Vibration-Hindered Rotation Interactions in Methyl Alcohol. The $J=0\rightarrow1$ Transition*

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(Received March 19, 1956)

The hindered rotation fine structure of the $J=0\rightarrow1$, $K=0\rightarrow0$ transition which has been observed by Venkateswarlu, Edwards, and Gordy in normal methanol as well as in five additional isotopic species can be understood only qualitatively on the basis of earlier investigations of the theory of hindered rotation in methanol. It has been shown that the frequency separations between the various torsional transitions and the splitting of each of these can be explained quantitatively by including in the theory the effects of the vibration-hindered rotation interactions during the rotation of the whole molecular framework in space. The effects of the asymmetry of the rigid hindered rotator, the Coriolis interactions, and the centrifugal distortion of the molecule are discussed separately. A frequency formula for the transition is derived which contains essentially only four new rotational constants. Three of these depend solely upon the known structure of the molecule and the elastic force constants and can therefore be calculated from a knowledge of the vibrational spectrum. Since this latter has never been analyzed in more than a rough way some small adjustments have been made in the indicated values of the elastic constants which are within the limits of uncertainty. This adjustment is made for the normal molecule after which the three rotational constants are calculated for the remaining isotopic species without further adjustment. The fourth constant in the frequency formula describes the dependence of the barrier height upon the normal coordinates and is the only constant which must be determined empirically for each isotopic species. It has thus been possible to predict the 30 observed separations and splittings with the aid of essentially only six empirical constants. The agreement with experiment is remarkably good with one possible exception where the theory predicts for the fully deuterated methanol a very large splitting of the normal state line whereas the line in question is observed to be single. It is not improbable, however, that the large splitting actually exists and that the second component lay too far away to be recognized.

INTRODUCTION

RECENTLY Venkateswarlu, Edwards, and Gordy[1] have reported the positions of the $J=0\rightarrow1$, $K=0\rightarrow0$ lines of methyl alcohol for the normal molecule as well as for five additional isotopic species. Since the transitions in the torsional states, characterized by $n=0$, 1, and 2, have been found to be split into two components these data comprise some 36 frequencies in all. The positions of the frequencies observed by Venkateswarlu, Edwards, and Gordy are shown in Fig. 1 together with a very qualitative indication of their intensities.[1] It will be observed that the positions of the doublets corresponding to the various n values as well as the doublet splittings vary in an apparently irregular fashion in going from one isotopic molecule to another.

The general qualitative appearance of this group of lines can be understood readily on the basis of previous work on the theory of hindered rotation in methanol.[2-4] The transitions in question are ones in which the quantum numbers most intimately connected with the internal rotation namely K, n, and τ, (using the notation of the papers cited), do not change, and in particular the K transition is $0\rightarrow0$. In zeroth approximation one would expect to observe a single line. This line would however be multiple with components corresponding to the possibilities $n=0\rightarrow0$, $1\rightarrow1$, $2\rightarrow2$, etc., as well as to the transitions $\tau=1\rightarrow1$, and $\tau=2$, $3\rightarrow2$, 3. (In general, τ may assume the values 1, 2, and 3 each of which denotes a different energy level. When $K=0$, however, the levels $\tau=2$ and 3 constitute a degenerate pair.) In higher approximation, various perturbations will separate the multiple line into distinct components. The largest effect might be expected to be a type of vibration-rotation interaction separating the various n transitions. The slight asymmetry of the methanol molecule should, moreover, split each n line into a doublet corresponding to the two τ transitions thus qualitatively producing the observed group of lines. The quantitative calculation of the various shifts (due to the n transitions) and the splittings (due to the τ transitions) cannot be made on the basis of the papers[2-4] where vibration-hindered rotation interactions were neglected. In particular, if these theories are employed the splittings in general turn out to be much smaller than those observed and to vary quite differently with isotopic species.

An advance towards incorporating the effects of vibrational perturbations into the theory of hindered rotation has been made by Kivelson[5] who applied his results very successfully to the $J=0\rightarrow1$ lines in the symmetric hindered rotator, methyl silane, CH_3SiH_3. He used a simple approximate frequency formula which contained a number of empirically determined con-

* The preparation of this manuscript was supported by Contract Nonr-1224(15) between the Office of Naval Research and the Engineering Research Institute of The University of Michigan.

[1] Venkateswarlu, Edwards, and Gordy, J. Chem. Phys. **23**, 1195 (1955).

[2] J. S. Koehler and D. M. Dennison, Phys. Rev. **57**, 1006 (1940).

[3] D. G. Burkhard and D. M. Dennison, Phys. Rev. **84**, 408 (1951).

[4] E. V. Ivash and D. M. Dennison, J. Chem. Phys. **21**, 1804 (1953).

[5] D. Kivelson, J. Chem. Phys. **22**, 1733 (1954); **23**, 2230 and 2236 (1955).

stants. This latter feature makes his theory somewhat unsatisfactory when extended to apply to methyl alcohol since additional vibration-hindered rotation interaction terms have been found to be of importance in this molecule, and the number of empirical constants needed would be too large for a convincing check between theory and experiment.

The program to be followed in the present paper consists in calculating the energy levels giving rise to the lines in the $J=0\rightarrow1$ group taking account of the interaction between the hindered and over-all rotations and the normal vibrations. These latter may be taken as known for, although no rigorous normal coordinate treatment is available for methanol, in molecules of this type it is well known that the normal vibrations may be well approximated by considering that the individual atoms vibrate either parallel or perpendicular to the bond directions. Consequently the observed fundamental infrared bands furnish the required elastic constants.

The various terms which contribute to the energy levels may be grouped in the following manner.

1. Rigid Hindered Rotator

In zeroth approximation the methanol molecule may be represented, as it was in the earlier papers, by a model consisting of a rigid methyl group and a rigid O−H bar which may perform a mutual internal rotation subject to a hindering sinusoidal potential. The only parameters which are involved are the dimensions of the molecule together with the magnitude of the potential barrier. These are all known from the earlier investigations. This model yields the dominant terms which determine the gross position of the $J=0\rightarrow1$ lines. It further introduces a splitting of the lines but the magnitude of the splitting depends upon the square of the product of inertia D. This quantity is very small in the case of normal methanol and the resulting splitting, as has been mentioned, is much smaller than that observed.

2. Coriolis Interaction

An important contribution to the detailed expression for the energy levels is the Coriolis interaction between the internal rotation and the angular momentum associated with the normal vibrations of the molecule. Although the actual calculations are complicated and lengthy the only constants which are involved are (a) the molecular dimensions and barrier height and (b) the elastic constants of the molecule. These may be taken to be known although there is some uncertainty as to their precise values since they are determined through the approximation that the atoms move either along or perpendicular to the bond directions. It is found that the best agreement between the observed and predicted $J=0\rightarrow1$ lines is found by making small and reasonable adjustments in the values of the elastic constants as determined from the positions of the near infrared bands.

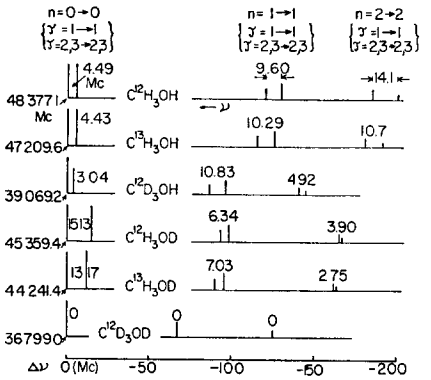

FIG. 1. The observed hindered rotation fine structure of the $J=0\rightarrow1$, $K=0\rightarrow0$ transition in six isotopic species of methyl alcohol (Venkateswarlu, Edwards, and Gordy). The numbers above the lines give the splittings in Mc/sec.

The actual calculation, as has been mentioned, is very lengthy, and it has been found advantageous to make it in two steps. The first step consists in examining in detail the principal contribution to the Coriolis interaction, namely the actual influence between the rotations and that normal vibration in which the O−H bar is allowed to move elastically in its own plane through a tipping motion relative to the methyl group. In this relatively simple model the remaining degrees of freedom are considered to be frozen. In the second step the smaller effects of these remaining normal vibrations are treated as additional vibration-hindered rotation perturbations; but at this point certain simplifying assumptions may be introduced without seriously affecting the accuracy of the resulting energy levels.

3. Centrifugal Distortion

The final set of terms arises from the fact that the molecule is distorted due to the balance between the centrifugal and the elastic restoring forces. Three effects may be distinguished. In the first place a centrifugal distortion will alter slightly the over-all rotational levels giving rise to terms proportional to the quartic combinations of the rotational quantum numbers J and K. These terms, which are present in all molecules, will affect all components of the line $J=0\rightarrow1$ equally and hence introduce neither shifts nor splittings. They can be ignored in the present discussion. The second set of terms arises from the influence of the centrifugal distortion upon the hindered rotation. One may say that the distorted molecule possesses effective moments and products of inertia which differ from those of the nonrotating molecule. This effect, which does contribute to the shifts and splittings, depends only upon the molecular dimensions, the barrier height, and the elastic constants, all of which may be taken as known.

The last effect of the centrifugal distortion is its

influence upon the barrier height and hence upon the hindered rotation levels. This dependence of the barrier height upon the displacements of the atoms cannot be calculated in any simple way although a qualitative classical argument may be made which does yield the correct orders of magnitude. In the present paper, however, the above-mentioned dependence will be represented through six empirically determined constants, one for each isotopic species. Thus with the aid of six constants it is hoped to predict the thirty observed shifts and splittings.

The actual mechanics of the vibration-hindered rotation perturbation calculations are simplified by performing a contact transformation on the Hamiltonian. The new form of the Hamiltonian is such that the interaction terms between the hindered rotation, the over-all space rotation, and the small vibrations appear as true perturbation terms; that is, of smaller order of magnitude than the rigid rotator terms. This can be accomplished by transforming to a new system of rotating axes with respect to which the hindered rotation and small vibration motions appear free of internal angular momentum, at least in zeroth order.[6] The zeroth-order internal rotation wave functions and energies still have the form given in the earlier papers but depend upon the molecular parameters in a slightly different manner since the transformation to the new Hamiltonian results in a change in the boundary conditions.

RIGID HINDERED ROTATOR

As a first step toward an understanding of the $J=0\rightarrow1$, $K=0\rightarrow0$ frequencies these will be computed on the basis of the simple theory of hindered rotation in which the molecule is represented by the rigid model hindered rotator. In a symmetric hindered rotator made up of two truly rigid components a $\Delta J=1$, $\Delta K=0$ transition, although consisting of several $\tau\rightarrow\tau$, $n\rightarrow n$ components, would, as mentioned previously, appear as a single frequency given solely by the rigid rotator energy since the hindered rotation splittings of the energy levels are independent of the quantum number J. In an asymmetric, vibrating molecule, however, there exists a J dependence of these splittings which would give rise to a splitting in the observed lines.

The frequencies predicted by the rigid model can be obtained most easily if the Hamiltonian of the hindered rotator is given in a form in which the interaction terms between the hindered rotation and the over-all rotation in space appear as small as possible, as was done in the preceding paper.[7] In methyl alcohol the off-diagonal matrix elements of this Hamiltonian arising solely through the slight asymmetry of the molecule are very small compared with the differences in the diagonal matrix elements, and for $J=1$ they can be treated as perturbation terms. The expression for the $J=0\rightarrow1$ frequencies is given with good accuracy by second-order perturbation theory

$$\underset{(J\,K\,\tau\,n)}{\nu_0{}^1{}_0{}^0{}_\tau{}^\tau{}_n{}^n}=\frac{h}{8\pi^2}\left(\frac{1}{A}+\frac{B}{B^2+D^2}\right)+\frac{2}{h}\sum_{K'=\substack{-1\\+1}}\frac{\left[\frac{h^2}{4}\frac{D}{B^2+D^2}\right]^2|\langle 0\tau n|e^{\pm ix}|K'\tau' n\rangle|^2}{(E_{0\tau n}-E_{K'\tau' n})+\frac{h^2}{4}\left[\frac{1}{A}+\frac{3B}{(B^2+D^2)}-\frac{2(B+C)}{(BC-D^2)}\right]}, \tag{1}$$

where

$$\langle 0\tau n|e^{\pm ix}|K'\tau' n\rangle=\int_0^{2\pi}P_{0\tau n}{}^*(x)e^{\pm ix}P_{K'\tau' n}(x)dx.$$

In the integral over the internal rotation angle, x, the $\pm$ signs belong to $K'=\mp1$, respectively. Using the new form of the Hamiltonian the contribution of the $n\rightarrow n'$, $(n'\neq n)$, matrix elements is completely negligible.

Since for all isotopic species of methanol $D^2\ll B^2$, to a very good approximation one is led to the following expression which is simply the rigid rotator frequency

$$\nu_0{}^1{}_0{}^0{}_\tau{}^\tau{}_n{}^n=\frac{h}{8\pi^2}\left(\frac{1}{A}+\frac{1}{B}\right). \tag{2}$$

Venkateswarlu and Gordy[8] have recomputed the six structural parameters of methyl alcohol under the assumption that the $n=0\rightarrow0$ lines are given by the simple formula (2). The Venkateswarlu-Gordy values of the moments and product of inertia, based on their small modifications in the structural parameters, will be used throughout the computations in this paper, while the Ivash-Dennison value of the barrier height ($H=374.82$ cm^{-1})[4] is employed for all isotopic species. A numerical substitution shows that (2) is an exceedingly accurate approximation to (1) for all the O—H isotopic species but may be in error by as much as 40 Mc/sec in the O—D isotopic species. However, since the bond distances and angles are only effective values it was not felt worthwhile to make further small changes in the structural parameters.[9]

[6] This process is illustrated in detail in the preceding paper for the hindered rotation—over-all space rotation interactions in the case of the simple theory of hindered rotation.

[7] The matrix elements of the Hamiltonian are given by Eqs. (12).

[8] P. Venkateswarlu and W. Gordy, J. Chem. Phys. **23**, 1200 (1955).

[9] Since the theory of the vibration-hindered rotation interactions in methyl alcohol is examined in detail in this paper it would have been possible to compute new effective bond distances and angles for which the averaging effects of the vibration-

TABLE I. Rigid hindered rotator splittings of the $n=0\rightarrow 0$ transitions in Mc/sec.

Isotopic molecule	$C^{12}H_3OH$	$C^{13}H_3OH$	$C^{12}D_3OH$	$C^{12}H_3OD$	$C^{13}H_3OD$	$C^{12}D_3OD$
Predicted Rigid hindered Rotator splittings	0.021	0.026	0.012	13.00	11.58	23.55
Observed Splittings	4.49	4.43	3.04	15.13	13.17	0

The splittings of the $n=0\rightarrow 0$ lines computed on the basis of the rigid model hindered rotator are shown in Table I for the six isotopic species. They are proportional to D^2/B^2, and for the O—H isotopic species are much smaller than those observed. Clearly the further effects of the Coriolis forces and of the centrifugal distortion must be considered. It will prove convenient to begin by discussing the centrifugal distortion.

