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GRADUATE COLLEGE

A THEORY OF INTERNAL ROTATION FOR COMPLETELY ASYMMETRIC MOLECULES WITH APPLICATIONS TO CH_2DCOH, CD_2HCOH AND C_6H_5COH

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CHARLES RICHARD QUADE

Norman, Oklahoma

1962

A THEORY OF INTERNAL ROTATION FOR COMPLETELY ASYMMETRIC MOLECULES

WITH APPLICATIONS TO CH_2DCOH, CD_2HCOH AND C_6H_5COH

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TABLE OF CONTENTS

		Page
LIST OF TABLES		vi
LIST OF ILLUSTRATIONS		vii
INTRODUCTION		1
Chapter		
I.	THE CLASSICAL HAMILTONIAN	5
	The Kinetic Energy	8
	The Angular Momentum	10
	Transformation of the Classical Kinetic Energy	13
	The Potential Energy	16
II.	THE QUANTUM MECHANICAL HAMILTONIAN	17
III.	APPLICATION OF THE THEORY TO CH_2DCOH AND CD_2HCOH	21
	Molecular Structure	21
	Rotational Constants	21
	The Torsional Equation	23
	The Rotational Hamiltonian	27
	The Rotational Torsional Interaction	28
	The Perturbation Calculation	33
	The Microwave Rotational Spectrum and Analysis	34
	Conclusions	42
IV.	APPLICATION OF THE GENERAL THEORY TO BENZALDEHYDE	43
	Molecular Structure	44
	Rotational Constants	44
	The Torsional Equation	46
	The Rotational Hamiltonian	48
	The Rotational Torsional Interaction	48
	The Perturbation Calculation	49
	The Microwave Rotational Spectrum of C_6H_5COH and Analysis	51
	The Case for High Barrier	59
	Conclusions	62

Chapter Page

V. A NOTE ON THE PARAMAGNETIC SUSCEPTIBILITY OF V^{+++} IN *CORUNDUM* 63

The Hamiltonian 63
Susceptibility in the Temperature Range 77° to 295°K..... 69
The Low Temperature Susceptibility 74

APPENDIX

I..... 75
II..... 81
III..... 85
IV..... 87

BIBLIOGRAPHY 90

LIST OF TABLES

TABLE		PAGE
I.	The Rotational Spectrum of CH_2DCOH	35
II.	The Rotational Spectrum of CHD_2COH	36
III.	The Rotational Spectrum of C_6H_5COH	53
IV.	The Matrix Elements of $\lambda \underline{L} \cdot \underline{S} + (\underline{L} + 2\underline{S}) \cdot \underline{H}$	65
V.	The Magnetic Susceptibility of V^{+++} in Corundum 77° to 295°K	71

LIST OF ILLUSTRATIONS

FIGURE		PAGE
1.	The General Molecule	7
2.	The Van Vleck Transformation	30
3.	The Torsional Functions for CH_2DCOH or CD_2HCOA	34
4.	A Graph of the Spectral Splitting of C_6H_5COH	57
5.	Energy Level Diagram for V^{+++} in Corundum	68
6.	A Graph of the Magnetic Susceptibility of V^{+++} in Corundum	72
7.	The Frame Structure of CH_2DCOH and CD_2HCOH	76
8.	The Top Structure of CH_2DCOH and CD_2HCOH	77
9.	The Structure of C_6H_5COH	82

INTRODUCTION

For several years the study of hindered internal rotation in molecules has been of interest. Many approaches have been utilized in studying the problem, one of which is microwave spectroscopy where the overall rotational spectrum is observed and the effective rotational constants of the molecule are quite sensitive to the internal motion.

The classic example of a molecule exhibiting internal rotation is ethane, CH_3-CH_3. In this case one methyl group is able to rotate relative to the other about the carbon-carbon bond. It is found that there is a force hindering the internal motion which has the three-fold symmetry of the molecule. Other examples of molecules exhibiting this property are acetaldehyde, CH_3COH, methyl alcohol, CH_3OH, and ethyl chloride, CH_3CH_2Cl.

One observes that a characteristic of these molecules is that the top, or internal rotor, has the rotational properties of a symmetric top, i.e. any set of orthogonal axes perpendicular to the symmetry axis of the top are principal axes with, of course, the same values for the moments of inertia. Therefore as the top rotates relative to the second part of the molecule, commonly designated the frame, the principal axes of the entire molecule do not change orientation, hence the moments of inertia of the molecule do not depend explicitly upon the angle of internal motion. The molecular dynamics of this class of molecules has received intensive

study. A semi-empirical expression for the potential hindering the internal motion has been found, with values for the potential barrier hindering the internal motion in different molecules being extensively tabulated. A review of the general theory has recently been made by Lin and Swalen (15). This review discusses various theoretical approches to the problem, works out some illustrative examples, and lists the values of the barrier heights known at the time of publication.

Although the empirical barrier heights for some forty molecules are known, the exact origin of the potential hindering the motion is subject to conjecture. In principle it should be possible to determine the potential from a straight-forward quantum mechanical calculation, but at this time the mathematical difficulties make such a treatment highly impractical. An alternative approach is to use physical insight and careful analysis of the data available to see if the behavior of the potential follows the pattern of any intermolecular interaction such as Van der Waals or resonance forces. Positive results of such an analysis would certainly be helpful to one making the quantum mechanical calculation in suggesting the proper physical or mathematical approximation in attacking the problem.

But even with the number of barrier heights which have been determined empirically, the second approach has not been successful. One difficulty might be that the known cases are all of a single type - where the top and hindering potential have a three-fold symmetry axis. Possibly the study of a more general class of molecules and the subsequent determination of their barrier heights would be useful in pinpointing the origin of the barrier. With this in mind an extended theory of the molecular dynamics in internal rotation has been developed.

The theory developed in this thesis is applicable to molecules where neither the internal rotor nor the frame have the rotational properties of a symmetric top. The complicating feature is that the moments of inertia now depend explicitly on the angle of internal rotation. A few examples of molecules of this type are deuterated acetaldehyde, CH_2DCOH and CD_2HCOH, benzaldehyde, C_6H_5COH, and nitronenzene, $C_6H_5NO_2$. This is not the first attempt to formulate the internal rotation problem for the more general molecules. Price (16) developed a theory for specific application to determine the barrier height from the vapor heat capacity of the molecule. Also Burkhard and Irwin (1,2) developed a complicated theory as applied to the microwave rotational spectrum, but so far it has been too formidable a task to apply to the barrier determination of a specific molecule.

The work in this thesis has been two-fold. First to see if a theory could be formulated with a minimum of complicating features in the application; and second to apply the theory specifically in the analysis of the microwave rotational spectrum of CD_2HCOH and CH_2DCOH (4), and of C_6H_5COH whose spectrum has recently been observed and interpreted by Kojima (12, 12a).

An outline of the material presented in the thesis is as follows: Chapter I contains the classical formulation of the problem. Expressions are obtained for the kinetic energy and angular momentum of the system. A brief discussion is devoted to the choice of a potential function hindering the internal motion. The relation between conjugate coordinates and momenta is established. Finally a transformation is applied to the classical Hamiltonian which puts it in a particularly desirable form for the quantum mechanical problem. In Chapter II the

quantum mechanical Hamiltonian is obtained. Also the method of expansion of the rotational constants in terms of the internal coordinate is developed; this is a key part of the formulation. Then in Chapter III the theory is applied to the specific problem of analyzing the rotational spectrum of CD_2HCOH and CH_2DCOH. Finally Chapter IV contains the application to C_6H_5COH and the attempt to determine this molecule's barrier height from its rotational spectrum.

A THEORY OF INTERNAL ROTATION FOR COMPLETELY ASYMMETRIC MOLECULES WITH APPLICATIONS TO CH_2DCOH, CD_2HCOH AND C_6H_5COH

CHAPTER I

THE CLASSICAL HAMILTONIAN

For problems concerned with molecular dynamics the customary procedure is to formulate the classical model of the molecule and then the transition to the quantum mechanical form follows in a straightforward manner. The method of approach for internal rotation will be recognized as quite similar to that of Wilson and Howard (20) in their consideration of vibration-rotation interaction, the primary differences being: 1) the internal degree of freedom in this problem is that of internal rotation, and 2) the internal axes of the molecule are specified by different criteria. A familiarity with the vibration-rotation problem, as well as the internal rotation of molecules such as CH_3OH, is helpful in following parts of the theory.

There are a few assumptions and approximations which are used in the development of the expressions for both the kinetic energy and angular momentum of the molecule. Some consist of no more than specification of the molecular axes, the choice of which does simplify the calculation, but others are a purely physical nature and limit the applicability of the theory and the "accuracy" of certain results. The approximations and assumptions are as follows:

1. The molecule is composed of two rigid parts which may rotate about a bond connecting them, for example the C-O bond in methyl alcohol. Other modes of internal vibration are neglected and could become important if the torsional and vibration modes have nearly the same frequency. Physically the interaction corresponds to a coupling between the two types of internal motion. The vibration-torsional interaction has been studied extensively by Kilvelson (7,8,9,10,11) and by Swan and Strandberg (17).

2. The molecular axes have their origin at the center of mass of the molecule, CM. Therefore the overall rotation and translation separate, as is not the situation in the formulation by Price (16). After separating out the translational terms the molecule has four degrees of freedom: three of overall rotation and one of internal motion (rotation about the bond connecting the top and the frame).

3. The frame has a plane of symmetry. An extension to the more general case is straightforward.

4. Neither the center of mass of the frame, CF, nor the center of mass of the top, CT, lie necessarily along the internal rotation axis.

5. The axes of the molecule always remain parallel to the axes fixed in the frame when the top rotates.

6. The z-axis of the molecule is parallel to the bond axis and is directed toward the top; the y-axis is parallel to the plane of symmetry of the frame; and the x-axis is perpendicular to the plane of symmetry of the frame. The coordinate system follows the right hand rule.

7. The internal coordinate, α, is measured from the equilibrium configuration which is assumed to be $\underline{\sigma} = \sigma_y \underline{j}$. (See Figure 1).

Figure 1 shows how various displacement vectors used in the derivation are related to the distances of the mass points from CM. They are defined as follows:

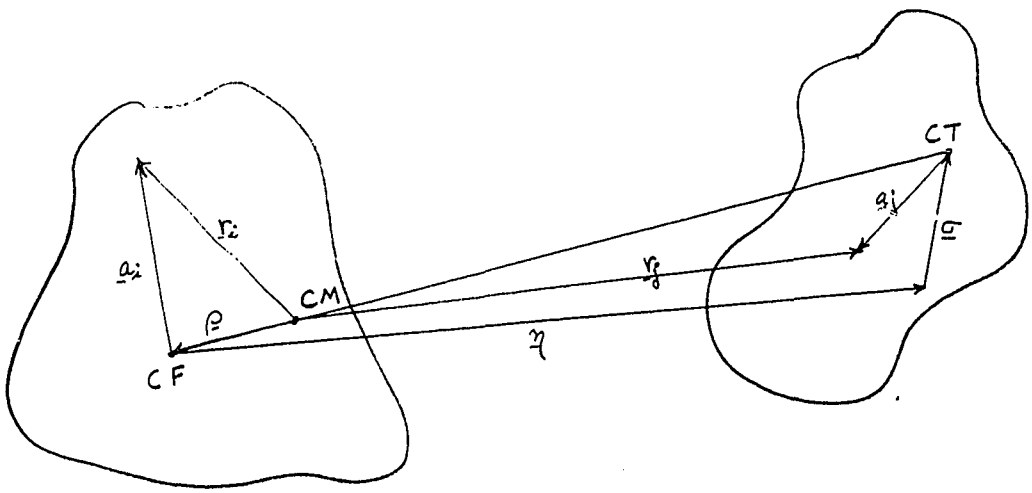


Figure 1.

CM: center of mass of the molecule

CF: center of mass of the frame

CT: center of mass of the top

$\underline{r}_i$: a vector from CM to a mass point of the frame, m_i.

$\underline{r}_j$: a vector from CM to a mass point of the top, m_j.

$\underline{\rho}$: a vector from CM to CF.

$\underline{\eta}$: a vector from CF to the "connection" of the top, (i.e., a bonded atom).

$\underline{\sigma}$: a vector from the connection of the top to CT.

$\underline{a}_i$: a vector from CF to a mass point of the frame.

$\underline{a}_j$: a vector from CT to a mass point of the top.

α: the angle of relative orientation between top and frame.

ω_i: the components of angular velocity projected on the body axes.

Then the following relations hold:

$$\begin{aligned} \underline{r}_i &= \underline{\rho} + \underline{a}_i & \underline{r}_j &= \underline{\eta} + \underline{\sigma} + \underline{\rho} + \underline{a}_j \\ \dot{\underline{r}}_i &= \dot{\underline{\rho}} & \dot{\underline{r}}_j &= \dot{\underline{\sigma}} + \dot{\underline{\rho}} + \dot{\underline{a}}_j \end{aligned} \tag{1-1}$$

and

$$\begin{aligned} \dot{\underline{\sigma}} &= \dot{\underline{\alpha}} \times \underline{\sigma} = - \dot{\alpha}\, \sigma_y\, \underline{i} + \dot{\alpha}\, \sigma_x\, \underline{j} \\ \dot{\underline{a}}_j &= \dot{\underline{\alpha}} \times \underline{a}_j = - \dot{\alpha}\, (a_j)_y\, \underline{i} + \dot{\alpha}\, (a_j)_x\, \underline{j} \end{aligned} \tag{1-2}$$

since

$$\dot{\underline{\alpha}} = \frac{\partial \alpha}{\partial t}\, \underline{k} \, .$$

Also the center of mass relation

$$M_F \underline{\rho} + M_T \, (\underline{\rho} + \underline{\eta} + \underline{\sigma}) = 0$$

implies that

$$\underline{\rho} = - \frac{M_T}{M} \, (\underline{\eta} + \underline{\sigma}); \qquad \dot{\underline{\rho}} = - \frac{M_T}{M} \, \dot{\underline{\sigma}} \tag{1-3}$$

M : mass of the entire molecule

M_F: mass of the frame

M_T: mass of the top.

The Kinetic Energy

The kinetic energy of a system of mass points relative to a set of axes fixed in space is

$$2T = \sum_i m_i \, \dot{\underline{R}}_i^2 + \sum_j m_j \, \dot{\underline{R}}_j^2 \, . \tag{1-4}$$

This may be separated into two independent parts if a new coordinate system is chosen with origin at the center of mass of the molecule. It will be assumed that the separation has been performed and we will be

concerned only with the kinetic energy relative to the center of mass of the molecule (3).

Then the kinetic energy may be expressed in the simpler form

$$2T = \sum m_i \left[\dot{\underline{r}}_i + \underline{\omega} \times \underline{r}_i \right]^2 + \sum m_j \left[\dot{\underline{r}}_j + \underline{\omega} \times \underline{r}_j \right]^2 \tag{1-5}$$

where $\underline{\omega}$ is the angular velocity relative to a set of axes fixed in the molecule. Substitution of the quantities defined in Eq. (1-1) and expanding the quadratic expressions lead to

$$\begin{aligned} 2T = {} & \underline{\omega}^+ \underline{I}\, \underline{\omega} + M_F \dot{\underline{\rho}}^2 + M_T \dot{\underline{\rho}}^2 + M_T \dot{\underline{\sigma}}^2 + 2M_T \underline{\sigma} \cdot \dot{\underline{\rho}} + \sum m_j \dot{\underline{a}}_j^2 \\ & + 2 \dot{\underline{\rho}} \cdot \sum m_j \dot{\underline{a}}_j + 2 \dot{\underline{\rho}} \cdot \underline{\omega} \times \sum m_i \underline{a}_i + 2M_F \dot{\underline{\rho}} \cdot \underline{\omega} \times \underline{\rho} \\ & + 2M_T \dot{\underline{\sigma}} \cdot \underline{\omega} \times \underline{\eta} + 2 \dot{\underline{\sigma}} \cdot \sum m_j \dot{\underline{a}}_j + 2M_T \dot{\underline{\sigma}} \cdot \underline{\omega} \times \underline{\sigma} \\ & + 2 \dot{\underline{\sigma}} \cdot \underline{\omega} \times \sum m_j \dot{\underline{a}}_j + 2M_T \dot{\underline{\sigma}} \cdot \underline{\omega} \times \underline{\rho} + 2 \sum m_j \dot{\underline{a}}_j \cdot \underline{\omega} \times \\ & \times (\underline{\eta} + \underline{\sigma} + \underline{\rho} + \underline{a}_j) + 2M_T \dot{\underline{\rho}} \cdot \underline{\omega} \times \underline{\eta} + 2M_T \dot{\underline{\rho}} \cdot \underline{\omega} \times \underline{\sigma} \\ & + 2 \dot{\underline{\rho}} \cdot \underline{\omega} \times \sum m_j \underline{a}_j + 2 M_T \dot{\underline{\rho}} \cdot \underline{\omega} \times \underline{\rho} \ , \end{aligned} \tag{1-6}$$

where $\underline{I}$ is the inertial tensor having components of the moments of inertia of the whole molecule about its center of mass. The expression reduces when use is made of the definition of $\underline{a}_j$, $\sum m_j \underline{a}_j = 0$, with the result

$$\begin{aligned} 2T = {} & \underline{\omega}^+ \underline{I}\, \underline{\omega} + M \dot{\underline{\rho}}^2 + M_T \dot{\underline{\sigma}}^2 + 2M_T \dot{\underline{\rho}} \cdot \dot{\underline{\sigma}} + 2M \dot{\underline{\rho}} \cdot \underline{\omega} \times \underline{\rho} \\ & + \sum m_j \dot{\underline{a}}_j^2 + 2 \sum m_j \dot{\underline{a}}_j \cdot \underline{\omega} \times \underline{a}_j + 2M_T \dot{\underline{\sigma}} \cdot \underline{\omega} \times \underline{\eta} \\ & + 2M_T \dot{\underline{\sigma}} \cdot \underline{\omega} \times \underline{\sigma} + 2M_T \dot{\underline{\sigma}} \cdot \underline{\omega} \times \underline{\rho} + 2M_T \dot{\underline{\rho}} \cdot \underline{\omega} \times \underline{\eta} \\ & + 2M_T \dot{\underline{\rho}} \cdot \underline{\omega} \times \underline{\sigma} . \end{aligned} \tag{1-7}$$

Finally introducing the assumptions listed in part one, the kinetic energy may be expressed in the form

$$
\begin{aligned}
2T = \; & \underline{\omega}^{*}\underline{I}\,\underline{\omega} + \frac{M_T\, M_F}{M}\,\sigma_{\perp}^{\,2}\,\dot{\alpha}^{\,2} + (I_{CT})_{zz}\,\dot{\alpha}^{\,2} \\
& + 2\dot{\alpha}\;\omega_z\left[\frac{M_T\, M_F}{M}\,(\sigma_{\perp}^{\,2} + \sigma_y\,\eta_y) + (I_{CT})_{zz}\right] \\
& - 2\dot{\alpha}\;\omega_y\left[\frac{M_T\, M_F}{M}\,\eta_z\,\sigma_y + (I_{CT})_{yz}\right] \\
& - 2\dot{\alpha}\;\omega_x\left[\frac{M_T\, M_F}{M}\,\eta_z\,\sigma_x + (I_{CT})_{xz}\right]
\end{aligned}
\qquad (1\text{-}8)
$$

where $(I_{CT})_{ij}$ is the moment of inertia of the particles comprising the top about the center of mass of the top, CT.

