fourier coefficients used in this work are based on the values

$$\frac{C_1}{C} = .189275, \quad C_2 = 5.33265 \times 10^{-40} \text{gm.cm}^2,$$

$$H = 374.821 \text{ cm}^{-1}$$

for the molecular constants.

$W_{K\tau_0}$ (in cm^{-1})

K	$\tau = 1$	$\tau = 2$	$\tau = 3$
0	128.82540	137.94889	137.94889
1	129.25292	140.00684	135.49014
2	130.49221	141.25606	133.04844
3	132.41046		130.97478
4		140.45849	129.52565

APPENDIX 2

FOURIER COEFFICIENTS

The Fourier coefficients a_τ in the following table are given for type 1 wave functions. However, using the relationships

$$a_{3n-1}(\sigma) = a_{3n}(\sigma-1) \qquad a_{3n-2}(\sigma) = a_{3n}(\sigma-2)$$

where $\sigma = -\frac{c_1}{c}K$ it is possible to determine the a_τ for the following states: $K=0, \tau=1,2,3$; $K=1, \tau=1,2,3$; $K=2, \tau=1,2$; $K=3, \tau=1,2,3$; $K=4, \tau=1,3$.

$-\sigma =$	0	.189275	.378550	.432175
a_{-12}	.0000240	.0000190	.0000150	.0000141
a_{-9}	.0010351	.0008435	.0006904	.0006525
a_{-6}	.025430	.021577	.018369	.017555
a_{-3}	.285724	.257096	.231585	.224808
a_0	.914017	.911676	.904393	.901337
a_3	.285724	.318393	.356104	.367846
a_6	.025430	.030129	.035925	.037808
a_9	.0010351	.0012785	.0015915	.0016956
a_{12}	.0C00240	.0000305	.0000393	.0000422

$-\sigma =$	.567825	.810725	1.000000
a_{-12}	.0000120	.000089	.0000070
a_{-9}	.0005660	.0004375	.0003556
a_{-6}	.015651	.012693	.010692
a_{-3}	.208369	.180788	.160297
a_0	.891392	.864211	.832730
a_3	.399863	.466110	.525624
a_6	.043130	.055017	.066764
a_9	.0019970	.0027009	.0034351
a_{12}	.0000509	.0000718	.0000945

$-\sigma =$	1.189275	1.242900	1.378550
a_{-12}	.0000055	.0000051	.0000044
a_{-9}	.0002852	.0002673	.0002255
a_{-6}	.0088993	.0084256	.0072922
a_{-3}	.140304	.134722	.120826
a_0	.790585	.776626	.737563
a_3	.590463	.609367	.657155
a_6	.080896	.085326	.097287
a_9	.004366	.004669	.005512
a_{12}	.0001244	.0001344	.0001629

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