CENTRIFUGAL DISTORTION IN METHYL ALCOHOL SIMPLIFIED SEMICLASSICAL DESCRIPTION

As a first step toward an understanding of the dominant vibration-hindered rotation interactions in methyl alcohol, the effect of the centrifugal distortion of the molecule on the observed frequencies will be examined on the basis of a simplified picture. If the small asymmetry of methyl alcohol is neglected the effect of the centrifugal distortion can be treated very simply on the basis of a semiclassical description of the molecule.

Since the transition of present interest is $K=0\rightarrow 0$ the classical motion corresponds to an end-over-end tumbling in space of the whole molecular framework. During this rotation in space the hydroxyl and methyl groups spin about each other in their mutual hindered rotation motion. The centrifugal forces arising from the two kinds of rotations tend to distort the molecule until the atoms have taken on new equilibrium positions depending upon the amount of rotation. The amount of rotation in a particular state, described by the quantum numbers J, τ, and n, $(K=0)$, is given by the quantum-mechanical expression for the rotational energy in that state, and the problem can be treated as a simple statics problem. Both the new equilibrium configuration and the change in energy due to the centrifugal distortion are determined from the condition that the total energy must be a minimum in the new equilibrium configuration, where both the energy due to the molecular forces and the two kinds of centrifugal forces must be considered.

If the small asymmetry of the molecule is neglected, this energy is simply

$$W_{\substack{J\tau n\\(K=0)}}=\frac{\hbar^2}{4}\left(\frac{1}{A}+\frac{1}{B}\right)(J^2+J)+\frac{1}{2}\left(\frac{1}{C_1}+\frac{1}{C_2}\right)\langle 0\tau n|p_x^2|0\tau n\rangle+\frac{H}{2}\langle 0\tau n|1-\cos 3x|0\tau n\rangle+\tfrac{1}{2}\sum_i k_i(\delta q_i)^2, \quad (3a)$$

where $\langle 0\tau n|p_x^2|0\tau n\rangle$, for example, is the diagonal matrix element of p_x^2:

$$-\hbar^2\int_0^{2\pi} P_{0\tau n}^*(x)\frac{\partial^2}{\partial x^2}P_{0\tau n}(x)dx.$$

The first term in (3a) represents the over-all rotation while the second and third terms give the average value of the kinetic and potential energies of hindered rotation. The δq_i are the chemical coordinates describing motions where the atoms move either along or perpendicular to the chemical bonds. For this type of molecule it is well known that cross terms in the potential, namely $k_{ij}\delta q_i\delta q_j$, while present are small enough to be neglected. Both the moments of inertia, A, B, C_1, and C_2, and the barrier height, H, are functions of the vibrational coordinates. For example

$$A=A_0+\sum_i A_i^{(1)}(\delta q_i)+\cdots,$$
$$H=H_0[1+\sum_i a_i^{(1)}(\delta q_i)+\cdots]. \quad (4)$$

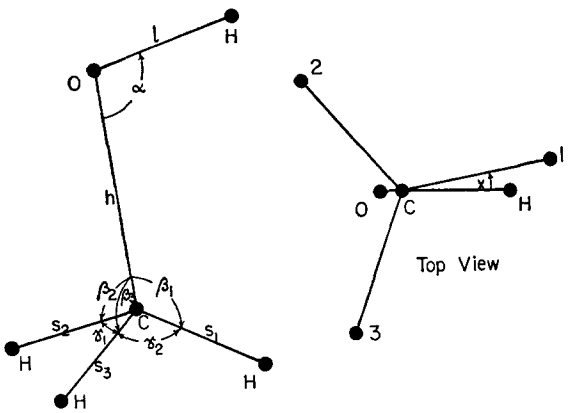

FIG. 2. The chemical coordinates and symmetry properties of the methyl alcohol molecule. The symmetry operation $x\rightarrow -x$, where the internal rotation angle, x, is defined by hydrogen atom 1 of the methyl group; $2\leftrightarrow 3$, an interchange of hydrogen atoms 2 and 3 of the methyl group, is equivalent to a reflection in the COH plane.

hindered rotation interactions (but not the ordinary vibration-rotation interactions) have been taken into account. It is certain that these would introduce only very minor changes.

However, to first order in the (δq_i) they are functions only of the totally symmetric vibrational coordinates since the energy must be invariant under the allowed symmetry operations of the molecule. Since the potential energy of methyl alcohol is invariant to the operation, $x \rightarrow -x$, $2 \rightarrow 3$, (Fig. 2), and since this operation is equivalent to a reflection in the COH plane, the vibrational degrees of freedom of methyl alcohol fall into the irreducible representations of the point group C_s. The molecule has eight vibrational degrees of freedom which are symmetric (+) and three, besides the hindered rotation, which are antisymmetric (−) with respect to reflections in the COH plane. Since the expression for W must be invariant under such reflections, the summations in Eqs. (4) must be carried out only over the eight (+) vibrational degrees of freedom. However, the expression for W may contain terms of the form

$$\sum_{\mu} b_{\mu}^{(1)}(\delta q_{\mu})\langle 0\tau n|\sin 3x|0\tau n\rangle, \tag{3b}$$

where this summation is now over the three (−) vibrational degrees of freedom only. Higher order terms in the δq_i, and terms involving $\cos 6x$, $\sin 6x$, $\cdots$ can be neglected.

The changes in the vibrational coordinates induced by the centrifugal distortion in a state characterized by J, τ, n, are determined from the condition of minimum energy

$$\frac{\partial W_{J\tau n}}{\partial(\delta q_i)}=0 \quad i=1, \cdots, 11. \tag{5}$$

With values of $(\delta q_i)_{J\tau n}$ given by these relations, the value of W is changed by the centrifugal distortion by an amount

$$\delta W_{\substack{J\tau n \\ (K=0)}} = -\sum_{\substack{i=1 \\ (+)}}^{8} \frac{\left[\frac{\hbar^2}{4}(J^2+J)\left\{\frac{A_i^{(1)}}{A_0^2}+\frac{B_i^{(1)}}{B_0^2}\right\}+\frac{1}{2}\langle 0\tau n|p_x^2|0\tau n\rangle\left\{\frac{C_{1i}^{(1)}}{C_{10}^2}+\frac{C_{2i}^{(1)}}{C_{20}^2}\right\}-\frac{H_0}{2}a_i^{(1)}\langle 0\tau n|1-\cos 3x|0\tau n\rangle\right]^2}{2k_{i(+)}}$$

$$-\sum_{\mu=9}^{11}\frac{[b_{\mu}^{(1)}\langle 0\tau n|\sin 3x|0\tau n\rangle]^2}{2k_{\mu(-)}}. \tag{6}$$

Formula (1) for the general $(J-1)\rightarrow J$, $K=0\rightarrow 0$ frequency is therefore modified by the centrifugal distortion terms

$$\nu_{(J-1)^{J}0^{0}\tau^{\tau}n^{n}}=\nu_{\text{rigid}}-4D_J J^3-2J\left[F_v\langle 0\tau n|1-\cos 3x|0\tau n\rangle+\frac{G_v}{\hbar^2}\langle 0\tau n|p_x^2|0\tau n\rangle\right], \tag{7}$$

where the first centrifugal distortion term, a function of J^3, arises from the ordinary vibration-rotation interactions. It has the same value for all the lines of the $J=0\rightarrow 1$ fine structure and merely shifts all of them to lower frequency by the same amount. The second term, linear in J, arises from the vibration-hindered rotation interactions and is the term proposed by Kivelson[5] for symmetric hindered rotators from a consideration of the complete Hamiltonian.

In the approximation in which methyl alcohol can be considered a symmetric molecule, F_v is given by

$$F_v=-\sum_{\substack{i=1 \\ (+)}}^{8}\frac{1}{k_{i(+)}}\left\{\frac{\hbar^2}{4}\left[\frac{A_i^{(1)}}{A_0^2}+\frac{B_i^{(1)}}{B_0^2}\right]\cdot\frac{H_0}{2}a_i^{(1)}\right\}. \tag{8}$$

Since the potential constants, $a_i^{(1)}$, can be determined neither from the pure vibration spectrum in the infrared nor from the pure hindered rotation microwave spectrum, the constant F_v can only be determined empirically from the observed $J=0\rightarrow 1$ frequencies themselves.

In the symmetric molecule approximation G_v is given by

$$G_v=+\sum_{\substack{i=1 \\ (+)}}^{8}\frac{1}{k_{i(+)}}\times\left\{\frac{\hbar^2}{4}\left(\frac{A_i^{(1)}}{A_0^2}+\frac{B_i^{(1)}}{B_0^2}\right)\cdot\frac{\hbar^2}{2}\left(\frac{C_{1i}^{(1)}}{C_{10}^2}+\frac{C_{2i}^{(1)}}{C_{20}^2}\right)\right\}. \tag{9}$$

Since the moments of inertia and their derivatives, $A_0, A_i^{(1)}, \cdots$ are functions only of the masses of the atoms and the known structure of the molecule, and since the elastic force constants can be estimated, with fair accuracy at least, from a knowledge of the infrared frequencies and their assignments,[10] the constant G_v can be computed for each isotopic molecule. For the normal molecule the following estimate has been made

$$G_v=-1.028+0.212+0.045$$
$$+(-0.138+0.097+0+0+0)=-0.81 \text{ Mc/sec},$$

[10] Ivash, Li, and Pitzer, J. Chem. Phys. **23**, 1814 (1955). References to earlier work are given in this paper.

where the first and largest term arises from the deformation of the COH angle, the next two terms from the stretching of the O—H and C—O bonds, respectively, and the terms in brackets from the five (+) degrees of freedom involving motions of the methyl group. These are to be discussed in more detail later. The contributions of the methyl group can be expected to be small, partly because the effect of the stretching modes cancels the effect of the bending modes and partly because the effective mass involved in the methyl motions is greater than that involved in the hydroxyl motions.

An attempt was made to fit the observed frequencies for $C^{12}H_3OH$ by means of (7) with this value for G_v and a value for F_v determined empirically to give the best possible fit. This attempt resulted in a failure to predict in any way satisfactorily the positions of the lines and pointed up the fact that Coriolis interactions play an important role. These will be considered next, starting with a discussion of the dominant terms.

O—H ROCKING MODEL FOR METHYL ALCOHOL THE DOMINANT CORIOLIS INTERACTION TERMS

The foregoing semiclassical description of the centrifugal distortion of the methyl alcohol molecule is based on an entirely static picture of the vibration-hindered rotation interactions and consequently fails to give the effects of the Coriolis forces which arise during the rotation of the whole molecular framework in space. These are somewhat complicated in form but the dominant Coriolis effects can be understood on the basis of an approximate description of the molecule.

From purely classical considerations it seems highly plausible that the Coriolis coupling between the hindered rotation and the vibrational degrees of freedom should receive its major contributions from the deformation of the COH bond angle resulting in a tipping or rocking motion of the O—H bar in the COH plane. If the atoms of the molecule move in this O—H tipping motion during the end-over-end tumbling in space of the whole molecular framework, (the $K=0$ space rotation), the O—H bar will be subject to a Coriolis force which causes it to precess about the symmetry axis of the CH_3 pyramid. During the O—H tipping motion the Coriolis forces therefore tend to excite the hindered rotation giving rise to an interaction between the two degrees of freedom. Since the vibrational motion is almost at right angles to the angular velocity vector for the end-over-end tumbling, and since the O—H tipping frequency is one of the lowest in methyl alcohol, the effect of this Coriolis interaction can be expected to be quite large, especially in the excited torsional states where the hindered rotation frequencies are not appreciably less than the O—H tipping frequency so that the effect of the Coriolis forces is not readily averaged out during a cycle of the tipping motion. In all the other normal coordinate motions the effect of this Coriolis interaction can be expected to be very much smaller. In the O—H stretching motion, for example, the vibrational velocities are almost parallel to the angular velocity vector for the end-over-end rotation, and the vibrational frequency is very much greater than the hindered rotation frequencies so that the small Coriolis interaction can be expected to be very largely averaged out during a vibrational cycle. The Coriolis interaction between the hindered rotation and all the other normal vibration motions can likewise be expected to exert a very small effect.

The major vibration-hindered rotation perturbations arising through the Coriolis coupling between the hindered rotation and the vibrational degrees of freedom can therefore be expected to come about largely through the deformation of the COH bond angle, and these can be understood on the basis of a new approximate model for the molecule. The molecule is still assumed to consist of a rigid O—H bar and a rigid CH_3 pyramid. Now, however, the mutual motion of the two portions of the molecule is to consist of the hindered rotation and a new degree of freedom, the deformation of the COH angle. The solution of this problem will of course lead to terms in the frequency formula such as those given by Eqs. (1) and (7) but should give additional terms arising largely through the Coriolis coupling between the hindered rotation and the COH deformation mode.

The kinetic energy for the new model of the molecule can be derived by the methods described previously.[11] The velocities of the atoms of the molecule relative to its over-all center of mass are described most easily in terms of the angular velocities of the two portions of the molecule and the intrinsic velocities of the atoms relative to a coordinate system which rotates in space with the equilibrium configuration of the hydroxyl group. With the introduction of the internal rotation angle x, the kinetic energy becomes

$$2T=A\omega_x^2+B\omega_y^2+C\omega_z^2-2D\omega_y\omega_z-2C_2\omega_z\dot{x} \\ +C_2\dot{x}^2+g_{11}\dot{\alpha}^2+2B_{11}\omega_x\dot{\alpha}. \quad (10)$$

The notation is that used in the preceding paper. The vector ω denotes the angular velocity of the hydroxyl group which can be expressed in terms of Euler angles θ, ψ, and ϕ_1; where the x-y-z coordinate system is an orthogonal system of axes rotating with the equilibrium configuration of the hydroxyl group, where the z-axis is parallel to the symmetry axis of the hindering potential and the y-axis lies in the COH plane. The variable COH angle is denoted by α, and the moments and product of inertia, A, B, C, and D, as well as the Coriolis interaction constant, B_{11}, are now all functions of α. Since the O—H rocking motion is confined to small angles about an equilibrium value, α_0, the solution of the problem will involve an expansion of α about this equilibrium value

$$\alpha=\alpha_0+\delta\alpha.$$

[11] See reference 3; also, D. G. Burkhard, "Coupling of the hindered rotation and the OH rocking motion in methyl alcohol" (private communiation).

In zeroth order the O—H tipping motion will be simple harmonic about α_0.