The origin of the various terms in the kinetic energy is obvious: the first term represents the energy of overall rotation, the second and third are the kinetic energy of internal motion, and then the remaining terms represent a coupling between the internal and external motions.

The Angular Momentum

When obtaining the quantum mechanical Hamiltonian from the classical formulation it is convenient to have the kinetic energy as a function of P_x, P_y, P_z, the components of total angular momentum about the body axes and commonly referred to as momentoids. In addition the momentoids must be expressible in terms of momenta conjugate to some coordinates which are usually chosen as the Eulerian angles.

The angular momentum, $\underline{P}$, is by definition (3)

$$
P = \sum m_i\left[\underline{r}_i \times (\dot{\underline{r}}_i + \underline{\omega} \times \underline{r}_i)\right] + \sum m_j\left[\underline{r}_j \times (\dot{\underline{r}}_j + \underline{\omega} \times \underline{r}_j)\right] \qquad (1\text{-}9)
$$

which easily reduces to

$$\mathbf{P} = \underline{\mathbf{I}}\,\underline{\omega} + \sum m_i\,(\underline{r}_i \times \dot{\underline{r}}_i) + \sum m_j\,(\underline{r}_j \times \dot{\underline{r}}_j). \tag{1-10}$$

After the substitution of Eqs. (1-1) and (1-2), and then simplifying in the same manner as for the kinetic energy, the form for the total angular momentum,

$$\begin{aligned}\mathbf{P} = \underline{\mathbf{I}}\,\underline{\omega} &- \dot{\alpha}\left[(I_{CT})_{xz} + \frac{M_T M_F}{M}\,\sigma_x\,\eta_z\right]\underline{i} \\ &- \dot{\alpha}\left[(I_{CT})_{yz} + \frac{M_T M_F}{M}\,\sigma_y\,\eta_z\right]\underline{j} \\ &+ \dot{\alpha}\left[(I_{CT})_{zz} + \frac{M_T M_F}{M}\,(\sigma_\perp^2 + \eta_y\,\sigma_y)\right]\underline{k}\end{aligned} \tag{1-11}$$

is obtained. One observes that P_x, P_y, P_z obtained in the following manner are identical with those of Eq. (1-11):

$$\begin{aligned}P_x &= \frac{\partial T}{\partial \omega_x} = I_{xx}\omega_x - I_{xy}\omega_y - I_{xz}\omega_z - \dot{\alpha}\left[(I_{CT})_{xz} + \frac{M_T M_F}{M}\,\eta_z\,\sigma_x\right] \\ P_y &= \frac{\partial T}{\partial \omega_y} = I_{yy}\omega_y - I_{xy}\omega_x - I_{yz}\omega_z - \dot{\alpha}\left[(I_{CT})_{yz} + \frac{M_T M_F}{M}\,\eta_z\,\sigma_y\right] \\ P_z &= \frac{\partial T}{\partial \omega_z} = I_{zz}\omega_z - I_{xz}\omega_x - I_{yz}\omega_y + \dot{\alpha}\left[(I_{CT})_{zz} + \frac{M_T M_F}{M}(\sigma_\perp^2 + \eta_y\,\sigma_y)\right]\end{aligned}$$

$$\begin{aligned}p = \frac{\partial T}{\partial \dot{\alpha}} &= \dot{\alpha}\left[(I_{CT})_{zz} + \frac{M_T M_F}{M}\,\sigma_\perp^2\right] \\ &- \omega_x\left[(I_{CT})_{xz} + \frac{M_T M_F}{M}\,\eta_z\,\sigma_x\right] \\ &- \omega_y\left[(I_{CT})_{yz} + \frac{M_T M_F}{M}\,\eta_z\,\sigma_y\right] \\ &+ \omega_z\left[(I_{CT})_{zz} + \frac{M_T M_F}{M}\,(\sigma_\perp^2 + \eta_y\,\sigma_y)\right].\end{aligned} \tag{1-12}$$

The momentum p, is that corresponding to the fourth degree of freedom. It is necessary to use a momentum which is conjugate to some coordinate in the quantum mechanical formulation and $p = \frac{\partial T}{\partial \dot{\alpha}}$ satisfies this condition.

The kinetic energy, T, may be expressed in terms of the Eulerian angles θ , φ , ψ by making use of the transformation

$$\begin{aligned} \omega_x &= \dot{\varphi} \sin\theta \sin\psi + \dot{\theta} \cos\psi \\ \omega_y &= \dot{\varphi} \sin\theta \cos\psi - \dot{\theta} \sin\psi \\ \omega_z &= \dot{\varphi} \cos\theta + \dot{\psi} \end{aligned} \tag{1-13}$$

After this substitution T has a quite complicated form and will not be reproduced here. The important thing is that T can be expressed in terms of coordinates to which there are conjugate moments p_θ , p_φ , p_ψ . To express P_x in this representation use is made of the relation

$$P_x = \frac{\partial T}{\partial \omega_x} = \frac{\partial T}{\partial \dot{\theta}} \frac{\partial \dot{\theta}}{\partial \omega_x} + \frac{\partial T}{\partial \dot{\varphi}} \frac{\partial \dot{\varphi}}{\partial \omega_x} + \frac{\partial T}{\partial \dot{\psi}} \frac{\partial \dot{\psi}}{\partial \omega_x} . \tag{1-14}$$

This leads to the expressions

$$\begin{aligned} P_x &= \cos\psi\, p_\theta + \csc\theta \sin\psi\, p_\varphi - \cot\theta \sin\psi\, p_\psi \\ P_y &= -\sin\psi\, p_\theta + \csc\theta \cos\psi\, p_\varphi - \cot\theta \cos\psi\, p_\psi \\ P_z &= p_\psi \end{aligned} \tag{1-15}$$

Note that P_x, P_y, P_z are functions <u>only</u> of the Eulerian angles and their conjugate moments; thus P_x, P_y, P_z commute with $p = \frac{\partial T}{\partial \dot{\alpha}}$, the momentum of internal rotation.

It is worthwhile to summarize the results of this section. It has been found that P_x, P_y, P_z depend only on θ , φ , ψ and their conjugate momenta - <u>not</u> on α or p; also they are the components of total angular momentum and therefore satisfy the commutation relations. Since p is conjugate to α , when the quantum mechanical formalism is developed p may be replaced by the operator $-i \frac{\partial}{\partial \alpha}$.

Transformation of the Classical Kinetic Energy

The formulation is now to the point where a transformation of the kinetic energy from the angular velocity to the angular momentum coordinates can be made. First it is necessary to solve the fourth of Eq. (1-12) for $\dot{\alpha}$, such that

$$\dot{\alpha} = \frac{1}{I'_z} p - \frac{I'_x}{I'_z} \sin\alpha \ \omega_x + \frac{I'_y}{I'_z} \cos\alpha \ \omega_y - (1+\eta\cos\alpha)\,\omega_z \qquad (1\text{-}16)$$

where the definitions

$$(I_{CT})_{xz} = -(I'_{CT})_{xz} \sin\alpha \qquad (I_{CT})_{yz} = (I'_{CT})_{yz} \cos\alpha$$

$$I'_x = (I'_{CT})_{xz} + \frac{M_T M_F}{M} \eta_z \sigma_\perp$$

$$I'_y = (I'_{CT})_{yz} + \frac{M_T M_F}{M} \eta_z \sigma_\perp$$

$$I'_z = (I_{CT})_{zz} + \frac{M_T M_F}{M} \sigma_\perp^2 \qquad (1\text{-}17)$$

$$(I_{CT})_{zz} + \frac{M_T M_F}{M} (\sigma_\perp^2 + \sigma_y \eta_z) = I'_z (1 + \eta\cos\alpha)$$

$$\eta = \frac{1}{I'_z} \frac{M_T M_F}{M} \eta_y \sigma_\perp$$

have been used. Next $\dot{\alpha}$ is eliminated from the first three of Eq. (1-12) by substitution of Eq. (1-16). After a slight rearrangement the results are

$$P_x - p_y = I_{xx}\omega_x - I_{xy}\omega_y - I_{xz}\omega_z$$

$$P_y - p_y = I_{yy}\omega_y - I_{xy}\omega_x - I_{yz}\omega_z \qquad (1\text{-}18)$$

$$P_z - p_z = I_{zz}\omega_z - I_{xz}\omega_x - I_{yz}\omega_y$$

where the I_{ij} are effective moments of inertia defined so that

$$
\begin{aligned}
I_{xx} &= (I_{CM})_{xx} - \frac{I_x'^2}{I_z'} \sin^2\alpha \\
I_{yy} &= (I_{CM})_{yy} - \frac{I_y'^2}{I_z'} \cos^2\alpha \\
I_{zz} &= (I_{CM})_{zz} - I_z' (1 + \eta \cos\alpha)^2 \\
I_{xy} &= (I_{CM})_{xy} - \frac{I_x' I_y'}{I_z'} \sin\alpha \cos\alpha \\
I_{xz} &= (I_{CM})_{xz} + I_x' (1 + \eta \cos\alpha) \sin\alpha \\
I_{yz} &= (I_{CM})_{yz} - I_y' (1 + \eta \cos\alpha) \cos\alpha \\
P_x &= \frac{I_x'}{I_z'} \sin\alpha \; p \\
P_y &= -\frac{I_y'}{I_z'} \cos\alpha \; p \\
P_z &= (1 + \eta \cos\alpha) \, p.
\end{aligned}
\tag{1-19}
$$

where $(I_{CM})_{ij}$ are the components of inertia of the entire molecule or the molecular axes through the center of mass of the entire molecule.

At this point it should be remembered that P_x, P_y, P_z are still the components of total angular momentum of the molecule referred to the body axes. The following physical significance can be attached to the p_x, p_y, p_z: they are the components of angular mementum of the top, including both the internal and overall rotation. Note in the fourth of Eq. (1-12) that when $\dot{\alpha} = 0$, as would be the case for a completely rigid molecule, p does not vanish.

Next we find that

$$
2T = (P_x - p_x)\,\omega_x + (P_y - p_y)\,\omega_y + (P_z - p_z)\,\omega_z + \frac{1}{I_z'} p^2 \tag{1-20}
$$

which may be verified by direct substitution of Eqs. (1-18) into Eq. (1-20). Now the inverse, μ , to the inertia tensor in Eqs. (1-18) is easily found and the results may be expressed as

$$\begin{aligned}
\omega_x &= 2\mu_{xx}(P_x - p_x) + 2\mu_{xy}(P_y - p_y) + 2\mu_{xz}(P_z - p_z) \\
\omega_y &= 2\mu_{yy}(P_y - p_y) + 2\mu_{xy}(P_x - p_x) + 2\mu_{yz}(P_z - p_z) \qquad (1\text{-}21) \\
\omega_z &= 2\mu_{zz}(P_z - p_z) + 2\mu_{xz}(P_x - p_x) + 2\mu_{yz}(P_y - p_y).
\end{aligned}$$

After substitution of Eqs. (1-21) into Eqs. (1-20) we finally obtain the result

$$\begin{aligned}
T = {} & \mu_{xx}(P_x - p_x)^2 + \mu_{yy}(P_y - p_y)^2 + \mu_{zz}(P_z - p_z)^2 \\
& + 2\mu_{xy}(P_x - p_x)(P_y - p_y) + 2\mu_{xz}(P_x - p_x)(P_z - p_z) \qquad (1\text{-}22) \\
& + 2\mu_{yz}(P_y - p_y)(P_z - p_z) + \mu\, p^2; \quad \mu = \frac{1}{2I'_z} .
\end{aligned}$$

Eq. (1-22) will be the starting point for the quantum mechanical formulation. General expressions for the moments of inertia and rotational constants depend upon the particular molecule under consideration and will be found in Chapters III and IV.

It is interesting to see how our formulation reduces for a symmetric top internal rotor. The alterations are: 1) $\mathcal{I} = 0$, 2) $(I_{CT})_{xz} = (I_{CT})_{yz} = 0$; from which it follows that $p_x = p_y = 0$. Therefore

$$\begin{aligned}
T = {} & \mu_{xx} P_x^2 + \mu_{yy} P_y^2 + \mu_{zz} (P_z - p)^2 + \mu p^2 \\
& + 2\mu_{xy} P_x P_y + 2\mu_{xz} P_x P_z + 2\mu_{yz} P_y P_z,
\end{aligned} \qquad (1\text{-}23)$$

and the result is the same as that used in the usual PAM formulation (15).

The Potential Energy

The ultimate goal of the calculation is to determine the height of the potential barrier hindering the internal motion. Since the exact origin of the barrier is not known, the only condition which we may impose upon its behavior is that it has the symmetry of the molecule under the internal rotation.

For the molecules CD_2HCOH and CH_2DCOH we will assume the customary three-fold barrier, neglecting six-fold and higher order terms:

$$V(\alpha) = \frac{V_3}{2} (1 - \cos 3\alpha) . \tag{1-24}$$

The benzaldehyde molecule is invariant under a rotation of $n\pi$, $n = 0, 1, \cdots$, so we will expand the potential in the Fourier series

$$V(\alpha) = \sum_{n=0} A_{2n} \cos 2n\alpha .$$

The first few terms are

$$V(\alpha) = \frac{V_2}{2} (1 - \cos 2\alpha) + \frac{V_4}{2} (1 - \cos 4\alpha) + , \cdots ; \tag{1-25}$$

the customary procedure will be followed and only the first order term will be kept. Under this assumption we obtain

$$V(\alpha) = \frac{V_2}{2} (1 - \cos 2\alpha) = V_2 \sin^2 \alpha . \tag{1-26}$$

For further discussion one is referred to the review article of Lin and Swalen (15).

CHAPTER II

THE QUANTUM MECHANICAL HAMILTONIAN

The results of the previous chapter lead directly to the correct formulation of the quantum mechanical Hamiltonian. The development of the theory has been presented in detail by Wilson et. al. (19, 20) for vibration-rotation interaction, and it is not necessary to review all of the details.

Essentially the results are that the kinetic energy operator has the complicated form (19)

$$T = g^{-\frac{1}{4}} \sum_{i,j} (P_i - p_i) \mu_{ij} g^{\frac{1}{2}} (P_j - p_j) g^{-\frac{1}{4}} + g^{-\frac{1}{4}} p \mu g^{\frac{1}{2}} p g^{-\frac{1}{4}} \quad (2\text{-}1)$$

where μ_{ij}, P_i, p_i, p, etc., are the same quantities as those appearing in Eq. (1-22) except that they have been replaced by the proper quantum mechanical operators; then $g = |\mu_{ij}|^{-1}$. Note that μ_{ij}, g, p_i are functions of the angle of internal rotation, α . This follows because the internal rotor is not a symmetric top. The P_i commute with all of these quantities except, of course, the other P_j, since they are functions only of the Eulerian angles and their conjugate momenta. The Hamiltonian operator is obtained by adding the potential energy $V(\alpha)$ to Eq. (2-1).

Partial expansion of the sum in Eq. (2-1) gives

$$H = H_R + H_{TR} + H_T \quad (2\text{-}2)$$

where

$$H_R = \mu_{xx}^{(0)} P_x^2 + \mu_{yy}^{(0)} P_y^2 + \mu_{zz}^{(0)} P_z^2 + \mu_{xy}^{(0)} (P_x P_y + P_y P_x) + \mu_{xz}^{(0)} (P_x P_z + P_z P_x) + \mu_{yz}^{(0)} (P_y P_z + P_z P_y) \tag{2-3}$$

$$H_T = g^{-\frac{1}{4}} \sum_{i,j} P_i \mu_{ij} g^{\frac{1}{2}} P_j g^{-\frac{1}{4}} + g^{-\frac{1}{4}} \mu\, p\, g^{\frac{1}{2}}\, p\, g^{-\frac{1}{4}} + V(\alpha) \tag{2-4}$$

$$H_{TR} = \mu_{xx}(\alpha) P_x^2 + \mu_{yy}(\alpha) P_y^2 + \mu_{zz}(\alpha) P_z^2 + \mu_{xy}(\alpha)(P_x P_y + P_y P_x) + \mu_{zz}(\alpha)(P_x P_z + P_z P_x) + \mu_{yz}(\alpha)(P_y P_z + P_z P_y) - g^{-\frac{1}{4}} \sum_{ij} P_i \mu_{ij} g^{\frac{1}{4}} P_j - g^{\frac{1}{4}} \sum_{i,j} \mu_{ij} P_i P_j g^{-\frac{1}{4}} . \tag{2-5}$$

Both H_R, H_T may be considered part of the unperturbed Hamiltonian, H^o; H_R is independent of the internal coordinate, α , and thus depends only on the over all rotational quantum numbers; while H_T is a function only of α , and therefore will be independent of the overall rotation. And then H_{TR} represents the coupling between the internal and overall motion. The last two terms of Eq. (2-5) may be combined with the simplification

$$- \sum_{ij} \left[2\mu_{ij} P_i - (P_i \mu_{ij}) \right] P_j \tag{2-6}$$

where P_i operates only on the quantity in parenthesis.

A convenient basis for the representation of H is the product function

$$\Psi_{RT}(R,\alpha) = \psi_R(R)\, \varphi_T(\alpha) \tag{2-7}$$

where Ψ_{RT} is an eigenfunction of $H^o = H_R + H_T$, ψ_R of H_R and φ_T of H_T:

$$H^o \Psi_{RT}(R,\alpha) = (H_R + H_T) \Psi_{RT}(R,\alpha) = (E_R + E_T) \Psi_{RT}(R,\alpha) \tag{2-8}$$

$$H_R \psi_R (R) = E_R \psi_R (R) \tag{2-9}$$

$$H_T \psi_T (\alpha) = E_T \psi_T (\alpha) \tag{2-10}$$

In practice the basic functions $\psi_R (R)$ will be either those of the symmetric top or the Wang representation, although at this time it is not necessary to specify the representation of R. The $\psi_T (\alpha)$ should be determined from H_T and their exact form will depend upon the choice of $V(\alpha)$; i.e., whether the potential energy has two or three fold symmetry.

The coupling between the internal and overall rotation, H_{TR}, will be treated as a perturbation, using as a basis the Ψ_{RT} of Eq. (2-7). From the choice of molecular axes, H_{RT} is <u>not</u> small, and even at the limit of $V \to \infty$ (i.e., the limit of a rigid molecule) its contribution to the rotational energy does not vanish. Therefore, in the application, there are situations when it might be necessary to use third or fourth order perturbation corrections. Quite often, though, first and second order theory are sufficient to determine the barrier height, but the higher order terms would be necessary to determine the complete rotational spectrum accurately.

For discussion of the details of the theory it is best to consider the application to a specific molecule, because the functional form of the rotational constants depend upon the structure of the molecule. But at this point it worthwhile to point out that it will be possible to express the $\mu_{ij}(\alpha)$ of Eq. (2-5) in a converging power series of $\sin^n \alpha$ and $\cos^m \alpha$. This will allow for the evaluation of certain integrals which otherwise would not be possible. The series arises from

$g = g^{o} + g(\alpha)$, Eq. (2-1) and the convergence of the series depends upon the ratio $g(\alpha)/g^{o}$. Therefore this theory will be applicable only if this ratio is less than one, which will be the case for the molecules considered in the next two chapters.

CHAPTER III

APPLICATION OF THE THEORY TO CDH_2COH AND CHD_2COH

Internal rotation in acetaldehyde, CH_3COH, and two of its deuterated species, CD_3COH and CD_3COD, has been studied quite intensively (4, 14). The potential barrier hindering the internal rotation has been determined conclusively to be of the order of 400 cm^{-1} and to be relatively independent of the isotopic species. In addition the microwave rotational spectrum of CHD_2COH and CH_2DCOH has been reported, but this spectrum has not been analyzed on the basis of internal rotation. In this chapter the theory developed earlier will be applied to these two molecules, and it will be found that the potential barrier for these molecules is in good agreement with those determined for CH_3COH, etc. Therefore these molecules for which the barrier height is presumably already known provide a good illustration and check of the theory.

Molecular Structure

The molecular structure of acetaldehyde is well determined (4). The same structure will be used for CH_2DCOH and CD_2HCOH. The actual evaluation of the moments of inertia is found in Appendix I.

Rotational Constants

The moments of inertia of the molecule have the general form

$$
\begin{aligned}
(I_{CM})_{xx} &= (I_{CM})^{(o)}_{xx} + (I_{CM})^{(o)}_{xx} \cos\alpha + (I_{CM})^{(2)}_{xx} \sin^2\alpha \\
(I_{CM})_{yy} &= (I_{CM})^{(o)}_{yy} + (I_{CM})^{(2)}_{yy} \sin^2\alpha \\
(I_{CM})_{zz} &= (I_{CM})^{(o)}_{zz} + (I_{CM})^{(o)}_{zz} \cos\alpha \\
(I_{CM})_{xy} &= (I_{CM})^{(o)}_{xy} \sin\alpha + (I_{CM})^{(1)}_{xy} \sin\alpha \cos\alpha \\
(I_{CM})_{xz} &= (I_{CM})^{(o)}_{xz} \sin\alpha \\
(I_{CM})_{yz} &= (I_{CM})^{(o)}_{yz} + (I_{CM})^{(o)}_{yz} \cos\alpha \quad .
\end{aligned}
\tag{3-1}
$$

In Chapter I the molecular axes were chosen so that z is parallel to the internal rotation axis, y parallel to the COH plane, and x perpendicular to this plane.

After the transformation to the effective moments of inertia, defined in Eq. (1-15, 16, 17, 18), one now has for I_{ij}

$$
\begin{aligned}
I_{xx} &= (I_{CM})^{(o)}_{xx} + (I_{CM})^{(1)}_{xx} \cos\alpha + \left[(I_{CM})^{(2)}_{xx} - \frac{(I'_x)^2}{I'_z}\right] \sin^2\alpha \\
I_{yy} &= (I_{CM})^{(o)}_{yy} - \frac{(I'_y)^2}{I'_z} + \left[(I_{CM})^{(2)}_{yy} + \frac{(I'_y)^2}{I'_z}\right] \sin^2\alpha \\
I_{zz} &= (I_{CM})^{(o)}_{zz} - I'_z(1+\eta^2) + \left[(I_{CM})^{(1)}_{zz} - 2I'_z\eta\right] \cos\alpha + I'_z\eta^2 \sin^2\alpha \\
I_{xy} &= (I_{CM})^{(o)}_{xy} \sin\alpha + \left[(I_{CM})^{(1)}_{xy} - \frac{I'_x I'_y}{I'_z}\right] \sin\alpha \cos\alpha \\
I_{xz} &= \left[(I_{CM})^{(o)}_{xz} + I'_x\right] \sin\alpha + I'_x \eta \sin\alpha \cos\alpha \\
I_{yz} &= (I_{CM})^{(o)}_{yz} - I'_y\eta + \left[(I_{CM})^{(1)}_{yz} - I'_y\right] \cos\alpha + I'_y \eta \sin^2\alpha \quad .
\end{aligned}
\tag{3-2}
$$

The transformation to obtain Eq. (1-20) is from the I_{ij} to the μ_{ij}. In their expanded form the μ_{ij} are

$$
\begin{aligned}
\mu_{xx} &= \mu_{xx}^{(o)} + \mu_{xx}^{(1)} \cos\alpha + \mu_{xx}^{(2)} \sin^2\alpha + \cdots \\
\mu_{yy} &= \mu_{yy}^{(o)} + \mu_{yy}^{(2)} \sin^2\alpha + \cdots \\
\mu_{zz} &= \mu_{zz}^{(o)} + \mu_{zz}^{(2)} \sin^2\alpha + \cdots \\
\mu_{xy} &= \mu_{xy}^{(o)} \sin\alpha + \mu_{xy}^{(1)} \sin\alpha \cos\alpha + \cdots \\
\mu_{xz} &= \mu_{xz}^{(o)} \sin\alpha + \mu_{xz}^{(1)} \sin\alpha \cos\alpha + \cdots \\
\mu_{yz} &= \mu_{yz}^{(o)} + \mu_{yz}^{(o)} \sin^2\alpha + \cdots
\end{aligned}
\tag{3-3}
$$

For CH_2DCOH and CD_2HCOH the convergence of the series is quite rapid; the next order terms are approximately 10^{-2} smaller than the $\mu_{ij}^{(2)}$.

The Torsional Equation

That part of the Hamiltonian which depends only on the internal coordinate, α, in Eq. (2-4),

$$
H_T = g^{-\frac{1}{4}} \sum p_i \mu_{ij} g^{\frac{1}{2}} p_j + g^{-\frac{1}{4}} \mu p\, g^{\frac{1}{2}} p\, g^{-\frac{1}{4}} + \frac{V_3}{2}(1-\cos 3\alpha), \tag{3-4}
$$

where the μ_{ij} are defined in Eq. (3-3) and

$$
\begin{aligned}
p_x &= \frac{I_x'}{I_z'}(\sin\alpha\, p + p \sin\alpha) & p_y &= \frac{-I_y'}{I_z'}(\cos\alpha\, p + p\cos\alpha) \\
p_z &= p + \eta(\cos\alpha\, p + p\cos\alpha) & p &= -i\frac{\partial}{\partial\alpha} \\
\mu &= \frac{1}{2I_z'} & g &= g^{(o)} + g^{(1)}\cos\alpha + g^{(2)}\sin^2\alpha
\end{aligned}
\tag{3-5}
$$

It is convenient to expand the summation in Eq. (3-4) with the result

$$
\begin{aligned}
H_T = {} & \mu_T^{(o)} p^2 + \mu_T^{(1)}(\cos\alpha\, p^2 + p^2 \cos\alpha) \\
& + \mu_T^{(2)}(\sin^2\alpha\, p^2 + p^2 \sin^2\alpha) + \frac{V_3}{2}(1-\cos 3\alpha)
\end{aligned}
\tag{3-6}
$$

$$\mu_T^{(o)} = \mu_{zz}^{(o)} (1 + \eta^2) + \left(\frac{I'_y}{I'_z}\right)^2 \mu_{yy}^{(o)} - 2\eta \frac{I'_y}{I'_z} \mu_{yz}^{(o)} + \mu$$

$$\mu_T^{(1)} = 2\left[\eta \mu_{zz}^{(o)} - \frac{I'_y}{I'_z} \mu_{yz}^{(o)}\right]$$

$$\mu_T^{(2)} = \mu_{zz}^{(2)} (1 + \eta^2) + 2 \frac{I'_x}{I'_z} \mu_{xz}^{(o)} - \mu_{zz}^{(o)} \eta^2 + \left(\frac{I'_x}{I'_z}\right)^2 \mu_{xx}^{(o)}$$
$$- \left(\frac{I'_y}{I'_z}\right)^2 \left[\mu_{yy}^{(o)} - \mu_{yy}^{(2)}\right] - 2 \frac{I'_x I'_y}{I'_z} \mu_{xy}^{(1)} + 2\eta \frac{I'_x}{I'_z} \mu_{xz}^{(1)}$$
$$+ 2\eta \frac{I'_y}{I'_z} \left[\mu_{zz}^{(o)} - \mu_{yz}^{(2)}\right] .$$

The higher order terms which have been neglected in Eq. (3-6) are 10^{-2} times smaller than those angular dependent terms which have been included.

The first thing one observes about Eq. (3-6) is that H_T is no longer invariant under a rotation of $\pm 2\pi/3$. Again this follows from the fact that the internal rotor is not a symmetric top. In CH_2DCOH, for example, there are two isometric configurations: in one case the hydrogen of the top can oppose the oxygen of the frame; and in the other configuration one of the deuteriums of the top opposes the oxygen of the frame. The former configuration is referred to as the symmetrical and the latter the asymmetrical.

If the angular dependent terms of the kinetic energy are neglected in Eq. (3-6), we obtain the differential equation

$$-\mu_T^{(o)} \frac{d^2U}{d\alpha^2} + \frac{V_3}{2} (1-\cos 3\alpha) U = EU. \qquad (3-7)$$

The solutions of this equation, which is related to Mathieu's equation and the eigenfunctions and eigenvalues have been tabulated (5, 18). Briefly the results are as follows: There are two types of eigenvalues, a non-degenerate level (A-type) and a two-fold degenerate level (E-type).

For $E_n << V_3$, the A and E levels are themselves nearly degenerate, and at $V_3 \to \infty$ would become degenerate. The splitting of the A and E levels is related to the probability of the top tunneling through the potential barrier. It has been customary to use two sets of quantum numbers to specify the torsional energy levels. One set of A and E levels are said to form a torsional state with quantum number n; and then the A and E levels are torsional substates denoted by $\sigma = 0$ for the A level and $\sigma = \pm 1$ for the degenerate E levels. It is found that

$$\left| E_{n=o,\sigma=o} - E_{n=o,\sigma=\pm 1} \right| << \left| E_{n=o,\sigma} - E_{n,\sigma} \right| \tag{3-8}$$

and therefore the nomenclature of state and substate is justified. The energy eigenvalues are $E_{n,\sigma}$ with corresponding eigenfunctions $U_{n,\sigma}$; (5, 18).

Now the inclusion of the angular dependent kinetic energy terms of Eq. (3-6) has similar qualitative features to those discussed above. Within each torsional state the degeneracy is completely removed. Consider the torsional state n = o; within this state there are three substates which will be denoted by the quantum numbers 0_o, 0_+, 0_- (the number for n, the subscript for the substate). The state 0_o corresponds to the symmetrical configuration at infinite barrier, and the states 0_+ and 0_- are those of the asymmetrical configuration, which at infinite potential barrier would become degenerate. The separation of the energy levels is roughly

$$\left| E_{0_+} - E_{0_-} \right| \sim \left| E_{o,\sigma=o} - E_{o,\sigma=1} \right| << \left| E_{0_{\pm}} - E_{0_o} \right| << \left| E_{0_{\substack{\pm \\ o}}} - E_{n,\sigma} \right| \tag{3-9}$$

Our procedure will be as follows: we are primarily interested in

the ground torsional state, and thus will use the 0_o, 0_+, 0_- representation for it. But for the higher torsional states, $n > o$, we will continue to use the symmetric top internal rotor representation of n, σ. These states only enter through the perturbation theory. For the ground torsional state, then, we have

$$\varphi_{0_o} = \frac{1}{\sqrt{3}}\left[U_{\sigma=o} + U_{\sigma=1} + U_{\sigma=-1}\right]$$

$$\varphi_{0_+} = \frac{1}{\sqrt{6}}\left[2U_{\sigma=o} - U_{\sigma=1} - U_{\sigma=-1}\right] \qquad (3\text{-}10)$$

$$\varphi_{0_-} = \frac{\beta}{\sqrt{6}}\left[U_{\sigma=1} - U_{\sigma=-1}\right] \quad (\beta = i\,2\sin 2\pi/3$$

(the phase of φ_{0_-} is arbitrarilly chosen for convenience). Also, if

$$H_T^o = \mu_T^{(o)} p^2 + \frac{V_3}{2}(1-\cos 3\alpha), \qquad (3\text{-}11)$$

$$H_T' = \tfrac{1}{2}\mu_T^{(1)}(\cos\alpha\, p^2 + p^2\cos\alpha) + \tfrac{1}{2}\mu_T^{(2)}(\sin^2\alpha\, p^2 + p^2\sin^2\alpha) \qquad (3\text{-}12)$$

then the energy matrix elements for the ground state are

$$(0_o|H_T|0_o) = \frac{1}{3}\Big[(0,0|H_T^o|0,0) + 2(0,1|H_T^o|0,1) + (0,0|H_T'|0,0)$$
$$+ 2(0,1|H_T'|0,L) + 4(0,0|H_T'|0,1) + 2(0,-1|H_T'|0,1)\Big] \qquad (3\text{-}13)$$

$$(0_+|H_T|0_+) = \frac{1}{3}\Big[2(0,0|H_T^o|0,0) + (0,1|H_T^o|0,1) + 2(0,0|H_T'|0,0)$$
$$+ (0,1|H_T'|0,1) - 4(0,0|H_T'|0,1) + (0,-1|H_T'|0,1)\Big]$$

$$(0_-|H_T|0_-) = (0,1|H_T^o|0,1) + (0,1|H_T'|0,1) - (0,-1|H_T'|0,1)$$

$$(0_o|H_T|0_+) = \frac{\sqrt{2}}{3}\Big[\,(0,0|H_T^o|0,0) - (0,1|H_T^o|0,1) + (0,0|H_T'|0,0)$$

$$- (0,1|H_T'|0,1) + (0,0|H_T'|0,1) - (0,-1|H_T'|0,1)\Big]$$

$$(0_o|H_T|0_-) = 0$$

$$(0_+|H_T|0_-) = 0.$$

The notation for the terms on the right of the equations is $(n,\sigma|H_T|n',\sigma')$. It turns out that the matrix element $(0_o|H_T|0_+)$ is quite small and may be neglected from now on.