With the introduction of angular momentum components, P_i, and the canonical momenta conjugate to α and x,

$$P_i=\frac{\partial T}{\partial \omega_i}, \quad p_\alpha=\frac{\partial T}{\partial \dot{\alpha}}, \quad p_x=\frac{\partial T}{\partial \dot{x}},$$

the classical Hamiltonian for the O—H rocking problem becomes

$$H=\frac{P_x^2}{2\left(A-\frac{B_{11}^2}{g_{11}}\right)}+\frac{P_y^2C_1}{2(BC_1-D^2)}+\frac{P_z^2B}{2(BC_1-D^2)}$$
$$+\frac{P_yP_zD}{(BC_1-D^2)}+\frac{P_xp_\alpha B_{11}}{g_{11}\left(A-\frac{B_{11}^2}{g_{11}}\right)}+\frac{p_xP_yD}{(BC_1-D^2)}$$
$$+\frac{p_xP_zB}{(BC_1-D^2)}+\tfrac{1}{2}p_\alpha^2\frac{A}{(g_{11}A-B_{11}^2)}$$
$$+\tfrac{1}{2}p_x^2\frac{(BC-D^2)}{C_2(BC_1-D^2)}+V(x,\alpha), \quad (11)$$

where $V(x,\alpha)=(H_0/2)(1-\cos 3x)+(k_\alpha/2)(\delta\alpha)^2+$higher-order terms involving both x and α.

In this Hamiltonian, however, the very small vibration-hindered rotation interactions do not appear as small perturbation terms. The Hamiltonian (11) is clearly not in a form in which it is simply that of an ordinary rigid rotator plus that of a simple hindered rotator plus that of a simple harmonic oscillator describing the O—H tipping motion in zeroth order with additional terms which are higher-order perturbation terms arising from the coupling of the O—H tipping motion, the hindered rotation, and the rotation of the whole molecular framework in space. As a first step in the solution of the O—H rocking problem, the Hamiltonian (11) will be transformed to one having such a simple form, so that the interaction between the O—H tipping motion and the hindered rotation can be treated as a simple perturbation problem. Before proceeding with the transformation, however, the difficulties inherent in the present form of the Hamiltonian must be understood.

It can be shown that P_x, P_y, and P_z are the components of the total angular momentum vector, but in this form of the Hamiltonian the total angular momentum contains contributions from the internal rotation and the angular momentum of the O—H tipping motion. The momentum p_x is a function of more than the hindered rotation degree of freedom alone. Likewise, p_α depends on the rotational degrees of freedom and is not a function of the O—H tipping motion alone. Even if the terms involving p_x and p_α were ignored completely the remaining terms in the Hamiltonian would not be the correct rigid rotator terms since the moment of inertia A is replaced by $A-(B_{11})^2/g_{11}$ and the moment of inertia C is replaced by $C_1=C-C_2$ in these terms. The coupling between the hindered rotation, the over-all rotation, and the vibrational motion is given largely by the terms containing the cross products p_xP_y, p_xP_z, and $p_\alpha P_x$; but the matrix elements arising from these terms in the quantum-mechanical formulation will give contributions also to the zeroth-order rotational energies.

These difficulties all arise from the fact that there is an internal angular momentum associated with both the hindered rotation and O—H tipping motion when viewed from a system of axes rotating in space with the equilibrium configuration of the hydroxyl group. The rotating axes which would serve as a proper framework for the description of the hindered rotation and O—H tipping motions have to be such that these motions appear free of internal angular momentum, at least in zeroth order. In the ordinary vibrating and rotating molecule any coordinate system fixed in the limiting rigid molecule can serve as such a proper system of molecule-fixed axes since the small-vibration coordinates can always be chosen as a linear combination of several chemical coordinates in such a way that the internal angular momentum vanishes, at least in zeroth order, during a change of any one small-vibration degree of freedom. In the simplified O—H rocking model for the methyl alcohol molecule, however, the nature of the molecular forces dictates the choice of the internal degrees of freedom, and since these are initially not free of internal angular momentum with respect to the system of rotating axes which seem the most natural choice from the point of view of the molecular forces, a proper molecule-fixed system of rotating axes must first be found if the vibration-hindered rotation interaction problem is to be formulated as a simple perturbation problem.

In the preceding paper it was shown how such a system of axes can be found in the case of the simple hindered rotator by a transformation of the Hamiltonian which removes zeroth-order terms containing products of the form p_xP_i. In the O—H rocking problem such a transformation must also remove the cross term between p_α and P_x arising from the angular momentum of the O—H rocking motion. The transformation must be a proper contact transformation from the old coordinates α, x, θ, ψ, and ϕ_1, and their canonically conjugate momenta to new canonical coordinates and momenta, α', x', θ', etc. . . . The mechanics of the transformation is much simpler in terms of the noncanonical angular momentum components, P_i, and the momenta p_α and p_x, where the new momentum and angular momentum components must again satisfy the Poisson bracket relations

$$(P_x',P_y')=P_z', \quad (12a)$$

and cyclically.

$$(P_i',p_\alpha')=0,\quad (P_i',p_x')=0,\quad (P_i',\alpha')=0,\quad (P_i',x')=0,\quad (p_\alpha',p_x')=0. \tag{12b}$$

The zeroth-order term containing the product between p_α and P_x can be transformed out of the Hamiltonian by means of the following transformation:

$$p_\alpha=p_\alpha'+\frac{B_{11}(\alpha)}{A(\alpha)}P_x',\qquad \alpha=\alpha', \tag{13a}$$

$$\begin{pmatrix}P_x\\P_y\\P_z\end{pmatrix}=\begin{pmatrix}1&0&0\\0&\cos u(\alpha)&-\sin u(\alpha)\\0&\sin u(\alpha)&\cos u(\alpha)\end{pmatrix}\begin{pmatrix}P_x'\\P_y'\\P_z'\end{pmatrix}, \tag{13b}$$

where transformation (13a) is chosen so that the coefficient of the $p_\alpha'P_x'$ term in the new Hamiltonian will be equal to zero for all values of α. Transformation (13b) is chosen to have the form of a rotation so that the relations (12a) are automatically satisfied, while $u(\alpha)$ is a function of α which must be chosen in such a way that the relations $(p_\alpha',P_i')=0$ are fulfilled. This will be the case if

$$\frac{du}{d\alpha}=\frac{B_{11}(\alpha)}{A(\alpha)},$$

or, expanding in the parameter of smallness $\delta\alpha=(\alpha-\alpha_0)$, if

$$\mu(\alpha)=\frac{B_{11}^{(0)}}{A_0}(\delta\alpha)+\left\{\frac{B_{11\alpha}^{(1)}}{A_0}-\frac{A_\alpha^{(1)}B_{11}^{(0)}}{A_0^2}\right\}\frac{(\delta\alpha)^2}{2}+\cdots, \tag{13c}$$

where

$$B_{11}^{(0)}=B_{11}(\alpha_0)\quad\text{and}\quad B_{11\alpha}^{(1)}=\left(\frac{\partial B_{11}}{\partial\alpha}\right)_{\alpha_0},\ \text{etc.}$$

The transformation (13) must be followed by a further transformation which makes the ordinary rotation-hindered rotation interaction terms in the Hamiltonian as mild as possible as discussed in the preceding paper. The complete transformation to the new form of the Hamiltonian is therefore

$$p_\alpha=p_\alpha'+\frac{B_{11}(\alpha)}{A(\alpha)}\left[P_x'\cos\left(\frac{C_2}{C}\right)_0^*x+P_y'\sin\left(\frac{C_2}{C}\right)_0^*x\right],$$

$$p_x=p_x'-\left(\frac{C_2}{C}\right)_0^*P_z',\quad\text{where}\quad\left(\frac{C_2}{C}\right)_0^*=\frac{C_2[B_0^2+D_0^2]^{\frac{1}{2}}}{(B_0C_0-D_0^2)},$$

$$\alpha=\alpha',\quad x=x',$$

$$\begin{pmatrix}P_x\\P_y\\P_z\end{pmatrix}=\begin{pmatrix}1&0&0\\0&\cos u(\alpha)&-\sin u(\alpha)\\0&\sin u(\alpha)&\cos u(\alpha)\end{pmatrix}\begin{pmatrix}1&0&0\\0&\dfrac{B_0}{[B_0^2+D_0^2]^{\frac{1}{2}}}&\dfrac{D_0}{[B_0^2+D_0^2]^{\frac{1}{2}}}\\0&\dfrac{-D_0}{[B_0^2+D_0^2]^{\frac{1}{2}}}&\dfrac{B_0}{[B_0^2+D_0^2]^{\frac{1}{2}}}\end{pmatrix}\begin{pmatrix}\cos\left(\frac{C_2}{C}\right)_0^*x&\sin\left(\frac{C_2}{C}\right)_0^*x&0\\-\sin\left(\frac{C_2}{C}\right)_0^*x&\cos\left(\frac{C_2}{C}\right)_0^*x&0\\0&0&1\end{pmatrix}\begin{pmatrix}P_x'\\P_y'\\P_z'\end{pmatrix}, \tag{14}$$

where B_0, C_0, and D_0 are the equilibrium values of the moments and product of inertia, e.g., $B_0=B(\alpha_0)$. They are therefore constants independent of α, as they must be if the Poisson bracket relations $(p_\alpha',P_i')=0$ are to be fulfilled for the complete transformation. Since the instantaneous values of B, C, and D cannot be used in transformation (14), this transformation removes only the zeroth-order part of the coupling terms of the form p_xP_i. In higher order there is an internal angular momentum associated with the combined hindered rotation and O—H tipping motion, and the new Hamiltonian will contain terms of the type $P_i'p_x'(\delta\alpha)$ due to the Coriolis interaction between the hindered rotation and the O—H tipping motion, but this Coriolis interaction now appears as a perturbation term.

Transformation (14) gives the new form of the classical Hamiltonian from which the correct symmetrized quantum-mechanical form of the Hamiltonian can be obtained as usual. The coefficients of this new Hamiltonian are somewhat complicated functions of the instantaneous and the equilibrium values of the moments of inertia. However, the Hamiltonian has the simple form

$$H=H^{(0)}_{\substack{\text{hindered rotation—}\\\text{over-all rotation}}}+H^{(0)+(1)+(2)+\cdots}_{\text{pure vibration}}+H^{(1)+(2)+\cdots}_{\substack{\text{vibration—hindered}\\\text{rotation-over-all}\\\text{rotation perturbations}}}, \tag{15}$$

and the coupling between the hindered rotation and

the O—H tipping motion during the over-all rotation of the whole molecular framework in space can therefore be treated as a simple perturbation problem.

The zeroth-order over-all rotation-hindered rotation Hamiltonian is in the form given in the preceding paper.[12] For the $J=1$ states in all isotopic species of methyl alcohol, the asymmetry terms can be treated as perturbation terms, and the solutions of the symmetric hindered rotator terms can be used as zeroth-order wave functions. The slight modifications in these wave functions in their dependence on the molecular parameters has also been discussed in the preceding paper.

The pure vibrational or O—H rocking part of the Hamiltonian is given by

$$H_{\text{pure vibration}}^{(0)+(1)+(2)+\cdots}=\tfrac{1}{2}G^{\frac{1}{4}}p_\alpha'\frac{A}{(g_{11}A-B_{11}^2)}G^{-\frac{1}{4}}p_\alpha'G^{\frac{1}{4}}+\tfrac{1}{2}k_\alpha(\delta\alpha)^2+\cdots, \quad (16)$$

in which $G=1/(g_{11}A-B_{11}^2)C_2(BC_1-D^2)$ is a function of α. In zeroth order, however, the vibrational part of the Hamiltonian has the harmonic oscillator form

$$H_{\text{pure vibration}}^{(0)}=\frac{1}{2\mu_\alpha}p_\alpha'^2+\frac{k_\alpha}{2}(\delta\alpha)^2, \quad (17)$$

in which μ_α, the reduced mass, or rather the reduced moment of inertia, for the O—H tipping motion is given by

$$\mu_\alpha=g_{11}-(B_{11}^{(0)})^2/A_0, \quad (18)$$

where

$$g_{11}=\left\{\frac{M_OM_H}{M_{OH}}+\frac{M_{OH}m_{CH_3}}{(M_{OH}+m_{CH_3})}\cdot\frac{M_H^2}{M_{OH}^2}\right\}l^2,$$

in which the masses are identified by the subscripts describing the components of the molecule and in which l is the OH bond length. With this value for μ_α the force constant for the OH rocking vibration, k_α, can be estimated from the observed infrared COH deformation frequency; $k_\alpha=\mu_\alpha\omega_\alpha^2$.

The perturbation terms arising through the coupling between the O—H rocking vibrational motion and the hindered and over-all rotations have the form

$$\begin{aligned}H_{\substack{\text{vibration—hindered}\\ \text{rotation-over all}\\ \text{rotation perturbations}}}^{(1)+(2)+\cdots}=&\tfrac{1}{4}(P_x'^2+P_y'^2)\left\{\mu_{11_\alpha}^{(1)}(\delta\alpha)+\mu_{11_{\alpha\alpha}}^{(2)}\frac{(\delta\alpha)^2}{2}+\cdots\right\}\\
&+\tfrac{1}{2}P_z'^2\left\{\mu_{33_\alpha}^{(1)}(\delta\alpha)+\mu_{33_{\alpha\alpha}}^{(2)}\frac{(\delta\alpha)^2}{2}+\cdots\right\}+\tfrac{1}{2}p_x'^2\left\{\mu_{44_\alpha}^{(1)}(\delta\alpha)+\mu_{44_{\alpha\alpha}}^{(2)}\frac{(\delta\alpha)^2}{2}+\cdots\right\}\\
&+\frac{H_0}{2}\left\{a_\alpha^{(1)}(\delta\alpha)+a_{\alpha\alpha}^{(2)}\frac{(\delta\alpha)^2}{2}+\cdots\right\}(1-\cos3x)+p_x'P_z'\left\{\mu_{34_\alpha}^{(1)}(\delta\alpha)+\mu_{34_{\alpha\alpha}}^{(2)}\frac{(\delta\alpha)^2}{2}+\cdots\right\}\\
&+\tfrac{1}{2}(P_+'p_x'+p_x'P_+')\left\{\mu_{14_\alpha}^{(1)}(\delta\alpha)+\mu_{14_{\alpha\alpha}}^{(2)}\frac{(\delta\alpha)^2}{2}+\cdots\right\}\\
&+\tfrac{1}{2}(P_+'P_z'+P_z'P_+')\left\{\mu_{13_\alpha}^{(1)}(\delta\alpha)+\mu_{13_{\alpha\alpha}}^{(2)}\frac{(\delta\alpha)^2}{2}+\cdots\right\}\\
&+\tfrac{1}{4}\left\{(P_x'^2-P_y'^2)\cos2\left(\frac{C_2}{C}\right)_0^*x+(P_x'P_y'+P_y'P_x')\sin2\left(\frac{C_2}{C}\right)_0^*x\right\}\\
&\cdot\left\{\mu_{12_\alpha}^{(1)}(\delta\alpha)+\mu_{12_{\alpha\alpha}}^{(2)}\frac{(\delta\alpha)^2}{2}+\cdots\right\}, \quad (19)\end{aligned}$$

in which

$$P_+'=P_y'\cos\left(\frac{C_2}{C}\right)_0^*x-P_x'\sin\left(\frac{C_2}{C}\right)_0^*x.$$

Only certain coefficients can give significant contributions to the $J=0\rightarrow1$, $K=0\rightarrow0$ frequencies, and these coefficients are listed as functions of the molecular constants and their derivatives in Table II. The vibration-hindered, rotation perturbation problem is now in a form in which it can be solved by standard perturbation methods using the zeroth-order rotational and vibrational wave functions discussed previously. The parameter of smallness in the perturbation calculation is given by $[\hbar/(\mu_\alpha\omega_\alpha)]^{\frac{1}{2}}$. Matrix elements of first order in this parameter, off-diagonal in the O—H rocking vibrational quantum number, v_α, and the torsional quantum number, n, can be transformed by

[12] See Eq. (9) of the preceding paper.

the usual methods[13] into second-order terms diagonal in v_α and n, but not necessarily diagonal in the rotational quantum number, K. Since the rotational matrix elements off-diagonal in K can themselves be treated as perturbation terms, the second-order contributions to these matrix elements arising from the vibrational perturbations can to good approximation be neglected.

The solution of the perturbation problem leads to the following $J=0\rightarrow 1$ frequency formula, valid to within the limitations of the O—H rocking model:

$$\underset{(J\,K\,\tau\,n\,v_\alpha)}{\nu_{0^1 0^0 \tau_n n_0^0}} = \frac{h}{8\pi^2}\left(\frac{1}{A_0}+\frac{B_0}{B_0^2+D_0^2}\right)-\tfrac{1}{2}(\alpha_{v_\alpha}{}^A+\alpha_{v_\alpha}{}^B)-4D_J \tag{20a}$$

$$-\frac{2}{h}\sum_{K'=\substack{+1\\-1}}\frac{\left|\frac{\hbar^2}{4}\frac{D_0}{B_0^2+D_0^2}\langle 0\tau n\,|\,e^{\mp ix}\,|\,K'\tau' n\rangle\right|^2}{E_{K'\tau' n}-E_{0\tau n}+\frac{\hbar^2}{2}\left[\frac{B_0+C_0}{(B_0C_0-D_0^2)}-\frac{1}{2}\left(\frac{1}{A_0}+\frac{3B_0}{(B_0^2+D_0^2)}\right)\right]} \tag{20b}$$

$$-2\left[F_{v_\alpha}\langle 0\tau n\,|\,1-\cos 3x\,|\,0\tau n\rangle+\frac{G_{v_\alpha}}{\hbar^2}\langle 0\tau n\,|\,p_x{}^2\,|\,0\tau n\rangle\right] \tag{20c}$$

$$-2\sum_{K'=\substack{+1\\-1}}\sum_{n'}\frac{\left|d_{v_\alpha}\left\langle 0\tau n\left|e^{\mp ix}\frac{1}{i}\frac{\partial}{\partial x}\mp\tfrac{1}{2}e^{\mp ix}\right|K'\tau' n'\right\rangle\pm c_{v_\alpha}\langle 0\tau n\,|\,e^{\mp ix}\,|\,K'\tau' n'\rangle\right|^2}{h\omega_\alpha+(E_{K'\tau' n'}-E_{0\tau n})}, \tag{20d}$$

where

$$\left\langle 0\tau n\left|e^{\mp ix}\frac{1}{i}\frac{\partial}{\partial x}\mp\tfrac{1}{2}e^{\mp ix}\right|K'\tau' n'\right\rangle=\int_0^{2\pi}P_{0\tau n}{}^*(x)\left(e^{\mp ix}\frac{1}{i}\frac{\partial}{\partial x}\mp\tfrac{1}{2}e^{\mp ix}\right)P_{K'\tau' n'}(x)dx,$$

for example, and where the upper sign applies when $K'=+1$ while the lower sign applies when $K'=-1$.

The first term in the new frequency formula, (20a), has the form of the symmetric rigid rotator expression (2), modified by the ordinary vibration-rotation interaction constants, the centrifugal distortion constant, D_J, and the constants, α_{v_α}, which account for the changes in the values of $1/A$ and $1/B$ resulting from the averaging effects during the COH deformation vibration.

The second term (20b) gives the contributions arising from the asymmetry of the molecule and has been discussed previously on the basis of the rigid model for the hindered rotator.

The terms (20c) give the COH deformation contributions to the centrifugal distortion terms and are the same as those derived previously from the simple semiclassical description of the centrifugal distortion, except that the constants F_v and G_v are modified by very small terms arising from the asymmetry of the molecule. F_v is the constant which must be determined empirically. G_v now has the value

$$G_{v_\alpha}=\frac{1}{k_\alpha}\frac{\hbar^2}{4}\left\{\frac{A_\alpha{}^{(1)}}{A_0{}^2}+\frac{B_\alpha{}^{(1)}}{B_0^2+D_0^2}-\frac{2D_0}{B_0^2+D_0^2}\frac{B_{11}{}^{(0)}}{A_0}\right\}$$
$$\cdot\frac{\hbar^2}{2}\left\{\frac{C_{1\alpha}{}^{(1)}}{C_{10}{}^2}-\frac{2D_0D_\alpha{}^{(1)}}{C_{10}(B_0C_{10}-D_0^2)}+\frac{D_0{}^2}{C_{10}(B_0C_{10}-D_0^2)}\left[\frac{C_{1\alpha}{}^{(1)}}{C_{10}}+\frac{C_{10}B_\alpha{}^{(1)}+C_{1\alpha}{}^{(1)}B_0-2D_0D_\alpha{}^{(1)}}{(B_0C_{10}-D_0^2)}\right]\right\}. \tag{21}$$

Except for terms smaller by an order of magnitude, D_0/B_0, this expression is exactly the same as that given previously by Eq. (9). Since D_0/B_0 has a value of about -0.003 for the O—H isotopic molecules and a value of about 0.03 for the O—D molecules, these terms can be neglected, especially since uncertainties in the rotational constants of about three percent must certainly be expected due to the uncertainties in the normal vibrations. To sufficient approximation therefore the constant G_v can be given by the simple formula (9).

The last term in the frequency formula is an entirely new term arising through the Coriolis interaction between the hindered rotation and O—H tipping motions, also partly through the asymmetry of the vibrating

[13] See, e.g., H. H. Nielsen, Revs. Modern Phys. **23**, 90 (1951); or E. B. Wilson and J. B. Howard, J. Chem. Phys. 4, 260 (1936).

molecule. This term can be written

$$-2\sum_{\substack{K'=+1\\-1}}\sum_{n'} D_{v\alpha}{}^2 \frac{\left|\left\langle 0\tau n\left|e^{\mp ix}\frac{1}{i}\frac{\partial}{\partial x}\mp\tfrac{1}{2}e^{\mp ix}\right|K'\tau'n'\right\rangle\right|^2}{1+\dfrac{(E_{K'\tau'n'}-E_{0\tau n})}{\hbar\omega_\alpha}} \tag{20d$_1$}$$

$$-2\sum_{\substack{K'=+1\\-1}}(\pm 1)\sum_{n'} 2C_{v\alpha}D_{v\alpha}\frac{\left|\left\langle 0\tau n\left|e^{\mp ix}\frac{1}{i}\frac{\partial}{\partial x}\mp\tfrac{1}{2}e^{\mp ix}\right|K'\tau'n'\right\rangle\langle K'\tau'n'\,|\,e^{\pm ix}\,|\,0\tau n\rangle\right|}{1+\dfrac{E_{K'\tau'n'}-E_{0\tau n}}{\hbar\omega_\alpha}} \tag{20d$_2$}$$

$$-2\sum_{\substack{K'=+1\\-1}}\sum_{n'} C_{v\alpha}{}^2\frac{|\langle 0\tau n\,|\,e^{\mp ix}\,|\,K'\tau'n'\rangle|^2}{1+\dfrac{E_{K'\tau'n'}-E_{0\tau n}}{\hbar\omega_\alpha}}. \tag{20d$_3$}$$

The matrix elements containing $(1/i)\partial/\partial x$ arise from terms in the Hamiltonian of the form $p_x'P_+'(\delta\alpha)$. Since these are the Coriolis interaction terms, (20d$_1$) can be expected to give large contributions to the $J=0\rightarrow 1$ frequencies, especially in the excited torsional states.

These matrix elements are somewhat complicated in form, and the summation cannot be carried out in general because of the dependence of the energy denominator on the hindered rotation quantum numbers.

TABLE II. Coefficients of the vibration-hindered rotation perturbation Hamiltonian.

$$\mu 11_\alpha{}^{(1)}=-\frac{A_\alpha{}^{(1)}}{A_0{}^2}-\frac{B_\alpha{}^{(1)}}{[B_0{}^2+D_0{}^2]}+\frac{2D_0}{[B_0{}^2+D_0{}^2]}\frac{B_{11}{}^{(0)}}{A_0}$$

$$\mu 44_\alpha{}^{(1)}=-\frac{C1_\alpha{}^{(1)}}{C1_0{}^2}+\frac{2D_0D_\alpha{}^{(1)}}{C1_0(B_0C1_0-D_0{}^2)}-\frac{D_0{}^2}{C1_0(B_0C1_0-D_0{}^2)}\times\left\{\frac{C1_\alpha{}^{(1)}}{C1_0}+\frac{C1_0B_\alpha{}^{(1)}+B_0C1_\alpha{}^{(1)}-2D_0D_\alpha{}^{(1)}}{(B_0C1_0-D_0{}^2)}\right\}$$

$a_\alpha{}^{(1)}$ = unknown potential constant

$$\mu 14_\alpha{}^{(1)}=\frac{[B_0{}^2+D_0{}^2]^{\frac{1}{2}}}{(B_0C1_0-D_0{}^2)}\frac{B_{11}{}^{(0)}}{A_0}+\frac{B_0D_\alpha{}^{(1)}-D_0B_\alpha{}^{(1)}}{[B_0{}^2+D_0{}^2]^{\frac{1}{2}}(B_0C1_0-D_0{}^2)}$$

$$\mu 13_\alpha{}^{(1)}=\frac{D_0B_\alpha{}^{(1)}}{(B_0C1_0-D_0{}^2)}\left\{\frac{C_2}{(B_0C_0-D_0{}^2)}-\frac{(B_0+C1_0)}{(B_0{}^2+D_0{}^2)}\right\}+\frac{D_\alpha{}^{(1)}}{(B_0C1_0-D_0{}^2)}\left\{1-\frac{B_0C_2}{(B_0C_0-D_0{}^2)}\right\}+\frac{B_{11}{}^{(0)}}{A_0}\left\{\frac{(B_0{}^2-D_0{}^2)(B_0-C1_0)+4B_0D_0{}^2}{(B_0C1_0-D_0{}^2)(B_0{}^2+D_0{}^2)}-\frac{C_2(B_0{}^2+D_0{}^2)}{(B_0C1_0-D_0{}^2)(B_0C_0-D_0{}^2)}\right\}$$

If the differences in the internal rotation energies could be neglected in comparison with the O—H rocking vibrational energy, $\hbar\omega_\alpha$, the summations over the quantum numbers n' and K' (with appropriate τ') could be carried out directly. In that approximation the sums over the internal rotation matrix elements in (20d$_2$) and (20d$_3$) turn out to be independent of the internal rotation quantum numbers, τ and n, while the summation in (20d$_1$) yields

$$\sum_{\substack{K'=+1\\-1}}\sum_{n'}\left|\left\langle 0\tau n\left|e^{\mp ix}\frac{1}{i}\frac{\partial}{\partial x}\mp\tfrac{1}{2}e^{\mp ix}\right|K'\tau'n'\right\rangle\right|^2 = \frac{2}{\hbar^2}\langle 0\tau n\,|\,p_x{}^2\,|\,0\tau n\rangle+\frac{1}{2}\left[\left(\frac{C_2}{C}\right)_0^*\right]^2. \tag{22}$$

In that approximation therefore the terms determined by the coefficients $C_v{}^2$ and C_vD_v shift all of the lines of the $J=0\rightarrow 1$ fine structure by the same amount so that the effect of these terms can be absorbed by the ordinary vibration-rotation interaction constants, α_v, while the term determined by the coefficient $D_v{}^2$ has much the same form as the centrifugal distortion term determined by G_v. It might, therefore, be expected that a simple formula of the Kivelson form, (7), should give an approximate fit for the frequencies provided that the constant G_v is replaced by $G_v+2D_v{}^2$. Actually, the differences in the internal rotation energy $(E_{K'\tau'n'}-E_{0\tau n})$, are for certain values of n' certainly not negligible compared with the vibrational energy, and since the integrals containing $(1/i)(\partial/\partial x)$ have significant values for several values of n' the approximations inherent in the use of (22), for example, might be expected to lead to errors in the frequency splittings of from 2 to 10 Mc/sec. Sums such as (22), however, are very useful as a check on the evaluation of the matrix elements. The summations over n' in (20d$_1$) and (20d$_2$) will usually contain

three or four significant terms. In the summation $(20d_3)$, on the other hand, there is usually only one dominant term so that the energy denominator can be replaced by an average value, and to a very good approximation, (about ± 0.05 Mc/sec), this term is independent of the hindered rotation quantum numbers n and τ. The effect of the vibration-hindered rotation interaction constant C_v^2 can therefore be absorbed by the ordinary vibration-rotation interaction rotational constants. This is a considerable simplification since each of the eleven vibrational degrees of freedom can be expected to contribute a term such as $(20d_3)$ with a significant value for the coefficient, C_v^2. Constants such as D_v, on the other hand, which give the strength of the Coriolis interaction between the hindered rotation and the vibrational degrees of freedom can be expected to have a large value only for the COH deformation mode, and complicated terms of the form $(20d_1)$ and $(20d_2)$ can therefore be expected to have significant coefficients only for this one vibrational mode.