At this point it is worth while to review the connection with experiment. The microwave rotational spectrum of the molecule depends upon its effective rotational constants. At ordinary temperatures, several of the molecules will be in different torsional states and substates, and each state will have its own set of characteristic rotational constants. The difference in rotational constants for the substates of the torsional state n = o is quite sensitive to V_3, the potential barrier hindering the internal motion.

The Rotational Hamiltonian

The pure rotational Hamiltonian is Eq. (2-3),

$$H_R = \mu_{xx}^{(o)} P_x^2 + \mu_{yy}^{(o)} P_y^2 + \mu_{zz}^{(o)} P_z^2 + \mu_{yz}^{(o)}(P_yP_z + P_zP_y). \qquad (3\text{-}14)$$

Note that the $\mu_{ij}^{(o)}$ are <u>not</u> the rotational constants of the molecule at infinite potential barrier since the contribution of H_{TR} to the rotational energy is not zero. It is convenient to choose the Wang representation for H_R when part of the perturbation theory is performed. But at this

point it is not necessary to specify the representation; only remember that P_x, P_y, P_z are the components of total angular momentum along the body axes. The spacing of the rotational energy levels is considerably less than that of the torsional states:

$$E_R \sim 10^{-2} E_n, \tag{3-15}$$

This will be particularly convenient when a perturbation treatment of H_{TR} is required.

The Rotational Torsional Interaction

The interaction between the overall rotation and internal motion is contained in H_{TR}, Eqs. (2-5,6),

$$\begin{aligned} H_{TR} = {} & \mu_{xx}(\alpha)\, P_x^2 + \mu_{yy}(\alpha)\, P_y^2 + \mu_{zz}(\alpha)\, P_z^2 \\ & + \mu_{xy}(\alpha)(P_xP_y + P_yP_x) + \mu_{xz}(\alpha)(P_xP_z + P_zP_x) \\ & + \mu_{yz}(\alpha)(P_yP_z + P_zP_y) - \sum_{ij}\left[2\mu_{ij}\, p_i - (p_i\mu_{ij})\right] P_j \end{aligned} \tag{3-16}$$

which for the specific case of CH_2DCOH or CDH_2COH becomes

$$\begin{aligned} H_{TR} = {} & \left[\mu_{xx}^{(2)} \sin^2\alpha + \mu_{xx}^{(1)} \cos\alpha\right] P_x^2 + \mu_{yy}^{(2)} \sin^2\alpha\, P_y^2 \\ & + \mu_{zz}^{(2)} \sin^2\alpha\, P_z^2 + \left[\mu_{xy}^{(o)} \sin\alpha + \mu_{xy}^{(1)} \sin\alpha \cos\alpha\right](P_xP_y + P_yP_x) \\ & + \left[\mu_{xz}^{(o)} \sin\alpha + \mu_{xz}^{(1)} \sin\alpha \cos\alpha\right](P_xP_z + P_zP_x) \\ & + \mu_{yz}^{(2)} \sin^2\alpha\, (P_yP_z + P_zP_y) \\ & - \left[a_x (\sin\alpha\, p + P \sin\alpha) + b_x(\sin\alpha \cos\alpha\, p + p \sin\alpha \cos\alpha)\right] P_x \\ & - \left[a_y\, p + b_y(\cos\alpha\, p + p \cos\alpha) + c_y(\sin^2\alpha\, p + p \sin^2\alpha)\right. \\ & \qquad \left. + d_y(\sin^2\alpha \cos\alpha\, p + p \sin^2\alpha \cos\alpha)\right] P_y \end{aligned} \tag{3-17}$$

$$- \Big[a_z\, p + b_z(\cos\alpha\, p + p\cos\alpha) + c_z(\sin^2\alpha\, p + p\sin^2\alpha) + d_z(\sin^2\alpha\cos\alpha\, p + p\sin^2\alpha\cos\alpha)\Big] P_z$$

where

$$a_x = \frac{I_x'}{I_z'}(\mu_{xx}^{(o)} - \mu_{xy}^{(1)}) + \mu_{xz}^{(o)} + \mu_{xz}^{(1)}$$

$$b_x = \frac{I_x'}{I_z'}(\mu_{xx}^{(1)} - \mu_{xy}^{(o)}) + \mu_{xz}^{(1)} + \mu_{xz}^{(o)}$$

$$a_y = 2\mu_{yz}^{(o)}$$

$$b_y = -\frac{I_x'}{I_z'}\mu_{yy}^{(o)} + \eta\mu_{yz}^{(o)}$$

$$c_y = \mu_{yz}^{(2)} + \frac{I_x'}{I_z'}\mu_{xy}^{(o)}$$

$$d_y = \frac{I_x'}{I_z'}(\mu_{xy}^{(1)} - \mu_{yy}^{(2)}) + \eta\mu_{yz}^{(2)}$$

$$a_z = 2\mu_{zz}^{(o)}$$

$$b_z = -\frac{I_x'}{I_z'}\mu_{yz}^{(o)} + \eta\mu_{zz}^{(o)}$$

$$c_z = \mu_{zz}^{(2)} + \frac{I_x'}{I_z'}\mu_{xz}^{(o)}$$

$$d_z = \frac{I_x'}{I_z'}(\mu_{xz}^{(1)} - \mu_{yz}^{(2)}) + \eta\mu_{zz}^{(2)} \quad .$$

Use has been made of Eqs. (3-3).

At this point it is convenient to write H_R and H_{TR} in a notation which is not so cumbersome. Let

$$H_R = A^o P_x^2 + B^o P_y^2 + C^o P_z^2 + F^o(P_y P_z + P_z P_y) \tag{3-18}$$

$$H_{TR} = A' P_x^2 + B' P_y^2 + C' P_z^2 + D'(P_x P_y + P_y P_x) \tag{3-19}$$

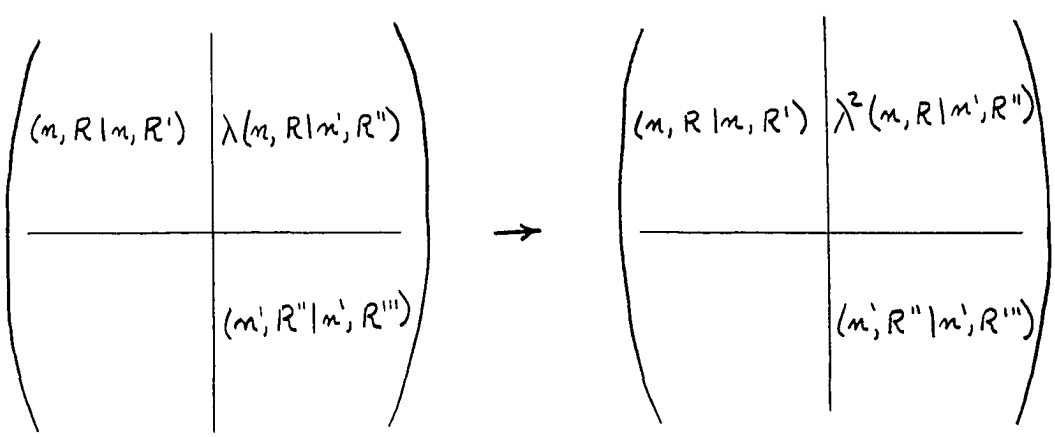
$$+ E'(P_x P_z + P_z P_x) + F'(P_y P_z + P_z P_y) - M' P_x - N' P_y - Q' P_z.$$

The coefficients should be compared with those in Eqs. (3-14,17) for identification.

It is observed that the coefficients of the P_i^2 or P_i in Eq. (3-19) are functions only of the internal coordinates α and p, hence depend only upon the torsional function $\varphi_n(\alpha)$; while the P_i^2 and P_i are functions only of the overall rotational coordinates, R. This, coupled with the fact that the torsional energies are much larger than the rotational, suggests that the function

$$\Psi_{R,n}(R,\alpha) = \psi_R(R)\ \varphi_n(\alpha) \tag{3-20}$$

forms a suitable basis for the representation of H, Eq. (2-2). The energy matrix in this representation will have the form indicated in Figure 2. To each torsional state, n, we may assign a set of rotational states. Both H_T and H_R are diagonal in n in this representation. Now H_{TR} will be considered the perturbation energy, and it has matrix elements



$$H = H_R + H_T + \lambda H_{TR}$$

Figure 2

connecting different torsional states as well as first order terms within a given n block. Our procedure will be to reduce the off-diagonal elements by a Van Vleck transformation; then in solving the rotational problem it is necessary to consider only a single torsional state. After applying the Van Vleck transformation, the torsional dependence is contained completely in the coefficients of $P_i P_j$.

A typical coefficient that needs to be calculated in the 0_o, 0_+, 0_- representation is Eq. (3-19)

$$(0_o|A'|0_o) = \int_o^{2\pi} \varphi_{0_o}(\alpha)\, A'(\alpha)\, \varphi_{0_o}(\alpha)\, d\alpha \qquad (3\text{-}21)$$

$$= \frac{1}{3}\int_o^{2\pi} (U^*_{\sigma=0} + U^*_{\sigma=1} + U^*_{\sigma=-1}) A' (U_{\sigma=0} + U_{\sigma=1} + U_{\sigma=-1})\, d\alpha$$

$$= \frac{1}{3}\int_o^{2\pi} U^*_{\sigma=0} A' U_{\sigma=0}\, d\alpha + \frac{1}{3}\int_o^{2\pi} U^*_{\sigma=0} A' U_{\sigma=1}\, d\alpha + \cdots .$$

It is convenient to introduce the notation

$$\int_o^{2\pi} U^*_{\sigma} A' U_{\sigma'}\, d\alpha = (0,\sigma|\, A'|0,\, \sigma') = A'_{\sigma,\sigma'} \quad .$$

Then we have

$$(0_o|A'|0_o) = \frac{1}{3}\left[A'_{00} + A'_{11} + A'_{-1-1} + A'_{01} + A'_{0-1} + A'_{10} + A'_{-10} + A'_{-11} + A'_{1-1}\right]. \qquad (3\text{-}21a)$$

The reason the integrals are referred to the unperturbed torsional representation is that the functions have been tabulated by Kilb (5), and the integrals are easily evaluated. Since only the ground state is in the 0_o, 0_+, 0_- representation, the matrix elements connecting excited torsional states are of the form [Eq. (3-19)]

$$(0_-|N|n,\sigma) = \frac{\beta}{\sqrt{6}}\left[(0,1|N|n,\sigma) - (0,-1|N|n,\sigma)\right] . \qquad (3\text{-}22)$$

After indroducing the notation of Eqs. (3-21a, 22) the matrix elements of H_{TR} may be expressed as

$$
\begin{aligned}
(0_o|H_{TR}|0_o) &= \frac{1}{3}\Big[3A'_{00} + 4A'_{01} + 2A'_{-11} + 3B'_{00} + 4B'_{01} + 2B'_{-11} \\
&\quad + 3C'_{00} + 4C'_{01} + 2C'_{-11} + 3F'_{00} + 4F'_{01} + 2F'_{-11}\Big] \\
(0_+|H_{TR}|0_+) &= \frac{1}{3}\Big[3A'_{00} - 4A'_{01} + A'_{-11} + 3B'_{00} - 4B'_{01} + B'_{-11} \\
&\quad + 3C'_{00} - 4C'_{01} + C'_{-11} + 3F'_{00} - 4F'_{01} + F'_{-11}\Big] \qquad (3\text{-}23) \\
(0_-|H_{TR}|0_-) &= A'_{00} - A'_{-11} + B'_{00} - B'_{-11} + C'_{00} - C'_{-11} + F'_{00} - F'_{-11} \\
(0_o|H_{TR}|0_+) &= \frac{\sqrt{2}}{3}\Big[A'_{01} - A'_{-11} + B'_{01} - B'_{-11} + C'_{01} - C'_{-11} + F'_{01} - F'_{-11} - 3M_{01}\Big] \\
(0_o|H_{TR}|0_-) &= \frac{\beta\sqrt{2}}{3}\Big[Q'_{01} + Q'_{11} + N'_{01} + N'_{11} + E'_{01} + E'_{-11} + D'_{01} + D'_{-11} + M'_{-11}\Big] \\
(0_+|H_{TR}|0_-) &= \frac{\beta}{3}\Big[2Q'_{01} - Q'_{11} + 2N'_{01} - N'_{11} + 2D'_{01} - D'_{-11} + 2E'_{01} - E'_{-11} - M_{-11}\Big]
\end{aligned}
$$

One should remember that A'_{00} actually stands for $A'_{00}P_x^2$, Q'_{01} for $Q'_{01}P_z$, etc. For those matrix elements to the excited torsional states we have

$$
\begin{aligned}
(0_o|H_{TR}|n,\sigma) &= \frac{-1}{\sqrt{3}}\Big[(0,0|M' + N' + Q'|n,\sigma) \\
&\quad + (0,1|M' + N' + Q'|n,\sigma) + (0,-1|M' + N' + Q'|n,\sigma)\Big] \\
(0_+|H_{TR}|n,\sigma) &= -\frac{1}{\sqrt{6}}\Big[2(0,0|M' + N' + Q'|n,\sigma) \qquad (3\text{-}24) \\
&\quad + (0,1|M' + N' + Q'|n,\sigma) - (0,-1|M' + N' + Q'|n,\sigma)\Big] \\
(0_-|H_{TR}|n,\sigma) &= -\frac{\beta}{\sqrt{6}}\Big[(0,1|M' + N' + Q'|n,\sigma) - (0,-1|M' + N' + Q'|n,\sigma)\Big]
\end{aligned}
$$

Also those terms which are quadratic in P_i (see Eq. (3-17)), connect different torsional states and would have a similar form.

The Perturbation Calculation

The Hamiltonian matrix is now in such a form that the Van Vleck transformation may be applied to reduce the off diagonal matrix elements in n. A general expression for the Van Vleck transformation through fourth order will be found in Appendix III. For the molecules CH_2DCOH and CD_2HCOH it is necessary to include only those terms which are linear or quadratic in P_i after the transformation. A complete expression for the rotational constants would have a form similar to Eqs. (4-24,25,26,27) in Chapter IV. The results are

$$
\begin{aligned}
(O_o|E|O_o) &= A_o P_x^2 + B_o P_y^2 + C_o P_z^2 + F_o(P_yP_z + P_zP_y) + E_o \\
(O_+|E|O_+) &= A_+ P_x^2 + B_+ P_y^2 + C_+ P_z^2 + F_+(P_yP_z + P_zP_y) + E_+ \\
(O_-|E|O_-) &= A_- P_x^2 + B_- P_y^2 + C_- P_z^2 + F_-(P_yP_z + P_zP_y) + E_- \\
(O_+|E|O_-) &= M_{+-} P_x + N_{+-} P_y + Q_{+-} P_z + D_{+-}(P_xP_y + P_yP_x) \\
&\quad + E_{+-}(P_xP_z + P_zP_x).
\end{aligned}
\tag{3-25}
$$

The notation has been simplified to the point where A_+ is the complete coefficient of P_x^2 in the O_+ torsional state after the Van Vleck transformation.

There is a simple explanation why the $P_xP_y + P_yP_x$ and $P_xP_z + P_zP_x$ terms connect different torsional states. The torsional functions, φ_{O_+} and φ_{O_-}, are not localized at either $2\pi/3$ or $-2\pi/3$, as shown in Figure 3. Since μ_{xy} and μ_{xz} change signs for these two orientations, they must have off-diagonal matrix elements, i.e. connect the states O_+ and O_-. If localized functions had been chosen in the torsional formulation, then μ_{xy} and μ_{xz} would be diagonal with the proper signs, but then all

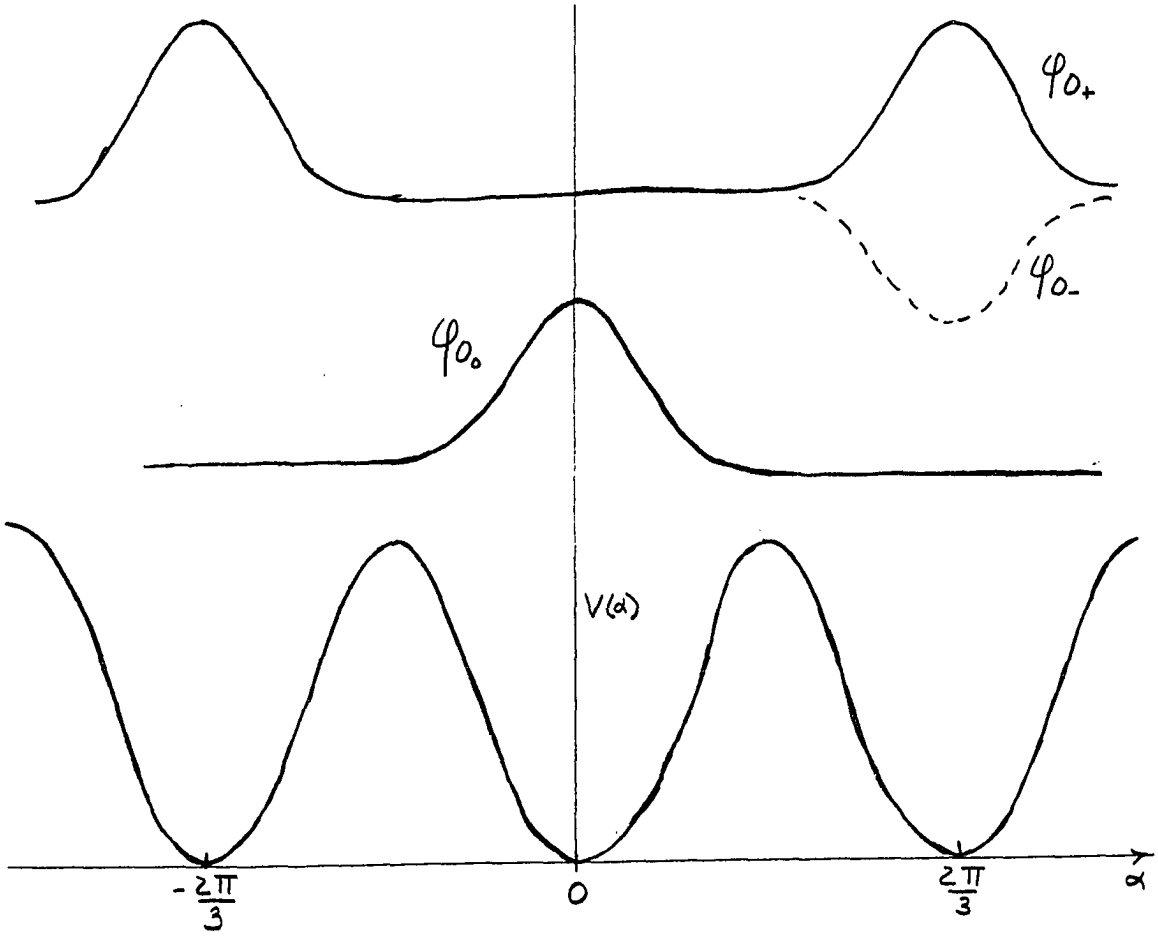


Figure 3

differences in rotational constants would connect the two states O_+ and O_-.

The Microwave Rotational Spectrum and Analysis

The microwave rotational spectrum of CH_2DCOH and CD_2HCOH has been reported in the literature by Kilb, Lin, and Wilson (4). Part of it is listed in Tables I and II, with the satellite lines being omitted.

The primary feature of the spectrum is the occurrence of three lines for each transition rather than two as would be the situation for molecules with a symmetric top internal rotor. One set of lines corresponds to the

TABLE I

ROTATIONAL SPECTRUM OF CH_2DCHO (in Mc)

Transition	Frequency (Symmetrical)	Frequency (Asymmetrical)	Splitting	Calculated Splitting
$0_{00} - 1_{01}$	18,501.87			
			493.3	503
		18,001.96		
			-3.19	-2.81
		18,005.15		
$1_{01} - 2_{02}$	36,975		984.2	1006.
		35,989.85		
			-1.85	-5.62
		35,991.70		
$5_{15} - 5_{14}$	18,402.40			
			6073.	6135.
		12,319.72		
			-19.97	-20.3
		12,339.69		
$6_{16} - 6_{15}$	25,748.55			
			8500.	8589.
		17,234.91		
			-28.14	-28.4
		17,263.05		
$7_{17} - 7_{16}$		22,964.06		
			-36.88	-37.8
		23,000.94		
$8_{18} - 8_{17}$		29,500.67		
			-47.64	-48.6
		29,548.31		

$(\Delta A - \Delta B)_{Data} = -1.32$ Mc.

$(\Delta A - \Delta B)_{Cal} = -1.35$ Mc.

TABLE II

ROTATIONAL SPECTRUM OF CHD_2CHO (in Mc)

Transition	Frequency (Symmetrical)	Frequency (Asymmetrical)	Splitting	Calculated Splitting
$0_{00} - 1_{01}$	16,953.90			
			-409.5	-421
		17,363.35		
$1_{01} - 2_{02}$		34,706.02		
			-1.3	-0.87
		34,707.32		
$5_{15} - 5_{14}$		14,827.5		
			-11.6	-10.1
		14,839.05		
$6_{16} - 6_{15}$		20,746.48		
			-14.72	-14.1
		20,761.20		
$7_{17} - 7_{16}$	16,926.85			
			-10,718	-10,612
		27,634.90		
			-20.11	-18.8
		27,655.01		

$(\Delta A - \Delta B)_{Data} = -7.30 \times 10^{-1}$ Mc.

$(\Delta A - \Delta B)_{Cal} = -6.72 \times 10^{-1}$ Mc.

symmetrical configuration, or to the torsional state 0_o. The splitting of these latter two lines is quite sensitive to the barrier hindering the internal motion.

The transitions which have been reported and are listed in Tables I and II are of two types: 1) from one of the K = 1 Wang doublets to the other, $\Delta J = 0$; or 2) $\Delta J = 1$, K = 0 in the Wang representation. The theoretical splittings for these transitions have been calculated accurately by the following method. First the cross terms in P_yP_z were removed by a rotation of axes with new coefficients B and C for P_y^2 and P_z^2 respectively. Although the coefficient of $P_yP_z + P_zP_y$ is different for the substates 0_+ and 0_-, the same rotation of axes is applied to the two states. Then a small term is left for each state but contributes a negligable amount to the splitting. Then the coefficients of $P_xP_y + P_yP_x$ and $P_xP_z + P_zP_x$ were calculated in this new representation and will be D and E respectively. Finally these terms connecting the states 0_+ and 0_- were removed by a perturbation calculation.

The resulting equations, which are similar to Eq. (3-25), are

$$(0_+|E|0_+) = AP_x^2 + BP_y^2 + CP_z^2 + E_+ \tag{3-27}$$

$$(0_-|E|0_-) = (A + \Delta A)P_x^2 + (B + \Delta B)P_y^2 + (C + \Delta C)P_z^2 + E_+ + \delta$$

$$(0_+|E|0_-) = D(P_xP_y + P_yP_x) + E(P_zP_y + P_yP_z) + MP_x + NP_y + QP_z$$

where $\Delta A = A_- - A_+$, (Eq. (3-25)), $\delta = E_- - E_+$, etc.

For an asymmetric top the rotational matrix is of the form

$$E = AP_x^2 + BP_y^2 + CP_z^2, \tag{3-28a}$$

with matrix elements in the symmetric top representation are

$$(K|E|K) = \frac{1}{2}(A+B)\,J(J+1) + MK^2 \tag{3-28b}$$

$$(K|E|K\pm2) = -\frac{1}{4}(A-B)\left[J(J+1) - K(K\pm1)\right]^{\frac{1}{2}}\left[J(J+1) - (K\pm1)(K\pm2)\right]^{\frac{1}{2}}$$

$$M = C - \frac{1}{2}(A+B).$$

The transformation to the Wang representation removes the degeneracy of the K = 1, -1 levels, such that

$$(K=1_+|E|K=1_+) = \frac{1}{2}(A+B)\,J(J+1) + M - \frac{1}{4}(A-B)\,J(J+1)$$

$$(K=1_-|E|K=1_-) = \frac{1}{2}(A+B)\,J(J+1) + M + \frac{1}{4}(A-B)\,J(J+1) \tag{3-29}$$

$$(K=1_+|E|K=1_-) = 0.$$

and for K = 0

$$(K=0|E|K=0) = \frac{1}{2}(A+B)\,J(J+1). \tag{3-30}$$

The A, B, C in these equations may be either those of the 0_+ or 0_- states in Eqs. (3-27).

The matrix elements of $P_xP_y + P_yP_x$ and $P_xP_z + P_zP_x$ when the torsional states are 0_+, 0_- and the rotational states are in the Wang representation are

$$(0_+,K=0|P_xP_z + P_zP_x|0_-,K=1_+) = 0$$

$$(0_+,K=0|P_xP_z + P_zP_x|0_-,K=1_-) = \frac{1}{\sqrt{2}}\left[J(J+1)\right]^{\frac{1}{2}} \tag{3-31}$$

$$(0_+,K=1_-|P_xP_y + P_yP_x|0_-,K=1_+) = \frac{-i}{2}J(J+1).$$

Also, the energy differences, in the representation specified above, which are necessary for the perturbation calculation are

$$E(0_+,K=0;\ 0_-,K=1_+) = -\delta - M - \Delta M + \frac{1}{4}(A-B)\,J(J+1)$$

$$E(0_+,K=0;\ 0_-,K=1_-) = -\delta - M - \Delta M - \frac{1}{4}(A-B)\,J(J+1)$$

$$E(0_+,K=1_-;\ 0_-,K=1_+) = -\delta + \frac{1}{2}(A-B)\,J(J+1)$$

$$E(0_+,K=1_+;\ 0_-,K=1_-) = -\delta - \frac{1}{2}(A-B)\,J(J+1) \qquad (3\text{-}32)$$

$$E(0_+,K=1_+;\ 0_-,K=0) = -\delta + M - \Delta M - \frac{1}{4}(A-B)\,J(J+1)$$

$$E(0_+,K=1_-;\ 0_-,K=0) = -\delta + M - \Delta M + \frac{1}{4}(A-B)\,J(J+1)$$

$$\Delta M = \Delta C - \frac{1}{2}(\Delta A + \Delta B).$$

The results of the perturbation calculation are

$$E(0_+,K=0) = \frac{1}{2}(A+B)\,J(J+1) - \frac{E^2}{2M}J(J+1)\left[1 - \frac{\delta+\Delta M}{M} - \frac{(A-B)\,J(J+1)}{4M}\right] \qquad (3\text{-}33a)$$

$$E(0_-,K=0) = \frac{1}{2}(A+B)\,J(J+1) + \frac{1}{2}(\Delta A + \Delta B)\,J(J+1) - \frac{E^2}{2M}J(J+1)\left[1 + \frac{\delta+\Delta M}{M} - \frac{(A-B)\,J(J+1)}{4M}\right] \qquad (3\text{-}33b)$$

$$E(0_-,K=1_-) = \frac{1}{2}(A+B)\,J(J+1) + M + \frac{1}{4}(A-B)\,J(J+1) + \frac{1}{2}(\Delta A + \Delta B)\,J(J+1) + \Delta M + \frac{1}{4}(\Delta A - \Delta B)\,J(J+1) + \frac{E^2}{2M}\left[1 - \frac{\delta+\Delta M}{M} - \frac{(A-B)\,J(J+1)}{4M}\right]J(J+1) + \frac{D^2}{8}(A-B)^{-1}\,J(J+1)\left[1 - \frac{2\delta}{(A-B)\,J(J+1)} + \frac{\Delta B}{A-B}\right] \qquad (3\text{-}33c)$$

$$E(0_-,K=1_+) = \frac{1}{2}(A+B)\,J(J+1) + M - \frac{1}{4}(A-B)\,J(J+1) + \frac{1}{2}(\Delta A + \Delta B)\,J(J+1) + \Delta M - \frac{1}{4}(\Delta A - \Delta B)\,J(J+1) - \qquad (3\text{-}33d)$$

$$- \frac{D^2}{8} (A-B)^{-1} J(J+1) \left[1 + \frac{2\delta}{(A-B)\ J(J+1)} + \frac{\Delta B}{A-B} \right]$$

$$E(0_+,K=1_-) = \frac{1}{2} (A+B)\ J(J+1) + M + \frac{1}{4} (A-B)\ J(J+1)$$

$$+ \frac{E^2}{2M} J(J+1) \left[1 + \frac{\delta + M}{M} - \frac{(A-B)\ J(J+1)}{4M} \right] \qquad (3\text{-}33e)$$

$$+ \frac{D^2}{8} (A-B)^{-1} J(J+1) \left[1 + \frac{2\delta}{(A-B)\ J(J+1)} - \frac{\Delta B}{A-B} \right]$$

$$E(0_+,K=1_+) = \frac{1}{2} (A+B)\ J(J+1) + M - \frac{1}{4} (A-B)\ J(J+1)$$

$$- \frac{D^2}{8} (A-B)^{-1} J(J+1) \left[1 - \frac{2\delta}{(A-B)\ J(J+1)} - \frac{\Delta B}{A-B} \right] \qquad (3\text{-}33f)$$

The terms which are linear in P_z connect the 0_- and 0_o substates. These may be removed by second order perturbation theory; Δ will be the separation of these states. Also 0_+ and 0_- are connected by the torsional equation; we have $(0_o\ H_T\ 0_+) = \frac{1}{\sqrt{2}}\ \delta$. The calculation is similar to those listed above for the 0_- and 0_+ blocks, and the results are given in Eq. (3-35).

The splitting for the transition from one K = 1 Wang doublet to the other is

$$E(0_-,K=1_-) - E(0_-,K=1_+) - E(0_+,K=1_-) - E(0_+,K=1_+) \qquad (3\text{-}34)$$

which is equal to

$$\frac{1}{2} J(J+1) \left\{ (\Delta A - \Delta B) - \frac{2E^2}{M} \frac{\delta + \Delta M}{M} + \frac{D^2}{2} (A-B)^{-1} \frac{\Delta B}{A-B} \right.$$

$$- \frac{2}{3} \left[(A_- - B_-) + (A_o - B_o) \right] \left(\frac{Q}{\Delta + \Delta M} \right)^2 \qquad (3\text{-}35)$$

$$\left. + \frac{1}{4} \left[(A_- - B_-) - (A_o - B_o) \right] \left(\frac{\delta}{\Delta + \Delta M} \right)^2 \right\} .$$

The dominating terms are the first and second; the last contributes a negligible amount. Then for the transition $\Delta J = 1$, $K = 0$ the splitting is

$$(J+1)\left[(\Delta A + \Delta B) - \frac{2E^2}{M}\frac{\delta+\Delta M}{M}\right]. \tag{3-36}$$

For the splittings calculated in Table I (CH_2DCOH) it has been assumed that $V = 413\ cm^{-1}$, $s = 29$, with the result

$$\begin{aligned}
&\Delta A = -0.06\ Mc.\\
&\Delta B = -2.10\ Mc.\\
&\frac{E^2}{M}\frac{\delta+\Delta M}{M} = 3.4 \times 10^{-1}\ Mc.\\
&\frac{2}{3}\left[(A_- - B_-) + (A_o - B_o)\right]\left(\frac{Q}{\Delta+M}\right)^2 = -3.16 \times 10^{-2}\ Mc.\\
&\frac{1}{4}\left[(A_- - B_-) - (A_o - B_o)\right]\left(\frac{\delta}{\Delta+\Delta M}\right)^2 = 6.3 \times 10^{-3}\ Mc.
\end{aligned} \tag{3-37}$$

Then for CD_2HCOH it has been assumed that $V = 380\ cm^{-1}$, $s = 29$, with the result

$$\begin{aligned}
&\Delta A = \text{negligible}\\
&\Delta B = -7.01 \times 10^{-1}\ Mc.\\
&\frac{E^2}{M}\frac{\delta+\Delta M}{M} = 1.7 \times 10^{-1}\ Mc.\\
&\frac{2}{3}\left[(A_- - B_-) + (A_o - B_o)\right]\left(\frac{Q}{\Delta+\Delta M}\right)^2 = -1.6 \times 10^{-1}\ Mc.\\
&\frac{1}{4}\left[(A_- - B_-) - (A_o - B_o)\right]\left(\frac{\delta}{\Delta+\Delta M}\right)^2 = -2.8 \times 10^{-2}\ Mc.
\end{aligned}$$

The difference in energy between the symmetrical and the asymmetrical configurations depends primarily on the difference in rotational constants at infinite barrier. For this case we have

CH_2DCOH	CD_2HCOH
$\Delta A = 47\ Mc.$	$\Delta A = -21\ Mc.$

$\Delta B = 456$ $\Delta B = -400$

$\Delta C = -3{,}699$ $\Delta C = 2{,}761$

These results are also reported in Tables I and II.

Conclusions

The results of the previous section show that the theory adequately explains the splitting of the spectral lines for CH_2DCOH and CD_2HCOH with the quantitative features of the calculation being acceptable. The value for the potential barrier is in good agreement with that determined for the other species of acetaldehyde. The splitting of the asymmetric lines is quite sensitive to the potential hindering the internal motion, while the difference in frequency of the symmetrical and asymmetrical lines depends more on the structure of the molecule.

The theory developed in this chapter is also applicable to molecules such as halogenated ethanes, etc., where the internal rotor is not a symmetric top. Of course for these molecules a more general potential energy would need to be assumed, but it is quite possible that this feature could be handled in a satisfactory manner.