The two new significant vibration-hindered rotation interaction constants $D_{v_\alpha}^2$ and $C_{v_\alpha}D_{v_\alpha}$, like G_v, are functions only of the elastic force constants and the known structural parameters. On the basis of the O—H rocking model they have the following values:

$$D_{v_\alpha}^2=\frac{1}{2k_\alpha}\left(\frac{\hbar^2}{2}\mu_{14_\alpha}^{(1)}\right)^2 \approx\frac{1}{2k_\alpha}\left\{\frac{\hbar^2}{2}\left[\frac{B_{11}^{(0)}}{C_{10}A_0}+\frac{D_\alpha^{(1)}}{C_{10}B_0}-\frac{D_0B_\alpha^{(1)}}{C_{10}B_0^2}\right]\right\}^2, \quad (23)$$

$$C_{v_\alpha}D_{v_\alpha}=\frac{1}{2k_\alpha}\left(\frac{\hbar^2}{2}\mu_{14_\alpha}^{(1)}\right)\left(\frac{\hbar^2}{2}\left[\mu_{13_\alpha}^{(1)}-\left(\frac{C_1}{C}\right)_0^*\mu_{14_\alpha}^{(1)}\right]\right) \approx\frac{1}{2k_\alpha}\left(\frac{\hbar^2}{2}\mu_{14_\alpha}^{(1)}\right)\cdot\left(\frac{\hbar^2}{4}\left[-\frac{B_{11}^{(0)}}{A_0B_0}\right]\right), \quad (24)$$

where most of the terms smaller by an order of magnitude, D_0/B_0, have been neglected in the approximate expressions. These constants can therefore be evaluated from known data. However, a certain amount of adjustment is possible due to the uncertainty in the elastic force constant, k_α, and the uncertainty in the actual form of the normal vibration motion. An adjustment in the force constant, k_α, however, must affect the rotational constants for all the molecules in exactly the same way, and the rotational constants for the isotopic species can therefore be expected to follow from the adjusted constants for the normal molecule. From an examination of the mass factors occurring in the expressions for the rotational constants it can be seen that the rotational constants for the isotopic species can be obtained, to sufficient approximation, from those for the normal molecule by the following very simple, approximate isotopic rules:

$$\frac{(D_{v_\alpha}^2)_{\text{isotope 1}}}{(D_{v_\alpha}^2)_{\text{isotope 2}}}=\frac{(C_{v_\alpha}D_{v_\alpha})_{\text{isotope 1}}}{(C_{v_\alpha}D_{v_\alpha})_{\text{isotope 2}}}\approx\frac{(A_0^2)_{\text{isotope 2}}}{(A_0^2)_{\text{isotope 1}}}, \quad (25)$$

$$\frac{(G_v)_{\text{isotope 1}}}{(G_v)_{\text{isotope 2}}}\approx\frac{\mu_{\text{isotope 1}}(A_0^2)_{\text{isotope 2}}}{\mu_{\text{isotope 2}}(A_0^2)_{\text{isotope 1}}}, \quad (26)$$

in which μ is the reduced mass involving the masses of the hydroxyl and methyl groups:

$$\mu=\frac{m_{CH_3}M_{OH}}{(m_{CH_3}+M_{OH})}.$$

The theory which has been developed up to this point uses a simplified model, and the physics behind the various terms is rather easily understood. It is satisfying that it gives the principal contributions and yields a fit with experiment which is quite good, (with a certain allowed adjustment in the constants for the normal molecule). A re-examination of the problem has been made and will be described in the following section in which all the degrees of vibrational freedom (not merely the O—H rocking) have been considered. Although this greatly increases the complexity of the calculations, it essentially introduces no new empirical constants, and it does result in a substantially better fit.

DETAILED EXAMINATION OF THE VIBRATION-HINDERED ROTATION INTERACTIONS

The detailed consideration of the vibration-hindered rotation perturbations in methanol is carried out in this section in order to incorporate into the theory the Coriolis effects of the vibrations other than the O—H rocking motion.

The eleven vibrational degrees of freedom of the molecule may be built up from the changes in the bond lengths and the bond angles which are illustrated in Fig. 2. There are eight (+) and three (−) degrees of freedom, symmetric and antisymmetric, respectively, with respect to reflections in the COH plane. The three chemical coordinates not involving the methyl group, namely the deformation of the COH angle, $\delta\alpha$, the stretching of the O—H bond, δl, and the stretching of the C—O bond, δh, are all (+) vibrational degrees of freedom. The degrees of freedom involving motions of the methyl group may be expressed through the changes in the three C—H bond lengths δs_i, the three HCH angles $\delta\gamma_i$, and the three HCO angles $\delta\beta_i$; but they must be built up in such a way as to have both the correct symmetry properties of the three fold methyl group and the correct symmetry, either (+) or (−), with respect to the symmetry operation, $x\rightarrow -x$, $2\leftrightarrow 3$, which leaves the potential energy of the molecule invariant. One possible choice having the correct symmetry is the

following:

$$\left.\begin{aligned}
\delta q_4 &= (\delta s)_0 = \frac{1}{\sqrt{3}}(\delta s_1+\delta s_2+\delta s_3) \\
\delta q_5 &= (\delta\gamma)_0 = \frac{1}{\sqrt{3}}(\delta\gamma_1+\delta\gamma_2+\delta\gamma_3) \\
\delta q_6 &= (\delta s)_+ = (\tfrac{2}{3})^{\frac{1}{2}}[\delta s_1-\tfrac{1}{2}(\delta s_2+\delta s_3)]\cos x-\frac{1}{\sqrt{2}}(\delta s_2-\delta s_3)\sin x \\
\delta q_7 &= (\delta\gamma)_+ = (\tfrac{2}{3})^{\frac{1}{2}}[\delta\gamma_1-\tfrac{1}{2}(\delta\gamma_2+\delta\gamma_3)]\cos x-\frac{1}{\sqrt{2}}(\delta\gamma_2-\delta\gamma_3)\sin x \\
\delta q_8 &= (\delta\beta)_+ = (\tfrac{2}{3})^{\frac{1}{2}}[\delta\beta_1-\tfrac{1}{2}(\delta\beta_2+\delta\beta_3)]\cos x-\frac{1}{\sqrt{2}}(\delta\beta_2-\delta\beta_3)\sin x
\end{aligned}\right\}(+)$$

$$\left.\begin{aligned}
\delta q_9 &= (\delta s)_- = (\tfrac{2}{3})^{\frac{1}{2}}[\delta s_1-\tfrac{1}{2}(\delta s_2+\delta s_3)]\sin x+\frac{1}{\sqrt{2}}(\delta s_2-\delta s_3)\cos x \\
\delta q_{10} &= (\delta\gamma)_- = (\tfrac{2}{3})^{\frac{1}{2}}[\delta\gamma_1-\tfrac{1}{2}(\delta\gamma_2+\delta\gamma_3)]\sin x+\frac{1}{\sqrt{2}}(\delta\gamma_2-\delta\gamma_3)\cos x \\
\delta q_{11} &= (\delta\beta)_- = (\tfrac{2}{3})^{\frac{1}{2}}[\delta\beta_1-\tfrac{1}{2}(\delta\beta_2+\delta\beta_3)]\sin x+\frac{1}{\sqrt{2}}(\delta\beta_2-\delta\beta_3)\cos x
\end{aligned}\right\}(-). \qquad (27)$$

In terms of these eleven vibrational coordinates the kinetic energy for the completely nonrigid hindered rotator can again be derived most easily in terms of the angular velocity ω of a framework of axes rotating in space with the equilibrium configuration of the hydroxyl group and the intrinsic velocities of the atoms of the two groups of the molecule relative to the equilibrium framework. With the introduction of the internal rotation angle, x, the kinetic energy of the vibrating hindered rotator becomes

$$\begin{aligned}
2T = {} & A\omega_x^2+B\omega_y^2+C\omega_z^2-2D\omega_y\omega_z-2E\omega_x\omega_y-2F\omega_x\omega_z \\
& +2\omega_x\sum_i B_{1i}\dot{q}_i+2\omega_y\sum_i B_{2i}\dot{q}_i+2\omega_z\sum_i B_{3i}\dot{q}_i \\
& +C_2\dot{x}^2-2C_2\omega_z\dot{x}+\sum_{i,j} g_{ij}\dot{q}_i\dot{q}_j \\
& +12m_{\mathrm{H}}(\dot{x}^2-\omega_z\dot{x}) \\
& \quad\times\{[(\delta\gamma)_+'-(\delta s)_+']^2+[(\delta\gamma)_-'-(\delta s)_-']^2\} \\
& +12m_{\mathrm{H}}\dot{x}\{[(\delta\gamma)_-'-(\delta s)_-'][(\delta\dot{\gamma})_+'-(\delta\dot{s})_+'] \\
& \quad-[(\delta\gamma)_+'-(\delta s)_+'][(\delta\dot{\gamma})_-'-(\delta\dot{s})_-']\}, \qquad (28)
\end{aligned}$$

in which m_{H} is the mass of one of the hydrogen atoms of the methyl group and $(\delta\gamma)_\pm'$, $(\delta s)_\pm'$ are given by

$$(\delta\gamma)_\pm' = \frac{\sqrt{2}}{3}s_0\left[1-\frac{3}{4}\frac{a^2}{s_0^2}\right](\delta\gamma)_\pm, \quad (\delta s)_\pm' = \frac{1}{\sqrt{6}}\frac{a}{s_0}(\delta s)_\pm,$$

s_0 is the equilibrium distance of the CH bonds, and a is the equilibrium distance from one of the hydrogen atoms to the center of gravity of the H_3 triangle. The last two terms arising through the distortion of the methyl group give an additional coupling between the vibrations and the hindered rotation but their effect on the $J=0\rightarrow 1$ frequencies can be shown to be completely negligible. The Coriolis interaction constants, B_{1i}, B_{2i}, B_{3i}, the moments of inertia, A, B, and C, the product of inertia, D, and the new products of inertia, E and F, arising from the complete asymmetry of the molecule in its distorted configurations, are functions not only of the eleven vibrational degrees of freedom but also of the internal rotation angle, x. This latter dependence comes about through the methyl degrees of freedom. First, there is an implicit dependence on x through vibrational degrees of freedom such as $(\delta\gamma)_+$ and $(\delta\gamma)_-$, but it gives rise to no new types of terms in the frequency formula. [In Appendix II it will be shown that vibrational coordinates such as $(\delta\gamma)_+$ and $(\delta\gamma)_-$ give contributions to the vibration-hindered rotation corrections to the energy of exactly the same form as the vibrational coordinate, $\delta\alpha$, for example.] However, there is an additional explicit dependence on x since the moments of inertia are in higher order functions of terms such as $(\delta\gamma)_+\cos 3x$ and $(\delta\gamma)_-\sin 3x$. This coupling between the hindered rotation and the methyl degrees of freedom does give rise to entirely new terms in the frequency formula. However, it can be shown that the

effects of these terms on the $J=0\rightarrow 1$ frequencies are numerically so small that they can be neglected.

The solution of the complete vibration-hindered rotation interaction problem is carried out in exactly the same way as the solution of the O—H rocking problem. With the introduction of the angular momentum components, P_i, and the momenta conjugate to x and the vibrational degrees of freedom, q_i

$$P_i=\frac{\partial T}{\partial \omega_i},\quad p_x=\frac{\partial T}{\partial \dot{x}},\quad p_i=\frac{\partial T}{\partial \dot{q}_i},$$

the classical Hamiltonian can be derived as before.

This form of the classical Hamiltonian, however, is subject to all the difficulties discussed in connection with the O—H rocking Hamiltonian in the form (11). The very small vibration-hindered rotation interactions do not appear as small perturbation terms, and the first step in the solution of the problem will again consist of a transformation to a new form for the Hamiltonian in which the interactions between the vibrational degrees of freedom and the hindered rotation can be treated as a simple perturbation problem. In the case of the completely nonrigid hindered rotator it would have been possible to choose vibrational coordinates which are in zeroth order free of internal angular momentum with respect to the framework of axes rotating with the equilibrium configuration of the hydroxyl group. Since there would still be zeroth-order interaction terms between the hindered rotation and the three (−) vibrational degrees of freedom and between the hindered rotation and the over-all rotation in space, it is just as convenient to make the transformation to the new form of the Hamiltonian without first forming linear combinations of the chemical coordinates which are free of internal angular momentum.

In the case of the completely nonrigid hindered rotator the transformation to the new form of the Hamiltonian is given by

$$p_x=p_x'-\left(\frac{C_2}{C}\right)_0^* P_z'$$

$$p_{i(+)}=p_{i(+)}'+\frac{B_{1i}^{(0)}}{A_0}P_-' \quad i=1,\cdots,8$$

$$p_{j(-)}=p_{j(-)}'+\lambda_j p_x'-\lambda_j \sin\mathcal{K} P_-'$$
$$+\left\{\lambda_j\cos\mathcal{K}\frac{(B_0\sin U-D_0\cos U)}{[B_0^2+D_0^2]^{\frac{1}{2}}}+\mathcal{K}_j\frac{(B_0\cos U+D_0\sin U)}{[B_0^2+D_0^2]^{\frac{1}{2}}}\right\}P_+'$$
$$+\left\{\lambda_j\cos\mathcal{K}\frac{(B_0\cos U+D_0\sin U)}{[B_0^2+D_0^2]^{\frac{1}{2}}}+\mathcal{K}_j\frac{(D_0\cos U-B_0\sin U)}{[B_0^2+D_0^2]^{\frac{1}{2}}}-\lambda_j\left(\frac{C_2}{C}\right)_0^*\right\}P_z' \quad j=9,10,11 \qquad (29)$$

$$q_i=q_i' \quad i=1,\cdots,11$$

$$x=x'-\lambda_9(\delta\lambda)_--\lambda_{10}(\delta\gamma)_--\lambda_{11}(\delta\beta)_-$$

$$\begin{pmatrix}P_x\\P_y\\P_z\end{pmatrix}=\begin{pmatrix}\cos\Lambda & -\sin\Lambda & 0\\ \sin\Lambda & \cos\Lambda & 0\\ 0 & 0 & 1\end{pmatrix}\begin{pmatrix}\cos\mathcal{K} & 0 & \sin\mathcal{K}\\ 0 & 1 & 0\\ -\sin\mathcal{K} & 0 & \cos\mathcal{K}\end{pmatrix}\begin{pmatrix}1 & 0 & 0\\ 0 & \cos U & -\sin U\\ 0 & \sin U & \cos U\end{pmatrix}\begin{pmatrix}1 & 0 & 0\\ 0 & \frac{B_0}{[B_0^2+D_0^2]^{\frac{1}{2}}} & \frac{D_0}{[B_0^2+D_0^2]^{\frac{1}{2}}}\\ 0 & \frac{-D_0}{[B_0^2+D_0^2]^{\frac{1}{2}}} & \frac{B_0}{[B_0^2+D_0^2]^{\frac{1}{2}}}\end{pmatrix}\begin{pmatrix}P_-'\\P_+'\\P_z'\end{pmatrix},$$

where the following abbreviations have been used

$$P_-'=P_x'\cos\left(\frac{C_2}{C}\right)_0^* x+P_y'\sin\left(\frac{C_2}{C}\right)_0^* x,$$

$$P_+'=-P_x'\sin\left(\frac{C_2}{C}\right)_0^* x+P_y'\cos\left(\frac{C_2}{C}\right)_0^* x,$$

and

$$\left(\frac{C_2}{C}\right)_0^*=\frac{C_2[B_0^2+D_0^2]^{\frac{1}{2}}}{(B_0C_0-D_0^2)},$$

$$\lambda_j=\frac{B_{2j}^{(0)}D_0+B_{3j}^{(0)}B_0}{(B_0C_{10}-D_0^2)},\quad \mathcal{K}_j=\frac{B_{2j}^{(0)}C_{10}+B_{3j}^{(0)}D_0}{(B_0C_{10}-D_0^2)},$$

$$j=9,10,11$$

and where the functions, $\Lambda(\delta q_{j-})$, $\mathcal{K}(\delta q_{j-})$, $U(\delta q_{i+})$ must be chosen in such a way that the Poisson bracket relations $(p_l', P_s')=0$ are fulfilled:

$$\Lambda(\delta q_{j-})=\sum_{j=9}^{11}\lambda_j\delta q_{j-},\quad \mathcal{K}(\delta q_{j-})=\sum_{j=9}^{11}\mathcal{K}_j\delta q_{j-},$$

$$U(\delta q_{i+})=\sum_{i=1}^{8}\frac{B_{1i}{}^{(0)}}{A_0}\delta q_{i+}+\cdots.$$

The quantities denoted by the subscript 0 and th eλ_j and $\mathcal{K}_j$ must be evaluated for the equilibrium configuration of the molecule since they must be constants independent of the vibrational coordinates if the Poisson bracket relations $(p_l', P_s')=0$ are to be fulfilled for the complete transformation.

The transformation (29) removes from the Hamiltonian zeroth-order terms of the form $p_x p_{j-}$ which arise through the coupling of the hindered rotation and the three $(-)$ vibrational degrees of freedom, but in doing so it alters the hindered rotation angle x to

$$x=x'-\lambda_9(\delta s)_- -\lambda_{10}(\delta\gamma)_- -\lambda_{11}(\delta\beta)_-.$$

As a result the coupling between the hindered rotation and the $(-)$ vibrational degrees of freedom reappears in the new Hamiltonian in the form of terms such as $H_0/2\sin 3x'(3\lambda_j\delta q_{j-})$ and $H_0/2\cos 3x'[9/2\lambda_j^2(\delta q_{j-})^2]$. Unlike the terms of the form $p_x p_{j-}$ these are now small perturbation terms, and since they have the form of potential energy terms their effect can be absorbed by the unknown potential constants of the general joint-vibration-hindered rotation potential field.

The new Hamiltonian is again in a form in which the coupling between the hindered rotation and the vibrational degrees of freedom can be treated as a simple perturbation problem. Since the vibrations parallel and perpendicular to the directions of the chemical bonds do not correspond to the exact normal coordinates, there are still cross terms in the zeroth-order vibrational part of the Hamiltonian. These could in principle be treated as additional perturbation terms, but no such refinements will be made since there will at best be some uncertainty in those rotational constants which can be evaluated from known data.

The vibration-over-all rotation-hindered rotation perturbation terms for the completely nonrigid molecule are very numerous. They will not be listed since they are for the most part analogous in form to the perturbation terms, (19), for the simple O—H rocking model. The form of the frequency formula given by the complete vibration-hindered rotation interaction problem is nearly the same as that given by the simple O—H rocking model, with the exception that there is not merely a single Coriolis term of the form (20d) involving only the O—H rocking motion, $\delta\alpha$, but there are now eleven terms of this form in all, one for each normal vibration, and each with its own rather complicated energy denominator. In the last section it was shown that the effect of the eleven constants, $C_{v_i}{}^2$, can be absorbed by the ordinary vibration-rotation constants. The constants, D_{v_i}, for the vibrational degrees of freedom other than the O—H tipping coordinate are very much smaller than the constant, D_{v_α}. The Coriolis interaction between the hindered rotation and the O—H tipping motion during the end-over-end tumbling in space is indeed the only Coriolis interaction of this form which gives significant contributions to the frequency formula. Since the effect of the Coriolis interaction between the hindered rotation and the other vibrational motions is so small, their contributions to the frequency formula can be given by the approximations inherent in the use of (22), and the effect of these Coriolis interaction constants can be absorbed by the centrifugal distortion constant, G_v, if this is replaced by $G_v+2\sum_i D_{v_i}{}^2$, with $i\neq\alpha$. It has been estimated that the effect of these Coriolis interactions is so small that the centrifugal distortion constant is modified only very little, (from a value of -0.81 Mc/sec to a value of -0.73 Mc/sec). The constant G_v is still given to a good approximation by the simple expression (9).

The constants $C_{v_\alpha}D_{v_\alpha}$ and $D_{v_\alpha}{}^2$ must be reevaluated on the basis of the complete theory since there are contributions to these constants arising through the interaction of the O—H rocking motion with the other vibrational degrees of freedom. The constant $C_{v_\alpha}D_{v_\alpha}$ now has the form

$$C_{v_\alpha}D_{v_\alpha}=\frac{1}{2k_\alpha}\left(\frac{\hbar^2}{2}\mu_{14_\alpha}{}^{(1)}\right)\frac{\hbar^2}{4}\left[\zeta_{\alpha\alpha\alpha}+\sum_j\zeta_{\alpha jj}\frac{\mu_\alpha\omega_\alpha}{\mu_j\omega_j}+\left(\mu_{13_\alpha}{}^{(1)}-\left(\frac{C_1}{C}\right)_0^*\mu_{14_\alpha}{}^{(1)}\right)\right], \quad (30)$$

where the new contributions determined by the constants $\zeta_{\alpha jj}$ arise through the interaction of the O—H rocking degree of freedom (α) with the other vibrational degrees of freedom.[14] To a good approximation these constants are given by

$$\zeta_{\alpha jj}=-\sum_{\substack{i\\ i\neq j}}\left(g^{(0)\alpha i}+\sum_{\mu,\nu}\frac{B_{1\mu}{}^{(0)}g^{(0)\mu i}B_{1\nu}{}^{(0)}g^{(0)\nu\alpha}}{A_0{}^*}\right)\frac{1}{2}\left[\frac{\partial^2(B_{1i}/A)}{\partial^2(\delta q_j)^2}\right]_{\delta q_j=0}$$
$$-\sum_{\substack{i\\ i\neq j}}\left[\frac{\partial}{\partial(\delta q_j)}\left(g^{\alpha i}+\sum_{\mu,\nu}\frac{B_{1\mu}g^{\mu i}B_{1\nu}g^{\nu\alpha}}{A^*}\right)\right]_{\delta q_j=0}\left[\frac{\partial(B_{1i}/A)}{\partial(\delta q_j)}\right]_{\delta q_j=0}, \quad (31)$$

in which g^{ij} are the inverse of the kinetic energy matrix elements and A^* is given by $A^*=A-\sum_{\mu,\nu}B_{1\mu}g^{\mu\nu}B_{1\nu}$.

[14] In the O—H rocking model the constant C_v was determined largely by a perturbation term of the form $1/2(P_+'P_z'+P_z'P_+')\mu_{13}(\delta\alpha)$. Now there are additional perturbation terms in the Hamiltonian of the form $P_-'p_\alpha'(\delta q_j)^2\zeta_{\alpha jj}$, for example, which give important contributions to this constant.

As in the case of the simple O—H rocking model the constant $D_{v_\alpha}{}^2$ is given by

$$D_{v_\alpha}{}^2=\frac{1}{2k_\alpha}\left[\frac{\hbar^2}{2}\mu_{14_\alpha}{}^{(1)}\right]^2, \tag{32}$$

in which

$$\begin{aligned}\mu_{14_\alpha}{}^{(1)}=&\frac{[B_0{}^2+D_0{}^2]^{\frac{1}{2}}}{(B_0C_{10}-D_0{}^2)}\frac{B_{11}{}^{(0)}}{A_0}\quad\text{Term 1}\\
&+\frac{(B_0-L_{22}{}^{(0)})(D_\alpha{}^{(1)}+L_{23\alpha}{}^{(1)})}{[B_0{}^2+D_0{}^2]^{\frac{1}{2}}[(B_0-L_{22}{}^{(0)})(C_{10}-L_{33}{}^{(0)})-(D_0+L_{23}{}^{(0)})^2]}\\
&\times\left\{1-\frac{(B_0L_{33}{}^{(0)}+D_0L_{23}{}^{(0)})-(B_0L_{23}{}^{(0)}+D_0L_{22}{}^{(0)})\dfrac{D_0+L_{23}{}^{(0)}}{B_0-L_{22}{}^{(0)}}}{(B_0C_{10}-D_0{}^2)}\right\}-\frac{B_0L_{23\alpha}{}^{(1)}}{[B_0{}^2+D_0{}^2]^{\frac{1}{2}}(B_0C_{10}-D_0{}^2)}\quad\text{Terms 2'}\\
&-\frac{(D_0+L_{23}{}^{(0)})(B_\alpha{}^{(1)}-L_{22\alpha}{}^{(1)})}{[B_0{}^2+D_0{}^2]^{\frac{1}{2}}[(B_0-L_{22}{}^{(0)})(C_{10}-L_{33}{}^{(0)})-(D_0+L_{23}{}^{(0)})^2]}\\
&\times\left\{1-\frac{B_0L_{33}{}^{(0)}+D_0L_{23}{}^{(0)}}{(B_0C_{10}-D_0{}^2)}\right\}-\frac{D_0L_{22\alpha}{}^{(1)}}{[B_0{}^2+D_0{}^2]^{\frac{1}{2}}(B_0C_{10}-D_0{}^2)}\quad\text{Terms 3'}\\
&+\frac{(C_{10}-L_{33}{}^{(0)})(B_\alpha{}^{(1)}-L_{22\alpha}{}^{(1)})(B_0L_{23}{}^{(0)}+D_0L_{22}{}^{(0)})}{[B_0{}^2+D_0{}^2]^{\frac{1}{2}}[(B_0-L_{22}{}^{(0)})(C_{10}-L_{33}{}^{(0)})-(D_0+L_{23}{}^{(0)})^2](B_0C_{10}-D_0{}^2)},\end{aligned} \tag{33}$$

where

$$L_{23}{}^{(0)}=\sum_{\mu,\nu=9}^{11}B_{2\mu}{}^{(0)}g^{(0)\mu\nu}B_{3\nu}{}^{(0)},$$

for example, and $(L_{23}{}^{(1)})_\alpha=(\partial L_{23}/\partial\alpha)_{\alpha 0}$ and in which 1 is the largest term and terms 2' and 3' are akin to similar terms derived on the basis of the simple O—H rocking model. The large number of complicated terms arises through higher order effects associated with the coupling between the hindered rotation and the three (—) vibrational degrees of freedom. For the most part the effect of these terms is quite small, but some of them do give significant contributions.

The constants $D_{v_\alpha}{}^2$ and $C_{v_\alpha}D_{v_\alpha}$ still are simple functions of the single elastic force constant, k_α, and to sufficient approximation the rotational constants for the other isotopic species follow from those of the normal molecule by the simple somewhat approximate isotope rules given by Eqs. (25) and (26) in the last section, with the exception of the constants, $D_{v_\alpha}{}^2$, for the O—D isotopic molecules for which the mass and structural factors of (33) are best evaluated for each isotopic molecule.

COMPARISON BETWEEN THEORY AND EXPERIMENT

From a detailed examination of the completely nonrigid hindered rotator therefore the frequency formula for the $J=0\rightarrow 1$ transition can to a very good approximation be expected to have the simple form derived on the basis of the O—H rocking model for the molecule, and such a formula must be expected to give a good fit between the predicted and the experimentally observed frequencies. Only one small modification has to be made, and the final frequency formula is taken to have the form

$$\begin{aligned}\nu_{0^1_0{}^0_\tau{}^\tau_n{}^n}=\nu_0(J\text{ only})&-\frac{2}{h}\sum_{K'=\substack{+1\\-1}}\frac{\left|\left(\dfrac{\hbar^2}{4}\dfrac{D_0}{[B_0{}^2+D_0{}^2]}+P_v\right)\langle 0\tau n|e^{\mp ix}|K'\tau' n\rangle\right|^2}{(E_{K'\tau' n}-E_{0\tau n})+\dfrac{\hbar^2}{2}\left[\dfrac{B_0+C_0}{(B_0C_0-D_0{}^2)}-\dfrac{1}{2}\left(\dfrac{1}{A_0}+\dfrac{3B_0}{B_0{}^2+D_0{}^2}\right)\right]}\\
&-2\left[F_v\langle 0\tau n|1-\cos 3x|0\tau n\rangle+\frac{G_v}{\hbar^2}\langle 0\tau n|p_x{}^2|0\tau n\rangle\right]\\
&-2\sum_{K'=\substack{+1\\-1}}\sum_{n'}\frac{D_{v_\alpha}{}^2\left|\left\langle 0\tau n\left|e^{\mp ix}\frac{1}{i}\frac{\partial}{\partial x}\mp\tfrac{1}{2}e^{\mp ix}\right|K'\tau' n'\right\rangle\right|^2\pm 2C_{v_\alpha}D_{v_\alpha}\left|\left\langle 0\tau n\left|e^{\mp ix}\frac{1}{i}\frac{\partial}{\partial x}\mp\tfrac{1}{2}e^{\mp ix}\right|K'\tau' n'\right\rangle\langle K'\tau' n'|e^{\pm ix}|0\tau n\rangle\right|}{1+\dfrac{E_{K'\tau' n'}-E_{0\tau n}}{\hbar\omega_\alpha}}.\end{aligned} \tag{34}$$

TABLE III. Matrix elements and matrix sums for CH_3OH.

		$\frac{1}{\hbar^2}\langle 0\tau n\vert p_x^2\vert 0\tau n\rangle$	$\langle 0\tau n\vert 1-\cos 3x\vert 0\tau n\rangle$	$\sum_{K'=-1}^{+1}\sum_{n'}\frac{\vert\langle 0\tau n\vert e^{\mp iz}\left(\frac{1}{i}\frac{\partial}{\partial x}\mp\frac{1}{2}\right)\vert K'\tau' n'\rangle\vert^2\cdot\langle K'\tau' n'\vert e^{\pm iz}\vert 0\tau n\rangle}{1+\frac{E_{K'\tau' n'}-E_{0\tau n}}{\hbar\omega_\alpha}}$	$\sum_{K'=-1}^{+1}\sum_{n'}\frac{\vert\langle 0\tau n\vert e^{\mp iz}\left(\frac{1}{i}\frac{\partial}{\partial x}\mp\frac{1}{2}\right)K'\tau' n'\rangle\vert^2}{1+\frac{E_{K'\tau' n'}-E_{0\tau n}}{\hbar\omega_\alpha}}$
$n=0$	$\tau=1$	1.5162	0.4631	0.8903	2.7785
	$\tau=2, 3$	2.3275	0.3918	0.8364	4.2270
$n=1$	$\tau=2, 3$	4.0193	1.2131	0.2792	8.4883
	$\tau=1$	9.4064	0.8779	0.7293	18.7239
$n=2$	$\tau=1$	7.9288	1.4076	0.3426	16.3624
	$\tau=2, 3$	15.5186	1.1294	0.7787	30.9173

The first term is determined by the rigid rotator energy and the ordinary vibration-rotation interactions. It determines the over-all position of the $J=0\rightarrow 1$ frequencies; but since it is independent of the hindered rotation quantum numbers n and τ, the shift in frequency due to the vibration-rotation interactions incorporated in this term must affect all of the lines of the $J=0\rightarrow 1$ fine structure in exactly the same way. No attempt has been made to evaluate the effects of the ordinary vibration-rotation interactions in methyl alcohol. Since the discussion has thus been limited to the vibration-hindered rotation interactions, the observed high frequency line is chosen as a reference line in each isotopic molecule and only the shifts in frequency from the high frequency line are studied.