CHAPTER IV

APPLICATION OF THE GENERAL THEORY TO BENZALDEHYDE

In this chapter the theory of internal rotation will be applied to molecules which have a structure similar to C_6H_5COH. The results for benzaldehyde are not conclusive. One difficulty is that this is the first molecule of this type (benzene derivative) in which it has been attempted to study internal rotation. Another is due to the limited spectral information that is available. Even so it is worthwhile to discuss the general theory on the basis that 1) more of the spectrum might be assigned and 2) some of the limiting features of the theory become evident.

There are two ways to formulate the problem within the framework of the theory developed earlier:

1. The benzene ring as the frame. At first sight this appears to be the best method for formulation because the top is so much lighter than the frame. The perturbation theory would converge rapidly and the angular dependence of the rotational constants is small. The difficulty is the non-equivalent configurations of the molecule when the top is rotated through 180°, which results in a mixing of the torsional substates in a manner similar to that for CH_2DCOH through the cross-terms P_xP_z and P_xP_y. For benzaldehyde, though, the correction is larger.

2. The aldehyde group as the frame. The chief advantage is that

the two torsional substates are not mixed through the torsional-rotational interaction - the molecule is invarient under a rotation of the benzene ring through 180°. The over-whelming disadvantage is the slow convergence (or even non-convergence) of the perturbation theory. The top contains such a large portion of the energy that too much of the rotational energy is contained in the rotational-torsional interaction. For an exceptionally high barrier it might be feasible to use this approach.

Under these circumstances then, the first procedure appears to be best. The modification of the theory in Chapters I and II is a simplifying feature: $\eta_y = 0$, Eq. (1-6,7,8,11,12), since the center of mass of the frame lies on the bond axis.

Molecular Structure

The molecular structure of benzaldehyde is not known; therefore some plausible structure must be assumed for this calculation. The structural parameters for the ring are assumed to be the same as those for benzene, and the aldehyde parameters similar to acetaldehyde. It is hoped that the splitting of the spectral lines is not so sensitive to the molecular structure as the actual frequency of the line. The assumed molecular structure is given in Appendix II.

Rotational Constants

The functional form of the moments of inertia is

$$\begin{aligned} (I_{CM})_{xx} &= (I_{CM})_{xx}^{(o)} + (I_{CM})_{xx}^{(2)} \sin^2\alpha \\ (I_{CM})_{yy} &= (I_{CM})_{yy}^{(o)} + (I_{CM})_{yy}^{(2)} \sin^2\alpha \\ (I_{CM})_{zz} &= (I_{CM})_{zz}^{(o)} \end{aligned} \qquad (4\text{-}1)$$

$$(I_{CM})_{xy} = (I_{CM})^{(1)}_{xy} \sin\alpha \quad \cos\alpha$$

$$(I_{CM})_{xz} = (I_{CM})^{(o)}_{xz} \sin\alpha \tag{4-1}$$

$$(I_{CM})_{yz} = (I_{CM})^{(o)}_{yz} \cos\alpha \ .$$

The effective moments of inertia, Eqs. (1-15,16,17,18) are

$$I_{xx} = (I_{CM})^{(o)}_{xx} + \left[(I_{CM})^{(2)}_{xx} - \frac{I'^2_x}{I'_z} \right] \sin^2\alpha$$

$$I_{yy} = (I_{CM})^{(o)}_{yy} - \frac{I'^2_y}{I'_z} + \left[(I_{CM})^{(2)}_{yy} + \frac{I'^2_y}{I'_z} \right] \sin^2\alpha \tag{4-2}$$

$$I_{zz} = (I_{CM})^{(o)}_{zz} - I'_z$$

$$I_{xy} = \left[(I_{CM})^{(o)}_{xy} - \frac{I'_x I'_y}{I'_z} \right] \sin\alpha \quad \cos\alpha$$

$$I_{xz} = I_{yz} = 0.$$

Then the result of the transformation to the μ_{ij} is

$$\mu_{xx} = \mu^{(o)}_{xx} + \mu^{(2)}_{xx} \sin^2\alpha + \mu^{(4)}_{xx} \sin^4\alpha + \mu^{(6)}_{xx} \sin^6\alpha + \cdots$$

$$\mu_{yy} = \sum_{n=o} \mu^{(2n)}_{yy} \sin^{2n}\alpha$$

$$\mu_{zz} = \mu^{(o)}_{zz} \tag{4-3}$$

$$\mu_{xy} = \sum \mu^{(2n+1)}_{xy} \sin^{2n+1}\alpha \quad \cos\alpha$$

$$\mu_{xz} = \mu_{yz} = 0.$$

The convergence of the series is much slower than for CH_2DCOH: here

$$\mu^{2n+2} \sim 1.5 \times 10^{-1} \mu^{2n} \ , \tag{4-4}$$

therefore it is necessary to include terms through $\mu_{ij}^{(6)}$. The numerical values for all coefficients are found in Appendix II.

The Torsional Equation

The general form of the torsional equation is found in Chapter II, Eq. (2-4),

$$H_T = g^{-\frac{1}{4}} \sum_{ij} p_i \mu_{ij} g^{\frac{1}{2}} p_j g^{-\frac{1}{4}} + g^{-\frac{1}{4}} \mu p g^{\frac{1}{2}} p g^{-\frac{1}{4}} + V_2 \sin^2\alpha \tag{4-5}$$

$$p_x = \frac{I_x'}{I_z'} (\sin\alpha\, p + p \sin\alpha) \qquad p_y = \frac{-I_y'}{I_z'} (\cos\alpha\, p + p \cos\alpha)$$

$$p_z = p \qquad p = -i \frac{\partial}{\partial\alpha} \tag{4-6}$$

$$\mu = \frac{1}{2I_z'} \qquad g = g^{(o)} + g^{(2)} \sin^2\alpha$$

and the μ_{ij} are defined in Eq. (4-3). Expansion of the sum in Eq. (4-5) results in

$$H_T = \mu_T^{(o)} p^2 + \mu_T^{(2)} (\sin^2\alpha\, p^2 + p^2 \sin^2\alpha) + \mu_T^{(4)} (\sin^4\alpha\, p^2 + p^2 \sin^4\alpha) + \mu_T^{(6)} (\sin^6\alpha\, p^2 + p^2 \sin^6\alpha) + V_2 \sin^2\alpha \tag{4-7}$$

where

$$\mu_T^{(o)} = \mu_{zz}^{(o)} + \mu + \left(\frac{I_y'}{I_z'}\right)^2 \mu_{yy}^{(o)}$$

$$\mu_T^{(2)} = \left[\mu_{xx}^{(o)} - 2\mu_{xy}^{(o)} + \mu_{yy}^{(2)}\right] \left(\frac{I_x'}{I_z'}\right)^2 \tag{4-8}$$

$$\mu_T^{(4)} = -R\mu_T^{(2)} \qquad \mu_T^{(6)} = R^2 \mu_T^{(2)}$$

The ratio $g^{(2)}/g^{(o)}$ occurs often in the formulation so it has been defined as the parameter

$$R = g^{(2)}/g^{(o)} \tag{4-9}$$

It is convenient to separate H_T into two parts

$$H_T^o = \mu_T^{(o)} p^2 + V_2 \sin^2\alpha \tag{4-10}$$

$$H_T' = \sum (-1)^n R^n \mu_T^{(2n+2)} (\sin^{2n+2}\alpha \; p^2 + p^2 \sin^{2n+2}\alpha \;). \tag{4-11}$$

When Eq. (4-10) is written as a differential equation it has the form

$$\left[-\mu_T^{(o)} \frac{d^2}{d\alpha^2} + V_2 \sin^2\alpha - E \right] U(\alpha) = 0. \tag{4-12}$$

The solutions of Eq. (4-12) are well known and have been extensively tabulated (18). They have the form

$$\begin{aligned}
U_{e_{2r}}(s,\alpha) &= \sum_{K=0} D_{e_{2K}}^{e_{2r}} (-1)^K \cos 2K\alpha && \text{A species} \\
U_{o_{2r}}(s,\alpha) &= \sum_{K=0} D_{o_{2K}}^{o_{2r}} (-1)^K \sin 2K\alpha && \text{A species} \\
U_{o_{2r+1}}(s,\alpha) &= \sum_{K=0} D_{o_{2K+1}}^{o_{2r+1}} (-1)^K \cos (2K+1)\alpha && \text{B species} \\
U_{e_{2r+1}}(s,\alpha) &= \sum_{K=0} D_{e_{2K+1}}^{e_{2r+1}} (-1)^{K+1} \sin (2K+1)\alpha && \text{B species}
\end{aligned} \tag{4-13}$$

The first few eigenvalues are

$$b_{e_o}, \; b_{o_1}, \; b_{e_1}, \; b_{o_2}, \; b_{e_2}, \; b_{o_3} \quad \cdots \tag{4-14}$$

This notation is used in reference (18). The parameter s will be referred to as the barrier height parameter, defined as

$$s = \frac{V_2}{\mu_T^{(o)}} . \tag{4-15}$$

Then the b's are related to the energy eigenvalues as

$$b_n = \frac{E_n}{\mu_T^{(o)}} . \tag{4-16}$$

For a two-fold barrier it is convenient to speak of torsional states and substates. The torsional states will be labeled by the quantum number n; the substates will be either A or B. If n = 0, for example, then the notation would be 0_A and 0_B. If n is an even integer the A functions are the $U_{e_{2r}}$, the B functions, $U_{0_{2r+1}}$. If n is odd the other functions apply.

Now H_T', Eq. (4-11), will be considered a perturbation. The results of the perturbation are a new set of functions

$$\varphi_{nA}(\alpha) = \sum_K a_K U_{KA}(\alpha)$$
$$\varphi_{nB}(\alpha) = \sum_K a_K' U_{KB}(\alpha) \qquad (4\text{-}17)$$

with eigenvalues b_{nA}' and b_{nB}' respectively. These will be the torsional functions for consideration of the overall rotation-torsional interaction.

The solutions of Eq. (4-12) are tabulated only for s in the range $0 \leqslant s \leqslant 100$. For benzaldehyde s = 100 would correspond to a barrier height ~ 200 cm^{-1}. For higher barriers it is necessary to formulate the torsional functions in another manner (Appendix IV).

The Rotational Hamiltonian

The pure rotational part of the Hamiltonian is Eq. (2-3),

$$H_R = \mu_{xx}^{(o)} P_x^2 + \mu_{yy}^{(o)} P_y^2 + \mu_{zz}^{(o)} P_z^2 \qquad (4\text{-}18)$$

Note that $\mu_{ij}^{(o)}$ are not the rotational constants in the limit of a rigid molecule.

The Rotational Torsional Interaction

The Hamiltonian, H_{TR}, contains the interaction between the internal

and overall rotation. From Eqs. (2-5,6) we have

$$H_{TR} = \mu_{xx}(\alpha)\, P_x^2 + \mu_{yy}(\alpha)\, P_y^2 + \mu_{xy}(\alpha)(P_xP_y + P_yP_x) - \sum_{i,j}\left[\, 2\mu_{ij}\, p_i - (p_i \mu_{ij})\right] P_j \tag{4-19a}$$

which for C_6H_5COH becomes

$$\begin{aligned} H_{TR} = {} & \sum_{n=o} (-1)^n R^n \mu_{xx}^{(2)} \sin^{2n+2}\alpha \;\; P_x^2 + \sum_{n=o} (-1)^n R^n \mu_{yy}^{(2)} \sin^{2n+2}\alpha \;\; P_y^2 \\ & + \sum_{n=o} (-1)^n R^n \mu_{xy}^{(1)} \sin^{2n+1}\alpha \;\; \cos\alpha \;\; (P_xP_y + P_yP_x) \\ & - \frac{I_x'}{I_z'} (\mu_{xx}^{(o)} - \mu_{xy}^{(1)}) \sum_{n=o} (-1)^n R^n (\sin^{2n+1}\alpha \;\; p + p \sin^{2n+1}\alpha \;\;) \; P_x \\ & + \frac{I_x'}{I_z'} \mu_{yy}^{(o)} \sum_{n=o} (-1)^n R^n (\cos\alpha \sin^{2n}\alpha \;\; p + p \cos\alpha \sin^{2n}\alpha \;\;) \; P_y \end{aligned} \tag{4-19}$$

where

$$R = g^{(2)}/g^{(o)} \qquad \text{and} \qquad p = -i\frac{\partial}{\partial\alpha}$$

It is convenient to rewrite H_R and H_{TR} in a new notation

$$H_R = A^o P_x^2 + B^o P_y^2 + C^o P_z^2 \tag{4-20}$$

$$H_{TR} = A' P_x^2 + B' P_y^2 + D'(P_xP_y + P_yP_x) - M'P_x - N'P_y - Q'P_z \tag{4-21}$$

and the coefficients may be compared with those in Eqs. (4-17,19) for identification. The coefficients of P_i^2 and P_i in Eq. (4-21) are functions only of the internal coordinates, while the P_i^2 and P_i are functions of the Eulerian angles.

The Perturbation Calculation

In the same manner described in detail in Chapter III, the matrix

elements connecting different torsional states will be removed by a Van Vleck transformation. The basis for the perturbation is the product function

$$\Psi_{R,n}(R,\alpha) = \psi_R(R)\ \varphi_n(\alpha) \tag{4-22}$$

where the $\varphi_n(\alpha)$ are eigenfunctions of H_T, Eq. (4-7). Again it is not necessary to specify the representation of $\psi_R(R)$. The torsional substates, A and B, will be mixed through the perturbation calculation only by the cross term and its coefficient, $P_y P_z + P_z P_y$.

For a torsional state, n, the matrix has the following form after the Van Vleck transformation

$$\begin{aligned}
(n_A|H|n_A) &= A_A P_x^2 + B_A P_y^2 + C_A P_z^2 \\
(n_B|H|n_B) &= A_B P_x^2 + B_B P_y^2 + C_B P_z^2 + \delta \\
(n_A|H|n_B) &= F_{AB}(P_y P_z + P_z P_y) \\
\delta &= E_{n_A} - E_{n_B};
\end{aligned} \tag{4-23}$$

δ is the energy spacing of the two torsional substates n_A and n_B. The coefficients A_i (A_A or A_B), etc, have been calculated through third order perturbation theory and are

$$\begin{aligned}
A_i = A^o &+ (n_i|A'|n_i) + \sum \frac{(n_i|M'|m_j)(m_j|M'|n_i)}{\Delta E(n_i\ ;\ m_j)} \\
&- 2\sum \frac{(n_i|Q'|m_j)(m_j|D'|n_i)}{\Delta E(n_i\ ;\ m_j)} + (C^o - A^o)\sum \frac{(n_i|N'|m_j)(m_j|N'|n_i)}{\Delta E(n_i\ ;\ m_j)^2} \\
&+ (B_o - A_o)\sum \frac{(n_i|Q'|m_j)(m_j|Q'|n_i)}{\Delta E(n_i\ ;\ m_j)^2} - \sum \frac{(n_i|Q'|m_j)(m_j|M'|\ell_k)(\ell_k|N'|n_i)}{\Delta E(n_i;m_j)\ \Delta E(n_i;\ell_k)}\ .
\end{aligned} \tag{4-24}$$

$$- \sum \frac{(n_i|N|m_j)(m_j|Q|\ell_k)(\ell_k|M|n_i)}{\Delta E(n_i;m_j)\ \Delta E(n_i;\ell_k)} + \sum \frac{(n_i|Q'|m_j)(m_j|N'|\ell_k)(\ell_k|M'|n_i)}{\Delta E(n_i;m_j)\ \Delta E(n_i;\ell_k)}$$

$$B_i = B^o + (n_i|B'|n_i) + \sum \frac{(n_i|N'|m_j)(m_j|N'|n_i)}{\Delta E(n_i;m_j)} \tag{4-25}$$

$$+ 2\sum \frac{(n_i|Q'|m_j)(m_j|D'|n_i)}{\Delta E(n_i;m_j)} - (B_o - A_o)\sum \frac{(n_i|Q'|m_j)(m_j|Q'|n_i)}{\Delta E(n_i;m_j)^2}$$

$$+ (C_o - B_o)\sum \frac{(n_i|N'|m_j)(m_j|N'|n_i)}{\Delta E(n_i;m_j)^2} - \sum \frac{(n_i|Q'|m_j)(m_j|N'|\ell_k)(\ell_k|M'|n_i)}{\Delta E(n_i;m_j)\ \Delta E(n_i;\ell_k)}$$

$$- \sum \frac{(n_i|N'|m_j)(m_j|Q'|\ell_k)(\ell_k|M'|n_i)}{\Delta E(n_i;m_j)\ \Delta E(n_i;\ell_k)} + \sum \frac{(n_i|Q'|m_j)(m_j|M'|\ell_k)(\ell_k|N'|n_i)}{\Delta E(n_i;m_j)\ \Delta E(n_i;\ell_k)}$$

$$C_i = C^o + \sum \frac{(n_i|Q'|m_j)(m_j|Q'|n_i)}{\Delta E(n_i;m_j)} - (C_o - A_o)\sum \frac{(n_i|N'|m_j)(m_j|N'|n_i)}{\Delta E(n_i;m_j)^2} \tag{4-26}$$

$$- (C_o - B_o)\sum \frac{(n_i|M'|m_j)(m_j|M'|n_i)}{\Delta E(n_i;m_j)} + \sum \frac{(n_i|N'|m_j)(m_j|Q'|\ell_k)(\ell_k|M'|n_i)}{\Delta E(n_i;m_j)\ \Delta E(n_i;\ell_k)}$$

$$+ \sum \frac{(n_i|Q'|m_j)(m_j|N'|\ell_k)(\ell_k|M'|n_i)}{\Delta E(n_i;m_j)\ \Delta E(n_i;\ell_k)} + \sum \frac{(n_i|Q'|m_j)(m_j|M'|\ell_k)(\ell_k|N'|n_i)}{\Delta E(n_i;m_j)\ \Delta E(n_i;\ell_k)}$$

$$F_{AB} = \sum \frac{(n_A|Q'|m_j)(m_j|N'|n_B)}{\Delta E(n;m_j)} - \sum \frac{(n_A|N'|m_i)(m_i|D'|n_B)}{\Delta E(n;m_i)} \tag{4-27}$$

$$+ \sum \frac{(n_A|M'|m_j)(m_j|B'|n_B)}{\Delta E(n;m_j)} + \tfrac{1}{2}(A_o + B_o - 2C_o)\sum \frac{(n_A|Q'|m_i)(m_i|N'|n_B)}{\Delta E(n;m_i)^2}$$

$$- \sum \frac{(n_A|Q'|m_j)(m_j|Q'|\ell_k)(\ell_k|M'|n_B)}{\Delta E(n;m_j)\ \Delta E(n;\ell_k)} + \sum \frac{(n_A|N'|m_i)(m_i|N'|\ell_k)(\ell_k|M'|n_B)}{\Delta E(n;m_j)\ \Delta E(n;\ell_k)} .$$

The Microwave Rotational Spectrum of C_6H_5COH and Analysis

Some of the lines in the microwave rotational spectrum of C_6H_5COH have been observed. The identification and assignment was made by Kojima

(12,12a). All transitions are of the same type: $\Delta J = 1$, $\Delta K = 0$. A complete set of lines has been found for J = 6,7,8,9. The spectrum and its assignment are listed in Table III.