A very small vibration-hindered rotation interaction constant, P_v, has been added to the second term, the term which comes about through the asymmetry of the rigid hindered rotator, for the following reason. Since the $K=0\rightarrow\pm 1$ matrix elements can themselves be regarded as perturbation terms, the second-order contributions to these matrix elements due to the vibration perturbations have previously been neglected. From an estimate based on the complete theory, however, it seems reasonable to assume that these may contribute as much as 10% to the $K=0\rightarrow\pm 1$ matrix elements. Unfortunately it is almost impossible to make an accurate estimate of these contributions since they arise through a large number of very small terms and are determined mainly by combinations with purely vibrational perturbation terms. For this reason it has been found necessary to choose the numerical value for P_v empirically to fit the $n=0\rightarrow 0$ splitting in $C^{12}H_3OD$. From considerations based on the O−H rocking model it seems plausible that P_v should obey the somewhat approximate isotope rule: $(P_v)_1/(P_v)_2=(A_0^2)_2/(A_0^2)_1$. It should be emphasized, however, that the constant, P_v, gives significant contributions, (of the order of 2 Mc/sec), *only* to the $n=0\rightarrow 0$ splittings of the O−D isotopic molecules and is otherwise completely negligible, so that the agreement between theory and experiment is not materially affected by this small constant.

The last four terms in the frequency formula give the contributions of the vibration-hindered rotation perturbations. Of the four rotational constants determined by the vibration-hindered rotation perturbations, only the constant F_v must be determined empirically for each isotopic species. It is chosen for each molecule to give the best possible fit between theory and experiment. The three constants, G_v, $D_{v\alpha}^2$, $C_{v\alpha}D_{v\alpha}$, can be computed exactly from the elastic force constants and the known structure of the molecule by the formulas derived in the last section. Due to the uncertainty in the normal vibration constants they are subject to a certain amount of adjustment. However, the rotational constants for the other isotopic species must follow from the adjusted constants for the normal molecule so that there should be a convincing number of checks between theory and experiment.

The values of the matrix elements and the matrix sums for the frequency formula are shown in Table III for the normal molecule, $C^{12}H_3OH$, as an example, to give an idea of the importance of the various terms.

In making the identification of the observed frequencies the observed intensities are of great importance. The intensity of a particular $n\rightarrow n$, $\tau\rightarrow\tau$, transition will depend on the population of the initial state and will thus be proportional to both the statistical weight and the exponential temperature factor of the initial state. For the two components of the $n=0\rightarrow 0$ transitions there is no observable intensity difference due to the exponential temperature factor. In the excited torsional states ($n=1$ and 2), however, the energy difference between the $\tau=1$ and $\tau=2, 3$ states is such that the exponential temperature factor will in all cases lead to an observable intensity difference between the two components of these $n\rightarrow n$ doublets. The transition in the lower energy state ($\tau=2, 3$ for $n=1$, and $\tau=1$ for $n=2$) always gives rise to the stronger line even in the $n=2$ transitions for CD_3OH where the statistical weight factor favors the $\tau=2, 3$ state. In the CH_3

isotopic molecules the statistical weight factors are in the ratio 4 to 4 for the two components of an $n \rightarrow n$ doublet. In the CD_3 isotopic molecules, on the other hand, the $\tau=2,\ 3\rightarrow 2,\ 3$ transition is favored by the statistical weight factor in the ratio 16 to 11. For the $n=0\rightarrow 0$ transitions in CD_3OH the high frequency line, which is the more intense, must therefore correspond to the $\tau=2,\ 3\rightarrow 2,\ 3$ transition. The $n=0\rightarrow 0$ transitions in the CH_3 isotopic molecules are the only ones in which the lines cannot be tagged with their τ quantum numbers from the observed intensities since neither the statistical weights nor the exponential temperature factor give rise to an observable intensity difference. It seems reasonable to assume that the high frequency line in the CH_3OH molecules corresponds to the $\tau=2,\ 3\rightarrow 2,\ 3$ transition as it does in CD_3OH, and this is borne out by the computations. In the O—D isotopic species the asymmetry of the molecule shifts the $\tau=2,\ 3\rightarrow 2,\ 3$ transition to lower frequencies, and the $\tau=1\rightarrow 1$ transition turns out to correspond to the high frequency line.

In making the fit between theory and experiment, the constants G_v, $D_{v\alpha}{}^2$, and $C_{v\alpha}D_{v\alpha}$ are computed first for the normal molecule. On the basis of the detailed theory, with the approximation that the small Coriolis effects of the vibrational degrees of freedom other than the O—H rocking motion can be absorbed by the centrifugal distortion constant G_v, the following estimates have been made for the values of these constants

$$G_v=-0.73 \text{ Mc/sec}, \quad D_{v\alpha}{}^2=1.60 \text{ Mc/sec},$$
$$2C_{v\alpha}D_{v\alpha}=0.62 \text{ Mc/sec}.$$

The largest contributions to the frequency shifts are given by the constants $D_{v\alpha}{}^2$ and F_v. $D_{v\alpha}{}^2$ involves only k_α, the elastic force constant associated with the O—H rocking motion. Unfortunately the spectrum of methyl alcohol does not furnish an unambiguous value for this constant since the O—H rocking vibration band has not been uniquely identified in normal methanol. In the deuterated molecule, CH_3OD, the band observed at 869 cm^{-1} would seem to be that of the COH deformation motion. However, on the basis of the simple O—H rocking model, this implies a band at 1165 cm^{-1} for CH_3OH, where however no band is observed, possibly because it is too weak. Using the 869 cm^{-1} frequency one obtains $k_\alpha/l^2=0.73\times 10^5$ dynes/cm, a value consistent with the elastic constant for the HOH bending frequency in water of 0.69×10^5 dynes/cm.[15] With this k_α, $D_{v\alpha}{}^2$ has been computed to be 1.60 Mc/sec.

In order to fit the observed frequencies, however, it became clear that $D_{v\alpha}{}^2$ must be adjusted upward to 2.20 Mc/sec. Working backwards this implies a value of k_α/l^2 of 0.51×10^5 dynes/cm and frequencies at 970 cm^{-1} and 720 cm^{-1} for normal methanol and the CH_3OD molecule, respectively. The situation is indeed somewhat unclear due to the fact that the O—H rocking frequency has not been definitely established as well as to the fact that a number of small effects which have not been calculated explicitly may serve to add to the contribution due to k_α by the amount required or may affect the magnitude of the Coriolis contributions due to the other normal modes. Undoubtedly some of the difficulty arises from the fact that none of the modes in methyl alcohol corresponds to a pure deformation of the COH bond angle since there must be a good deal of interaction between the frequencies. Even though the interactions between the various chemical coordinates may be very significant in the determination of the actual normal modes and frequencies, however, the rotational constants $D_{v\alpha}{}^2$, $C_{v\alpha}D_{v\alpha}$, and G_v should be given largely by the magnitude of the elastic force constants and should be less sensitive to the actual form of the normal vibration motions. As a result the rotational constants for the isotopic molecules should follow from those for the normal molecule to a sufficiently good approximation.

TABLE IV. Final values for the rotational constants in mc/sec.

Molecule	G_v	$D_{v\alpha}{}^2$	$2C_{v\alpha}D_{v\alpha}$	F_v
$C^{12}H_3OH$	−0.73	(2.20)	0.62	(68.85)
$C^{13}H_3OH$	−0.72	2.09	0.59	(67.34)
$C^{12}D_3OH$	−0.52	1.43	0.41	(54.60)
$C^{12}H_3OD$	−0.64	1.63	0.53	(64.05)
$C^{13}H_3OD$	−0.63	1.55	0.50	(62.80)
$C^{12}H_3OD$	−0.48	1.22	0.35	(44.20)

$$\left(P_v=0.135-\frac{\hbar^2}{4}\frac{D_0}{B_0{}^2+D_0{}^2}\right) \text{ for } C^{12}H_3OD$$

Only the energy denominator occurring in the Coriolis interaction term is a function of the observed COH deformation frequency rather than mainly a function of the elastic force constants. In the computations presented here a value of 1165 cm^{-1} has been used for the normal molecule. In the lower torsional states the results are not too sensitive to a small error in this frequency. In the $n=3$ states, on the other hand, there would be a possibility of a near-resonance between the hindered rotation and COH deformation frequencies, and an observation of the $n=3\rightarrow 3$ transitions might give some new information about the "COH deformation frequency" in CH_3OH.

The constants G_v, $D_{v\alpha}{}^2$, and $C_{v\alpha}D_{v\alpha}$ for the other isotopic species are taken to follow from the adjusted constants for the normal molecule and have been computed by means of the isotope rules discussed in the last two sections. They are listed in Table IV together with the empirically determined values for the constant F_v. In Table IV the empirical constants and the constants which have undergone a significant adjustment in the normal molecule have been enclosed in brackets.

The agreement between the experimentally observed frequencies and the values calculated with these rota-

[15] As listed by Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 170.

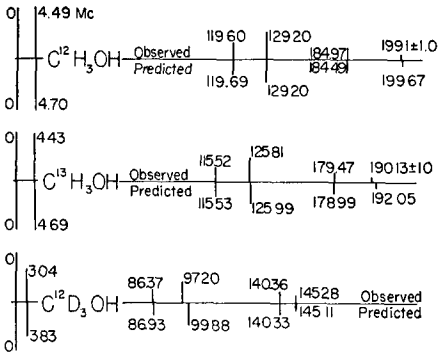

FIG. 3. Comparison between the predicted and observed frequencies I. The O—H molecules. The numbers give the shifts in Mc/sec from the high frequency line.

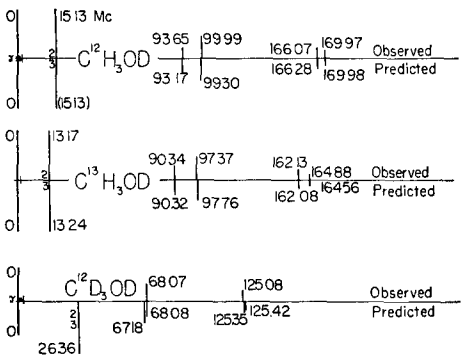

FIG. 4. Comparison between the predicted and observed frequencies II. The O—D molecules. The numbers give the shifts in Mc/sec from the high frequency line.

tional constants is illustrated in Fig. 3 for the O—H isotopic molecules, and in Fig. 4 for the O—D isotopic molecules. Differences of the order of 0.5 Mc/sec between the predicted and the observed frequencies must certainly be expected, since a large number of very small effects have been neglected for simplicity. On the whole therefore the agreement between theory and experiment is quite good. One very serious discrepancy between theory and experiment occurs in the completely deuterated molecule. Apparently only a single $n=0\rightarrow0$ line is observed, while theory predicts a very large splitting into two lines, separated by 26 Mc/sec. In the $n=1\rightarrow1$ and $n=2\rightarrow2$ transitions in CD_3OD the agreement is quite good. In each case theory predicts a closely spaced doublet in good agreement with the single observed frequency. The large predicted $n=0$ splitting is due partly to a very small energy denominator in the rigid hindered rotator asymmetry term and is therefore very sensitive to small errors in the energies of the $K=0$ and $K=1$ hindered rotator states. However such errors could not result in a shift of the $\tau=2,3\rightarrow2,3$ line to higher frequency by 26 Mc/sec. A large shift to even lower frequency seems much more likely.[16]

Two competing effects come into play in the deuterated isotopes. The moments of inertia, C_1 and C_2, about the symmetry axis of the hindering potential are increased on deuterium substitution. This brings about an increase in the effective barrier height since the value of $H'=H/(\hbar^2/2)(C/C_1C_2)^*$ defined in the preceding paper is increased. A twofold increase in H' can bring about a significant decrease in the line splittings. This seems to be the dominant effect in the $n=1\rightarrow1$ and the $n=2\rightarrow2$ transitions in the O—D isotopic molecules even though these energy levels lie near the top or above the top of the hindering barrier. On the other hand, the O—D molecules have a comparatively large product of inertia, D, giving rise to a large asymmetry splitting, especially in the ground state where there is only a small energy difference between the $K=0$ and $K=1$ states, and is the reason for the large $n=0\rightarrow0$ splitting in the O—D molecules.

The six empirically determined rotational constants F_v are functions of the eight unknown potential constants, $a_i^{(1)}$, for the (+) vibrational degrees of freedom, so that no careful evaluation of these potential constants is possible. Since the contributions of certain of the $a_i^{(1)}$ to the values of F_v can be expected to be very small, it is possible to make a very rough order of magnitude estimate of some of the potential constants, $a_i^{(1)}$. From the six empirically determined values for F_v it seems reasonable to assign the following rough order of magnitude values

$$\begin{aligned} &a_h^{(1)}=-3 \text{ to } -8, \quad a_{\gamma_0}^{(1)}=0 \text{ to } 2.0, \\ &a_{s_0}^{(1)}=0 \text{ to } -1.0, \quad a_\alpha^{(1)}=0 \text{ to } -0.4, \end{aligned} \tag{35}$$

in which h, α, γ_0, and s_0 refer to the CO stretching, COH deformation, and the completely symmetric CH bending and stretching coordinates, respectively. The constants for the bending frequencies are dimensionless quantities, while the constants for the stretching frequencies are given in units of $(10^{-8}$ cm$)^{-1}$. No rigorous theory exists whereby these potential constants could be calculated from the electronic structure of the methyl alcohol molecule. However, it is possible to make a rough order of magnitude estimate from approximate classical arguments. The constants $a_i^{(1)}$ can be computed if the electronic distributions of the O—H and C—H bonds in methyl alcohol can be represented by classical charge distributions fixed to the moving O—H and C—H bonds. The estimates turn out to be of the right order of magnitude for the larger potential constants and may perhaps give some confidence that the empirically determined rotational constants F_v are at least of a sensible order of magnitude. The constant $a_h^{(1)}$, for example, has been computed to have the value -2.7 if the classical charge distributions are assumed to be simple point charges at the extremities of the O—H and C—H bonds, while a value of -4.3 is obtained if they are dipoles located at the midpoints of the bonds.

[16] A large $n=0\rightarrow0$ splitting for this isotopic molecule has also been predicted on the basis of the rigid model hindered rotator by J. D. Swalen by a different method [J. Chem. Phys. **23**, 1739 (1955)].

Considering the irregularities in the line splittings for the various isotopic molecules, it is perhaps quite satisfying that the theory with the aid of essentially only one empirical constant per isotopic molecule, and this of sensible order of magnitude, reproduces the irregularities as well as it does. If we count as empirical constants the constants which for the normal molecule have undergone a significant adjustment, then it can be claimed that some 30 frequency shifts have been predicted with the use of only eight empirical constants, with only one possible serious discrepancy between theory and experiment.

APPENDIX I. INTERNAL ROTATION WAVE FUNCTIONS AND ENERGIES

In order to evaluate the matrix elements needed for the $J=0\rightarrow1$ frequency formula the internal rotation wave functions and energies must be known for the $K=0, \pm1$; $n=0$, 1, 2, 3, and 4 states of $C^{12}H_3OH$ and its five isotopic species. The same wave functions can be used for both $C^{12}H_3OH$ and $C^{13}H_3OH$, however; also for both $C^{12}H_3OD$ and $C^{13}H_3OD$, since the molecular parameters in the hindered rotator part of the Hamiltonian are very nearly the same for the C^{12} and C^{13} isotopic molecules.

The wave functions and energies for the $n=0$, 1, and 2 and some of the $n=3$ states have been calculated by the continued fractions technique discussed in reference 2. The remaining $n=3$ and $n=4$ wave functions and energies have been calculated by a perturbation method. These states correspond to nearly free rotation states, and for them the barrier height, H, can be treated as a perturbation. The wave functions and energies can be given as power series in the parameter $H'=H/(\hbar^2/2)(C/C_1C_2)_0$*

$$P_m(x)=e^{imx}+H'c_1(x)+H'^2c_2(x)+H'^3c_3(x)+\cdots, \quad (36)$$

where this wave function is not yet normalized, and where m is the free rotation quantum number which can be correlated with K, τ, and n.[2]

$$E_{m,\sigma}'=\frac{H'}{2}+(m+\sigma)^2+\alpha_1H'+\alpha_2H'^2+\alpha_3H'^3+\alpha_4'H'^4+\cdots, \quad (37)$$

where

$$E_{m,\sigma}'=E_{m,\sigma}^{\text{int}}\Big/\frac{\hbar^2}{2}\left(\frac{C}{C_1C_2}\right)_0^*,$$

and

$$\sigma=-K\left[1-\left(\frac{C_2}{C}\right)_0^*\right].$$

The functions $c_i(x)$ and the constants α_i can be computed by ordinary perturbation theory or by the methods discussed for the ordinary Mathieu differential equation by McLachlan.[17]

$$\alpha_1=0, \qquad \alpha_3=0,$$

$$\alpha_2=-\frac{1}{8}\frac{1}{[4(m+\sigma)^2-9]}, \qquad \alpha_4=\frac{20(m+\sigma)^2+63}{128[4(m+\sigma)^2-9]^3[4(m+\sigma)^2-36]},$$

$$c_1(x)=\frac{e^{i(m+3)x}}{3\cdot2^2[2(m+\sigma)+3]}-\frac{e^{+i(m-3)x}}{3\cdot2^2[2(m+\sigma)-3]},$$

$$c_2(x)=\frac{e^{i(m+6)x}}{3^2\cdot2^5[2(m+\sigma)+3][2(m+\sigma)+6]}+\frac{e^{i(m-6)x}}{3^2\cdot2^5[2(m+\sigma)-3][2(m+\sigma)-6]}, \quad (38)$$

$$c_3(x)=\frac{[4(m+\sigma)^2+24(m+\sigma)+63]e^{i(m+3)x}}{3^3\cdot2^7[2(m+\sigma)+3]^2[2(m+\sigma)+6][4(m+\sigma)^2-9]}-\frac{[4(m+\sigma)^2-24(m+\sigma)+63]e^{i(m-3)x}}{3^3\cdot2^7[2(m+\sigma)-3]^2[2(m+\sigma)-6][4(m+\sigma)^2-9]}$$

$$+\frac{e^{i(m+9)x}}{3^4\cdot2^7[2(m+\sigma)+3][2(m+\sigma)+6][2(m+\sigma)+9]}-\frac{e^{i(m-9)x}}{3^4\cdot2^7[2(m+\sigma)-3][2(m+\sigma)-6][2(m+\sigma)-9]}.$$

II. APPENDIX II. STUDY OF THE METHYL DEGREES OF FREEDOM

The effects of vibrational degrees of freedom such as $(\delta\gamma)_+$ and $(\delta\gamma)_-$, involving the coordinates of the methyl group, must be discussed separately since these degrees of freedom are implicit functions of the internal rotation angle, x, and may thus give rise to an additional coupling between the hindered rotation and the vibrational degrees of freedom. It is the purpose of this appendix to show that vibrational degrees of freedom such as $(\delta\gamma)_+$ and $(\delta\gamma)_-$ give contributions to the vibration-hindered rotation corrections to the energy of exactly the same form as the O—H rocking vibrational coordinate, $\delta\alpha$. For this purpose it is convenient to introduce polar vibrational coordinates, r_γ and χ_γ, for

[17] N. W. McLachlan, *Theory and Application of Mathieu Functions* (The Clarendon Press, Oxford, England, 1946), p. 19.

example:

$$r_\gamma=[\tfrac{1}{2}(\delta\gamma_2-\delta\gamma_3)^2+\tfrac{2}{3}(\delta\gamma_1-\tfrac{1}{2}\{\delta\gamma_2+\delta\gamma_3\})^2]^{\frac{1}{2}},$$
$$\chi_\gamma=\tan^{-1}\left\{\frac{1/\sqrt{2}(\delta\gamma_2-\delta\gamma_3)}{\sqrt{2}/\sqrt{3}[\delta\gamma_1-\frac{1}{2}(\delta\gamma_2+\delta\gamma_3)]}\right\}, \tag{39}$$

so that the vibrational coordinates can be written

$$(\delta\gamma)_+=r_\gamma\cos(\chi_\gamma+x)=r_\gamma\cos\chi_\gamma',$$
$$(\delta\gamma)_-=r_\gamma\sin(\chi_\gamma+x)=r_\gamma\sin\chi_\gamma'.$$

With the introduction of the angle, $\chi_\gamma'=\chi_\gamma+x$, the explicit dependence on the internal rotation angle has been transformed out of the vibrational coordinates and the coupling between the hindered rotation and these vibrational degrees of freedom appears instead in the boundary conditions which must be modified for the methyl degrees of freedom. The coordinates $(\delta\gamma)_+$ and $(\delta\gamma)_-$ do not correspond to doubly degenerate frequencies; but the distinct frequencies, $\nu_{\gamma+}$ and $\nu_{\gamma-}$, can be expected to have nearly the same value, and it proves convenient to use zeroth-order wave functions which have the form of a doubly degenerate pair. This would correspond to the physical situation if it could be assumed that the coupling between the methyl degrees of freedom and the other degrees of freedom of the molecule can be neglected, at least in zeroth order.

The complete wave function which is a solution of the zeroth-order symmetric hindered rotator-pure vibrational problem is therefore chosen to have the form

$$\psi_{JKM,n\tau,v_il_i}=\frac{1}{2\pi}\Theta(\theta')\cdot e^{iM\psi'}e^{iK\varphi'}e^{i\sigma x'}$$
$$\times P_{\sigma\tau n}(x')\prod_i\psi_{v_i}(q_i)\prod_j[e^{il_j\chi_j'}\psi_{v_j,l_j}(r_j)], \tag{40}$$

in which the rotational part of the wave function has the usual form, and in which the one-dimensional harmonic oscillator wave functions, $\psi_{v_i}(q_i)$, are used as zeroth-order wave functions for degrees of freedom such as $\delta\alpha$, and two-dimensional harmonic oscillator wave functions in polar coordinates, $e^{il_j\chi_j'}\psi_{v_jl_j}(r_j)$, are used for the methyl degrees of freedom. This complete wave function must be invariant under the transformation

$$\varphi_1\to\varphi_1+2n_1\pi,\quad \varphi_2\to\varphi_2+2n_2\pi,$$
$$\chi_\gamma\to\chi_\gamma+2n_3\pi,\quad \chi_s\to\chi_s+2n_4\pi,\quad \chi_\beta\to\chi_\beta+2n_5\pi, \tag{41}$$

since this transformation leaves the physical situation unchanged. ϕ_1 and ϕ_2 are the azimuth angles which describe the rotation of the hydroxyl and methyl groups, respectively, about the symmetry axis of the hindering potential; and $n_1,\cdots,n_5$ can be any integers. As usual, the value of σ is determined from this boundary condition since it leads to the condition

$$Kn_1-K\left(\frac{C_2}{C}\right)_0^*(n_1-n_2)+\sigma(n_1-n_2)+l_\gamma n_3$$
$$+l_sn_4+l_\beta n_5+(l_\gamma+l_s+l_\beta)(n_1-n_2)=n, \tag{42}$$

where n is any arbitrary integer. This condition can be fulfilled only if K, l_γ, l_s, and l_β are all integers, and if σ has the value

$$\sigma=-K\left[1-\left(\frac{C_2}{C}\right)_0^*\right]-(l_\gamma+l_s+l_\beta). \tag{43}$$

σ is therefore a function both of the quantum number K and of the quantum numbers, l_γ, l_s, and l_β. Through the value of σ the internal rotation wave function is therefore also a function both of K and the l_i and must be labeled, $P_{Kl_\gamma l_sl_\beta\tau n}(x)$.

Despite this dependence of the internal rotation wave function on the vibrational quantum numbers of the methyl group, it can be shown that the methyl degrees of freedom do not give rise to any new *types* of vibration-hindered rotation corrections to the energy. For this purpose a specific perturbation term is studied, as an example. The perturbation term, $\mu_{11\alpha}^{(1)}(P_x'^2+P_y'^2)(\delta\alpha)$, gives rise to the matrix element

$$\langle JK\tau nv_\alpha|\mu_{11\alpha}^{(1)}(P_x'^2+P_y'^2)\delta\alpha|JK\tau n(v_\alpha+1)\rangle$$
$$=\mu_{11\alpha}^{(1)}\left[\frac{\hbar}{\mu_\alpha\omega_\alpha}\right]^{\frac{1}{2}}\left[\frac{v_\alpha+1}{2}\right]^{\frac{1}{2}}\hbar^2(J^2+J-K^2). \tag{44}$$

The same type of perturbation term involving the methyl degree of freedom, $(\delta\gamma)_+$, on the other hand, gives rise to the corresponding matrix elements

$$\langle JK\tau nv_\gamma l_\gamma|\mu_{77\gamma}^{(1)}(P_x'^2+P_y'^2)(\delta\gamma)_+|JK\tau'n(v_\gamma+1)(l_\gamma+1)\rangle$$
$$=-\mu_{77\gamma}^{(1)}\left[\frac{\hbar}{\mu_\gamma\omega_\gamma}\right]^{\frac{1}{2}}\left[\frac{v_\gamma+l_\gamma+2}{2}\right]^{\frac{1}{2}}\frac{\hbar^2}{2}(J^2+J-K^2)\int_0^{2\pi}P_{Kl_\gamma\tau n}^*(x)e^{-ix}P_{K(l_\gamma+1)\tau'n}(x)dx, \tag{45}$$

and

$$\langle JK\tau nv_\gamma l_\gamma|\mu_{77\gamma}^{(1)}(P_x'^2+P_y'^2)(\delta\gamma)_+|JK\tau''n(v_\gamma+1)(l_\gamma-1)\rangle$$
$$=+\mu_{77\gamma}^{(1)}\left[\frac{\hbar}{\mu_\gamma\omega_\gamma}\right]^{\frac{1}{2}}\left[\frac{v_\gamma-l_\gamma+2}{2}\right]^{\frac{1}{2}}\frac{\hbar^2}{2}(J^2+J-K^2)\int_0^{2\pi}P_{Kl_\gamma\tau n}^*(x)e^{+ix}P_{K(l_\gamma-1)\tau''n}(x)dx. \tag{46}$$

From the symmetry properties of the wave functions, however, it can be shown that the integrals over the internal rotation angle, x, in these matrix elements are equal to unity; and when these first-order matrix elements, off-diagonal in v_γ and l_γ are transformed to second-order elements diagonal in v_γ and l_γ, they result in exactly the same type of vibration-rotation corrections to the energy as the matrix elements, (44), involving the O—H rocking degree of freedom. For this purpose the internal rotation wave functions must be studied in more detail. In particular, it must be seen how the hindered rotation quantum number, τ, for a particular state is determined by the quantum numbers K and l_i.

The wave functions, $P_{Kl_\gamma l_s l_\beta \tau n}(x)$, can be given as linear combinations of free internal rotation wave functions

$$P_{Kl_\gamma l_s l_\beta \tau n}(x)=e^{i\rho x}\sum_{m=-\infty}^{\infty} a_m e^{3imx}, \qquad (47)$$

where the coefficients a_m are functions of n and σ, and therefore of K and the l_i; and where $\rho=0$ for $\tau=1$, $\rho=-1$ for $\tau=2$, and $\rho=+1$ for $\tau=3$. From the form of the wave functions it follows that the only nonvanishing matrix elements of the complete Hamiltonian are those for which τ' and τ'' obey the following rules. For the $K\rightarrow K+1$, $l_i\rightarrow l_i$ matrix elements the only possible τ connections are those given in reference 3: $\tau=1\rightarrow 3$, $3\rightarrow 2$, and $2\rightarrow 1$. For the $K\rightarrow K$, $l_i\rightarrow(l_i+1)$, matrix elements such as (45) the only possible τ connections are again $\tau=1\rightarrow 3$, $3\rightarrow 2$, and $2\rightarrow 1$, while the only possible τ connections for the $K\rightarrow K+1$, $l_i\rightarrow(l_i+1)$, matrix elements are now $\tau=1\rightarrow 2$, $2\rightarrow 3$, and $3\rightarrow 1$; and, last, the only possible τ connections for the $K\rightarrow K+1$, $l_i\rightarrow(l_i-1)$, matrix elements are $\tau=1\rightarrow 1$, $2\rightarrow 2$, and $3\rightarrow 3$. As a result the complete energy determinant for the vibration-hindered rotation problem factors into three subdeterminants as it did for the rigid hindered rotator[3]; but now each subdeterminant is characterized by the specific τ values which are associated with both the K and l_i values which characterize the diagonal elements of the Hamiltonian as shown in Table V. From the symmetry properties of the hindered rotation states[2,3] it can be seen that the roots of determinants No. 1 and No. 2 are identical and that the wave functions, $e^{-ix}P_{K(l_i+1)\tau' n}(x,\sigma-1)$, characterized by (l_i+1) and τ' are identically equal to the wave functions, $P_{Kl_i\tau n}(x,\sigma)$ characterized by l_i and τ where

$$\text{for } \tau'=\begin{matrix}3\\2\end{matrix}\rightarrow\tau=\begin{matrix}1\\3\end{matrix}\text{, respectively.}$$

Similarly the wave functions $e^{+ix}P_{K(l_i-1)\tau'' n}(x,\sigma+1)$ are identically equal to the wave functions, $P_{Kl_i\tau n}(x,\sigma)$, where now

$$\text{for } \tau''=\begin{matrix}2\\1\end{matrix}\rightarrow\tau=\begin{matrix}1\\3\end{matrix}\text{, respectively.}$$

It can therefore be seen that the integrals occurring in Eqs. (45) and (46) are merely normalization integrals and are equal to unity.

TABLE V.

	$l_s=l_\beta=0$, $l_\gamma=-1$			$l_s=l_\beta=0$, $l_\gamma=0$			$l_s=l_\beta=0$, $l_\gamma=+1$		
	$K=-1$	0	$+1$	$K=-1$	0	$+1$	$K=-1$	0	$+1$
Determinant No. 3	3	2	1	2	1	3	1	3	2
Determinant No. 2	1	3	2	3	2	1	2	1	3
Determinant No. 1	2	1	3	1	3	2	3	2	1