An important feature of the spectrum is the occurrence of a doublet for each transition. It is found that for a given J and high K the splitting is independent of K. If this splitting is expressed as a function of J, see Figure 4, the points lie on a straight line with slope equal to the extrapolated intercept. If it is assumed that each set of lines is approximately an asymmetric top spectrum, then for high K the splitting should be

$$(\Delta A + \Delta B)\ (J + 1). \tag{4-28}$$

From the spectrum we find

$$\Delta A + \Delta B = 2.4 \text{ Mc}. \tag{4-29}$$

Kojima has attempted to fit each set of transitions with a set of rotational constants. The spectrum for these constants is found in Table III, along with the values for the rotational constants. From this analysis he finds

$$\begin{aligned} \Delta A + \Delta B &= 2.6 \text{ Mc}. \\ \Delta A - \Delta B &= 1.2 \text{ Mc}. \\ \Delta C &= -21.7 \text{ Mc}. \end{aligned} \tag{4-30}$$

It should be noted that $\Delta A - \Delta B$ and ΔC depend quite sensitively on the Wang doublets K = 1, and these lines probably have the least certain assignment.

The theoretical considerations become complicated in the analysis when the fact that J is large is coupled with the mixing of the torsional states through the cross term $P_y P_z + P_z P_y$. The following procedure will

TABLE III

THE ROTATIONAL SPECTRUM OF C_6H_5COH (in Mc)

Transition	Observed Frequency	Splitting	Calculated Frequency
$6_{6,0} - 7_{7,0}$	18,255.7 18,274.3	18.6	18,255.6 18,274.6
$6_{6,1} - 7_{7,1}$	17,857.6 17,878.1	20.5	17,857.0 17,878.7
$6_{5,1} - 7_{6,1}$	20,240.9 20,254.2	13.3	20,241.6 20,254.3
$6_{5,2} - 7_{6,2}$	19,188.9 19,206.4	17.5	19,188.8 19,206.1
$6_{4,2} - 7_{5,2}$	20,311.5 20,326.9	15.4	20,311.1 20,326.7
$6_{4,3} - 7_{5,3}$	19,528.3 19,545.2	16.9	19,528.5 19,545.4*
$6_{3,3} - 7_{4,3}$	19,661.9 19,679.1	17.2	19,661.5 19,678.8
$6_{3,4} - 7_{4,4}$	19,506.1 19,523.3	17.2	19,506.1 19,523.2
$6_{2,4} - 7_{3,4}$	19,511.0 19,528.3	17.3	19,510.8 19,528.0
$6_{2,5} - 7_{3,5}$ $6_{1,5} - 7_{2,5}$	19,472.1 19,489.3	17.2	19,472.1 19,489.4
$6_{1,6} - 7_{2,6}$ $6_{0,6} - 7_{1,6}$	19,453.1 19,470.2	17.1	19,453.3 19,470.5
$7_{7,0} - 8_{8,0}$	20,637.8 20,660.2	22.4	20,637.7 20,660.2
$7_{7,1} - 8_{8,1}$	20,331.9 20,356.8	24.9	20,331.9 20,356.8
$7_{6,1} - 8_{7,1}$	22,951.1 22,966.3	15.2	22,951.1 22,966.3

TABLE III (continued)

Transition	Observed Frequency	Splitting	Calculated Frequency
$^{7}_{6,2} - {}^{8}_{7,2}$	21,849.2 21,869.2	20.0	21,849.2 21.869.1
$^{7}_{5,2} - {}^{8}_{6,2}$	23,350.2 23,367.3	17.1	23.350.2 23,367.3
$^{7}_{5,3} - {}^{8}_{6,3}$	22,331.5 22,350.6	19.1	22,331.5 22,350.8
$^{7}_{4,3} - {}^{8}_{5,3}$	22,588.6 22,608.4	19.8	22,588.6 22,608.4
$^{7}_{4,4} - {}^{8}_{5,4}$	22,322.9 22,342.5	19.6	22,323.0 22,342.6
$^{7}_{3,4} - {}^{8}_{4,4}$	22,336.1 22,355.5	19.4	22,336.0 22,355.6
$^{7}_{3,5} - {}^{8}_{4,5}$ $^{7}_{2,5} - {}^{8}_{3,5}$	22,275.2 22,294.6	19.4	22,275.0 22,294.5
$^{7}_{2,6} - {}^{8}_{3,6}$	22,246.7 22,266.3	19.6	22,246.7 22,266.4
$^{7}_{1,7} - {}^{8}_{2,7}$	22,230.1 22,249.6	19.5	22,230.0 22,249.7
$^{8}_{8,0} - {}^{9}_{9,0}$	23,010.5 23,036.4	25.9	23,010.4 23.036.6
$^{8}_{8,1} - {}^{9}_{9,1}$	22,789.6 22,817.8	28.2	22,789.8 22,818.0
$^{8}_{7,1} - {}^{9}_{8,1}$	25,576.7 25,593.9	17.2	25,577.0 25,594.1
$^{8}_{7,2} - {}^{9}_{8,2}$	24,479.8 24,502.3	22.5	24,480.0 24,502.5
$^{8}_{6,2} - {}^{9}_{7,2}$	26,359.5 26,377.8	18.3	26,360.0 26,377.9
$^{8}_{6,3} - {}^{9}_{7,3}$	25,126.1 25,147.6	21.5	25,126.3 25,147.9

TABLE III (continued)

Transition	Observed Frequency	Splitting	Calculated Frequency
$8_{5,3} - 9_{6,3}$	25,574.1 25,596.0	21.9	25,574.4 25,596.6
$8_{5,4} - 9_{6,4}$	25,149.4 25,171.0	21.6	25,149.5 25,171.5
$8_{4,4} - 9_{5,4}$	25,179.8 25,202.5	21.7	25,180.1 25,202.2
$8_{4,5} - 9_{5,5}$ $8_{3,5} - 9_{4,5}$	25,086.2 25,108.3	22.1	25,086.3 25,108.0
$8_{3,6} - 9_{4,6}$ $8_{2,6} - 9_{3,6}$	25,045.8 25,067.8	22.0	25,046.0 25,068.1
$8_{2,7} - 9_{3,7}$ $8_{1,7} - 9_{2,7}$	25,021.9 25,044.0	22.1	25,022.0 25,044.3
$8_{1,8} - 9_{2,8}$ $8_{0,8} - 9_{1,8}$	25,006.7 25,028.8	22.1	25,007.0 25,029.1
$9_{9,0} - 10_{10,0}$	25,385.5 25,415.7	30.2	25,385.7 25,415.8
$9_{9,1} - 10_{10,1}$	25,233.4 25,265.0	31.6	25,234.1 25,265.3
$9_{8,1} - 10_{9,1}$	28,112.5 28,131.8	19.3	28,112.9 28,132.2
$9_{8,2} - 10_{9,2}$	27,079.6 27,104.7	25.1	27,079.8 27,105.0
$9_{7,2} - 10_{8,2}$	29,318.1 29,337.8	19.7	29,318.5 29,338.0
$9_{7,3} - 10_{8,3}$	27,906.4 27,930.5	24.1	27,906.8 27,930.6
$9_{6,3} - 10_{7,3}$	28,620.8 28,645.2	24.4	28,620.9 28,645.4
$9_{6,4} - 10_{7,4}$	27,984.1 28,008.5	24.4	27,984.1 28,008.5

TABLE III (concluded)

Transition	Observed Frequency	Splitting	Calculated Frequency
$9_{5,4} - 10_{6,4}$	28,048.8 28,073.4	24.6	28,049.2 28,073.8
$9_{5,5} - 10_{6,5}$	27,906.1 27,930.7	24.6	27,906.1 27,930.7
$9_{4,5} - 10_{5,5}$	27,908.0 27,932.4	24.4	27,908.7 27,933.3
$9_{4,6} - 10_{5,6}$ $9_{3,6} - 10_{4,6}$	27,851.5 27,876.1	24.6	27,851.7 27,876.3
$9_{3,7} - 10_{4,7}$ $9_{2,7} - 10_{3,7}$	27,818.9 27,843.4	24.5	27,819.1 27,843.7
$9_{2,8} - 10_{3,8}$ $9_{1,8} - 10_{2,8}$	27,798.0 27,822.6	24.6	27,798.2 27,822.8
$9_{1,9} - 10_{2,9}$ $9_{0,9} - 10_{1,9}$	27,783.6 27,808.5	24.9	27,784.1 27,808.7

EMPIRICAL ROTATIONAL CONSTANTS

Lower	Higher
A = 1204.7	A = 1206.5
B = 1564.3	B = 1564.9
C = 5235.2	C = 5213.9
K = 0.82157	K = 0.82112

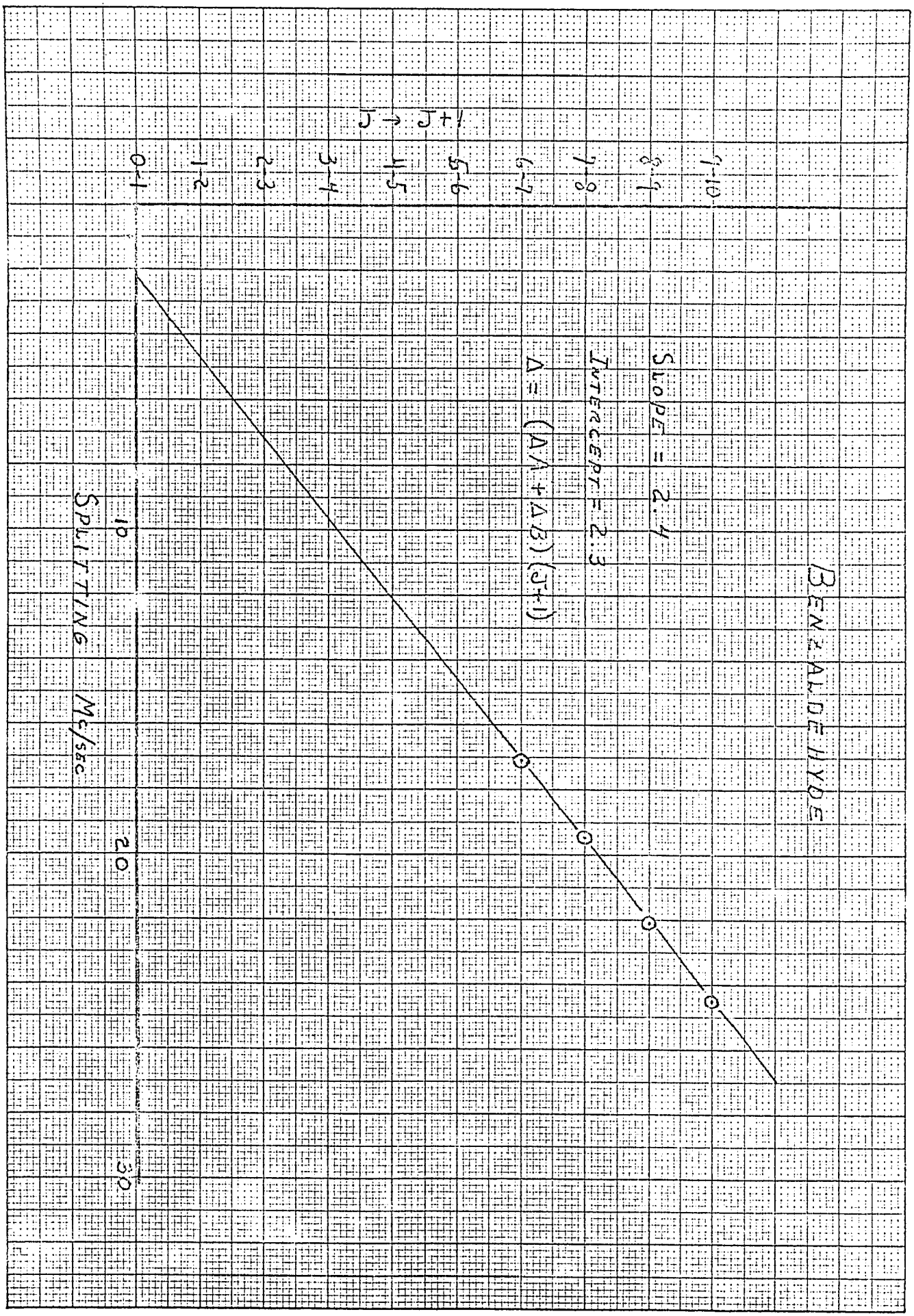

BENZALDEHYDE
SLOPE = 2.4
INTERCEPT = 2.3
Δ = (A/λ + Δ B) (J+1)
J → J+1
10
SPLITTING
MC/SEC
20
30

Figure 4

be applicable to obtain the splitting of the high K doublets. The method is similar to that used in Chapter III for the cross-terms $P_xP_z + P_zP_x$ and $P_xP_y + P_yP_x$. Eqs. (4-23) may be rewritten in the form

$$\begin{aligned}
(O_A|H|O_A) &= AP_x^2 + BP_y^2 + CP_z^2 \\
(O_B|H|O_B) &= (A+\Delta A)P_x^2 + (B+\Delta B)P_y^2 + (C+\Delta C)P_z^2 + \delta \\
(O_A|H|O_B) &= F(P_yP_z + P_zP_y)
\end{aligned} \tag{4-31}$$

where $\Delta A = A_B - A_A$ and δ is the splitting of the torsional substates.

The matrix elements of $P_yP_z + P_zP_y$ in this representation are

$$\begin{aligned}
(O_A,K|P_yP_z + P_zP_y|O_B,K+1) &= -\frac{i}{2}(2K+1)\left[J(J+1) - K(K+1)\right]^{\frac{1}{2}} \\
(O_A,K|P_yP_z + P_zP_y|O_B,K-1) &= \frac{i}{2}(2K-1)\left[J(J+1) - K(K-1)\right]^{\frac{1}{2}}
\end{aligned} \tag{4-32}$$

The energy differences which are necessary in the perturbation calculation are

$$\begin{aligned}
E(O_B,K;\ O_A,K+1) &= \delta - (M+\Delta M)(2K+1) \\
E(O_B,K;\ O_A,K-1) &= \delta + (M+\Delta M)(2K-1)
\end{aligned} \tag{4-33}$$

$$\begin{aligned}
E(O_A,K;\ O_B,K+1) &= -\delta - (M-\Delta M)(2K+1) \\
E(O_A,K;\ O_B,K-1) &= -\delta + (M-\Delta M)(2K-1).
\end{aligned} \tag{4-33}$$

where δ is the splitting of the torsional substates, $M = C - \frac{1}{2}(A+B)$ and $\Delta M = \Delta C - \frac{1}{2}(\Delta A + \Delta B)$. For an estimation of the relative size of M and δ we find

$$\delta \sim 10^{-3} M, \tag{4-33a}$$

therefore an expansion in $\frac{\delta}{M}$ is convenient for the perturbation

correction. Finally the corrections to the energy are

$$(O_A,K|E'|O_A,K) = -\frac{F^2}{2M}\left[J(J+1)-3K^2\right] + \frac{F^2}{2M}\,\frac{\delta-\Delta M}{M}\left[J(J+1)-K(K+1)\right]$$
$$(O_B,K|E'|O_B,K) = -\frac{F^2}{2M}\left[J(J+1)-3K^2\right] - \frac{F^2}{2M}\,\frac{\delta-\Delta M}{M}\left[J(J+1)-K(K+1)\right]. \qquad (4\text{-}34)$$

When Eqs. (4-31,34) are combined, the result for the splitting of the high K states for the transition $\Delta J = 1$, $\Delta K = 0$ is

$$\left[(\Delta A + \Delta B) - \frac{F^2}{M}\cdot\frac{\delta-\Delta M}{M}\right](J+1). \qquad (4\text{-}35)$$

If it is assumed that s = 31, which corresponds to a barrier height V = 59 cm^{-1}, then the theoretical result for the parameters is

$$\begin{aligned} \Delta A &= -\ 8.1234 \times 10^{-1}\ \text{Mc.} \\ \Delta B &=\ \ 1.7416 \times 10^{-1}\ \text{Mc.} \\ \delta &=\ \ 5.9986 \times 10^{-2}\ \text{Mc.} \\ \frac{F^2}{M^2} &= 1.922\ \text{Mc.} \end{aligned} \qquad (4\text{-}36)$$

which gives for the coefficient of J + 1

$$2.56\ \text{Mc.} \qquad (4\text{-}36a)$$

This result compares favorably with the empirical value of 2.4 Mc., Eq. (4-29).

At this point it is worthwhile to mention the effect of H_T', Eq. (4-11), on the splitting. If we neglect this torsional correction all Δ's in Eq. (3-36) are approximately 30% larger, which has an effect of changing the barrier height about 10%. If H_T' is neglected we obtain a value of s = 34 and V_2 = 65 cm^{-1} for the barrier height.

The Case for a High Barrier

The theoretical barrier obtained in the last section is quite low.

One would expect a value much higher from the double bond character of the C-C bond connecting the top and frame. Also there is another consideration. A comparison of the potential barriers for CH_3COH and CH_3OH shows that they have about the same height ~ 400 cm^{-1}. One would expect that possibly a similar comparison might be made for benzaldehyde and phenol. Kojima (13) has estimated the barrier of phenol at around 1100 cm^{-1}, and on this basis one would expect about the same value for C_6H_5COH. This is contrary to the barrier of 60 cm^{-1} calculated in the last section.

One thing is certain; if the barrier is around 1000 cm^{-1} then the assumption that the doublets are due to different torsional substates is incorrect. One set of lines must correspond to an excited torsional state. For molecules with a symmetric top internal rotor it has been found that the assumption of a rigid molecule is <u>not</u> sufficient to explain the shift in the spectral lines for the excited torsional states - interaction with other vibrational modes must be taken into account. The theory for this interaction has been formulated and applied from a parametric approach by Kivelson (7,8,9,10,11) and by Swan and Strandberg (17). Also a simpler treatment has been worked out by Swalen (15) which we will use to estimate this effect.

The change in rotational constant due to interaction with other vibrations is

$$\begin{aligned} B_n &= B^o - \alpha_B(n + \tfrac{1}{2}) \\ A_n &= A^o - \alpha_A(n + \tfrac{1}{2}) \end{aligned} \qquad (4\text{-}37)$$

Now

$$\alpha_A \sim \frac{(A^o)^2}{h \nu_T} \qquad \alpha_B \sim \frac{(B^o)^2}{h \nu_T} \qquad (4\text{-}38)$$

where ν_T is the torsional frequency

$$h\nu_T = 2\mu_T \left(\frac{V_2}{\mu_T}\right)^{\frac{1}{2}} = 2\mu_T (s)^{\frac{1}{2}} \tag{4-39}$$

For C_6H_5COH

$$A^o \sim 1.2 \times 10^3 \text{ Mc.} \qquad B^o \sim 1.5 \times 10^3 \text{ Mc.}$$
$$\mu_T \sim 5.7 \times 10^4 \text{ Mc.} \tag{4-40}$$

from which it follows

$$\frac{(A^o)^2}{2\mu_T} \sim 1.2 \times 10 \text{ Mc.} \qquad \frac{(B^o)^2}{2\mu_T} \sim 2 \times 10 \text{ Mc.} \tag{4-41}$$

so that for

$s = 100$	$s = 1000$
$\Delta A + \Delta B = 3.2$ Mc.	$\Delta A + \Delta B = 1$ Mc.

(4-42)

Therefore for the Kilvelson effect to account for all of the splitting the barrier height would be about 300 cm^{-1}.

So far the splitting from internal rotation has been neglected. The functional form of the Hamiltonian and method of approach is in Appendix IV. The results of the calculation would be

$s = 100$	$s = 1000$
$\Delta A = 3.0$ Mc.	$\Delta A = 0.8$ Mc.
$\Delta B = -3.0$ Mc.	$\Delta B = -0.8$ Mc.

so that

$$\Delta A + \Delta B = 0.$$

Therefore for excited torsional states the splitting would be due entirely to the Kilvelson effect and the potential barrier is still not as high as one would expect.

Conclusions

The results for C_6H_5COH are not nearly as conclusive as for CH_2DCOH and CD_2HCOH. The low potential barrier is almost impossible to explain. There are two alternatives which might be worthwhile to try.

1. Obtain the spectrum of a deuterated species of benzaldehyde, for example C_6H_5COD. If the splitting is due to different torsional substates then we should be able to obtain the same barrier as that for C_6H_5COH.

2. Obtain more of the spectrum of C_6H_5COH, but with possibly different selection rules. Some transitions might be more dependent upon one parameter than another. If the high barrier solution is real, then the spectrum for more torsional states must be obtained to determine the barrier height.

Essentially we have shown that it is possible to develop and apply a theory of internal rotation for asymmetric internal rotors. The procedure from here would seem to be to obtain the spectrum and barrier heights for more molecules of this type.

CHAPTER V

A NOTE ON THE PARAMAGNETIC SUSCEPTIBILITY OF V^{+++} IN CORUNDUM

Earlier the author formulated a theory for the paramagnetic susceptibility of vanadium, V^{+++}, in corundum crystals (4) and found that susceptibility data would provide a good means of determining certain structural parameters and ionic constants for the crystal. But at that time no measurements had been made of the susceptibility. Lately, however, measurements have been made for the temperature range 77° to $295^{o}K$ by Brumage (1,1a,5), so that quantitative results may be obtained. Also some simplifications of the theory have become apparent and will be presented in detail. This section essentially replaced everything from page 49 on in reference (4).

The Hamiltonian

The Hamiltonian operator describing the behavior of the $(d)^2$ electrons of V^{+++} in 1) the crystal Al_2O_3 which has trigonal symmetry and 2) an external applied magnetic field is

$$H = H^{o} + H' \tag{1}$$

$$H' = \lambda \underline{L} \cdot \underline{S} + (\underline{L} + g\,\underline{S}) \cdot \underline{\mathcal{H}} \tag{2}$$

where H^{o} contains all crystalline and atomic energy terms except those included in H'. The basic functions of H^{o} will be found on pages 17,21, 28 of reference (4). The cubic crystalline potential splits ^3F of $(d)^2$

into $^3T_1$, $^3T_2$, and $^3A_2$ levels whose separation is quite large ($\sim$20,000 cm^{-1}). The small trigonal component further splits the $^3T_1$ and $^3T_2$ levels: $^3T_1 \rightarrow {}^3A_2 + {}^3E$ and $^3T_2 \rightarrow {}^3A_1 + {}^3E$. The A-E separation is of the order of 1000 cm^{-1}. For the energy level structure see Figure 5.

We will handle H' in the following way: the basic functions of the trigonal field will be chosen as the representation of H'. Then a Van Vleck Transformation will be applied to bring the off-diagonal elements into the $^3A_2$ block. For temperatures less than 750°K only these levels will contribute to the paramagnetic susceptibility since ^3E will have a negligible population. After the perturbation calculation, then those terms which are linear in the magnetic field, will contribute to the temperature dependent susceptibility, and those which are quadratic in H will form the constant or Van Vleck susceptibility. The matrix elements of H' are listed in Table IV; H_z is the magnetic field along the trigonal axis and H_x the field perpendicular to this axis.

The matrix elements of the $^3A_2$ block after the Van Vleck transformation has been carried through fourth order are

$\underline{H = H_x}$

$$(M_s=0|E|M_s=0) = -\beta^2\left[\frac{\gamma^2}{\Delta_C} + \frac{\alpha^2}{\Delta_T}\left(1 - \frac{10\alpha^2\lambda^2}{\Delta_T^2}\right)\right]\mathcal{H}_x^2 - \left[2\frac{(\alpha\lambda)^2}{\Delta_T} + \frac{(\gamma\lambda)^2}{\Delta_C} - \frac{2(\alpha\lambda)^4}{\Delta_T^3} + \frac{1}{2}\frac{(\alpha\lambda)^3}{\Delta_T^2}\right]$$

$$(M_s = \pm 1|E|M_s = \pm 1) = -\beta^2\left[\frac{\gamma^2}{\Delta_C} + \frac{\alpha^2}{\Delta_T}\left(1-(3\alpha^2+2\alpha-4)\frac{\lambda^2}{\Delta_T^2}\right)\right]\mathcal{H}_x^2 \qquad (3)$$

$$(M_s = 0|E|M_s = \pm 1) = g_\perp \beta \frac{\sqrt{2}}{2}\mathcal{H}_x$$

TABLE IV

MATRIX ELEMENTS OF $\lambda\, \underline{L} \cdot \underline{S} + (\underline{L} + g\,\underline{S}) \cdot \underline{H}$

$(\gamma\, M_S \mid \gamma'\, M_S')$

$(2,0|2,1) = g\, s_x\, H_x = g\, \frac{\sqrt{2}}{2}\, H_x$

$(2,0|2,-1) = g\, \frac{\sqrt{2}}{2}\, H_x$

$(2,1|2,1) = g\, s_z\, H_z = g\, H_z$

$(2,-1|2,-1) = -g\, H_z$

$(5,0|5,0) = -\alpha H_z$

$(5,1|5,1) = -\alpha\lambda - \alpha H_z + g\, H_z$

$(5,-1|5,-1) = \alpha\lambda - \alpha H_z - g\, H_z$

$(7,0|7,0) = \alpha H_z$

$(7,1|7,1) = \alpha\lambda + \alpha H_z + g\, H_z$

$(7,-1\ 7,-1) = -\alpha\lambda + \alpha H_z - g\, H_z$

$(5,0|5,1) = g\, \frac{\sqrt{2}}{2}\, H_x$

$(5,0|5,-1) = g\, \frac{\sqrt{2}}{2}\, H_x$

$(7,0|7,1) = g\, \frac{\sqrt{2}}{2}\, H_x$

$(2,0|7,-1) = g\, \frac{\sqrt{2}}{2}\, H_x$

$(2,0|5,-1) = -\alpha\lambda$

$(2,1|5,0) = -\alpha\lambda$

$(2,0|7,1) = -\alpha\lambda$

$(2,-1|7,0) = -\alpha\lambda$

$(2,0|5,0) = L_x\, H_x = -\alpha\, \frac{\sqrt{2}}{2}\, H_x$

$(2,1|5,1) = -\alpha\, \frac{\sqrt{2}}{2}\, H_x$

$(2,-1|5,-1) = -\alpha\, \frac{\sqrt{2}}{2}\, H_x$

$(2,0|7,0) = -\alpha\, \frac{\sqrt{2}}{2}\, H_x$

$(2,1|3,1) = 2\sqrt{2}\,\gamma\lambda + 2\sqrt{2}\,\gamma H_z$

$(2,-1|3,-1) = -2\sqrt{2}\,\gamma\lambda + 2\sqrt{2}\,\gamma H_z$

$(5,1|4,1) = -\sqrt{2}\,\gamma\lambda - \sqrt{2}\,\gamma H_z$

$(5,-1|4,-1) = \sqrt{2}\,\gamma\lambda - \sqrt{2}\,\gamma H_z$

$(7,1|6,1) = \sqrt{2}\,\gamma\lambda + \sqrt{2}\,\gamma H_z$

$(7,-1|6,-1) = -\sqrt{2}\,\gamma\lambda + \sqrt{2}\,\gamma H_z$

$(2,1|4,0) = \sqrt{2}\,\gamma\,\lambda$

$(2,0|4,-1) = \sqrt{2}\,\gamma\lambda$

$(2,0|6,1) = \sqrt{2}\,\gamma\lambda$

$(2,-1\ 6,0) = \sqrt{2}\,\gamma\lambda$

$(5,1|6,0) = -2\sqrt{2}\,\gamma\lambda$

$(5,0|3,1) = \sqrt{2}\,\gamma\,\lambda$

$(5,0|6,-1) = -2\sqrt{2}\,\gamma\lambda$

$(5,-1|3,0) = \sqrt{2}\,\gamma\,\lambda$

$(2,0|4,0) = \gamma\, H_x$

$(2,1|4,1) = \gamma H_x$

$(2,-1|4,-1) = \gamma\, H_x$

$(2,0|6,0) = \gamma\, H_x$

$(2,-1|6,-1) = \gamma\, H_x$

$(2,-1|6,-1) = \gamma H_x$

$(7,1|3,0) = -\sqrt{2}\,\gamma\lambda$

$(7,0|3,-1) = -\sqrt{2}\,\gamma\lambda$

TABLE IV (concluded)

$(2,1\|7,1) = -\alpha \frac{\sqrt{2}}{2} H_x$	$(7,0\|4,1) = -2\sqrt{2}\,\gamma\lambda$
$(2,-1\|7,-1) = -\alpha \frac{\sqrt{2}}{2} H_x$	$(7,-1\|4,0) = -2\sqrt{2}\,\gamma\lambda$
$(5,1\|6,1) = -2\,\delta H_x$	$(7,1\|3,1) = -\delta H_x$
$(5,0\|6,0) = -2\,\delta H_x$	$(7,0\|3,0) = -\delta H_x$
$(5,-1\|6,-1) = -2\,\delta H_x$	$(7,-1\|3,-1) = -\delta H_x$
$(5,1\|3,1) = \delta H_x$	$(7,1\|4,1) = -2\,\delta H_x$
$(5,0\|3,0) = \delta H_x$	$(7,0\|6,0) = -2\,\delta H_x$
$(5,-1\|3,-1) = \delta H_x$	$(7,-1\|6,-1) = -2\,\delta H_x$

$$g_{\perp} = g - \frac{2\alpha^2\lambda}{\Delta_T} - \frac{\gamma^2\lambda}{\Delta_C} + \frac{\alpha^3\lambda^2}{\Delta_T^2} - \frac{\gamma^2\alpha\lambda}{\Delta_T\Delta_C}$$

$\underline{H = H_z}$

$$(M_s=0|E|M_s=0) = -\beta^2\left[\frac{2\gamma^2}{\Delta_C} + \frac{2(\alpha+2)^2\alpha^2\lambda^2}{\Delta_T^3}\right]\mathcal{H}_z^2 - \left[2\frac{(\alpha\lambda)^2}{\Delta_T} + \frac{(\gamma\lambda)^2}{\Delta_C} - \frac{2(\alpha\lambda)^4}{\Delta_T^3} + 2\frac{(\alpha\lambda)^3}{\Delta_T^2}\right]$$

$$(M_s=\pm 1|E|M_s=\pm 1) = \pm g_{\parallel}\beta\mathcal{H}_z - \beta^2\left[2\frac{\gamma^2}{\Delta_C} + \frac{(\alpha+2)^2\alpha^2\lambda^2}{\Delta_T^3}\right]\mathcal{H}_z^2 - \left[\frac{(\alpha\lambda)^2}{\Delta_T} + \frac{5}{2}\frac{(\gamma\lambda)^2}{\Delta_C} - \frac{(\alpha\lambda)^4}{\Delta_T^3}\right] \quad (4)$$

$$g_{\parallel} = g - (2+\alpha)\frac{\alpha^2\lambda^2}{\Delta_T^2} - 4\frac{\gamma^2\lambda}{\Delta_C} + 4(2+\alpha)\frac{\alpha^4\lambda^4}{\Delta_T^4} - \frac{\gamma^2\lambda^2}{\Delta_C^2} - \frac{\alpha\gamma^2\lambda^2}{\Delta_C\Delta_T}$$

The energy denominators are defined in Figure 5; the coefficients α and γ depend upon the mixing of atomic states through the cubic field with values $\frac{3}{2}$ and $\sqrt{10}/4$ in the case of no mixing, but in the cubic field are 1.29 and 1.52 respectively; λ is the spin-orbit coupling constant, and β is the Bohr magneton. These expressions are applicable either to the spin-Hamiltonian formulation of electron spin resonance or to the direct determination of the susceptibility equations. The field independent terms contribute to the zero magnetic field splitting of $^3A_2$.

The general expression for the paramagnetic susceptibility is (7)

$$\chi = \frac{N\sum\omega_n\left\{\left[m_{\mathcal{H}}^{(1)}(n;n)\right]^2/kT - 2\,m_{\mathcal{H}}^{(2)}(n;n)\right\}e^{-E_n^o/kT}}{\sum\omega_n e^{-E_n^o/kT}} \quad (5)$$

where $m^{(1)}(n;n)$ are the diagonal terms in Eqs. (3,4) which are linear

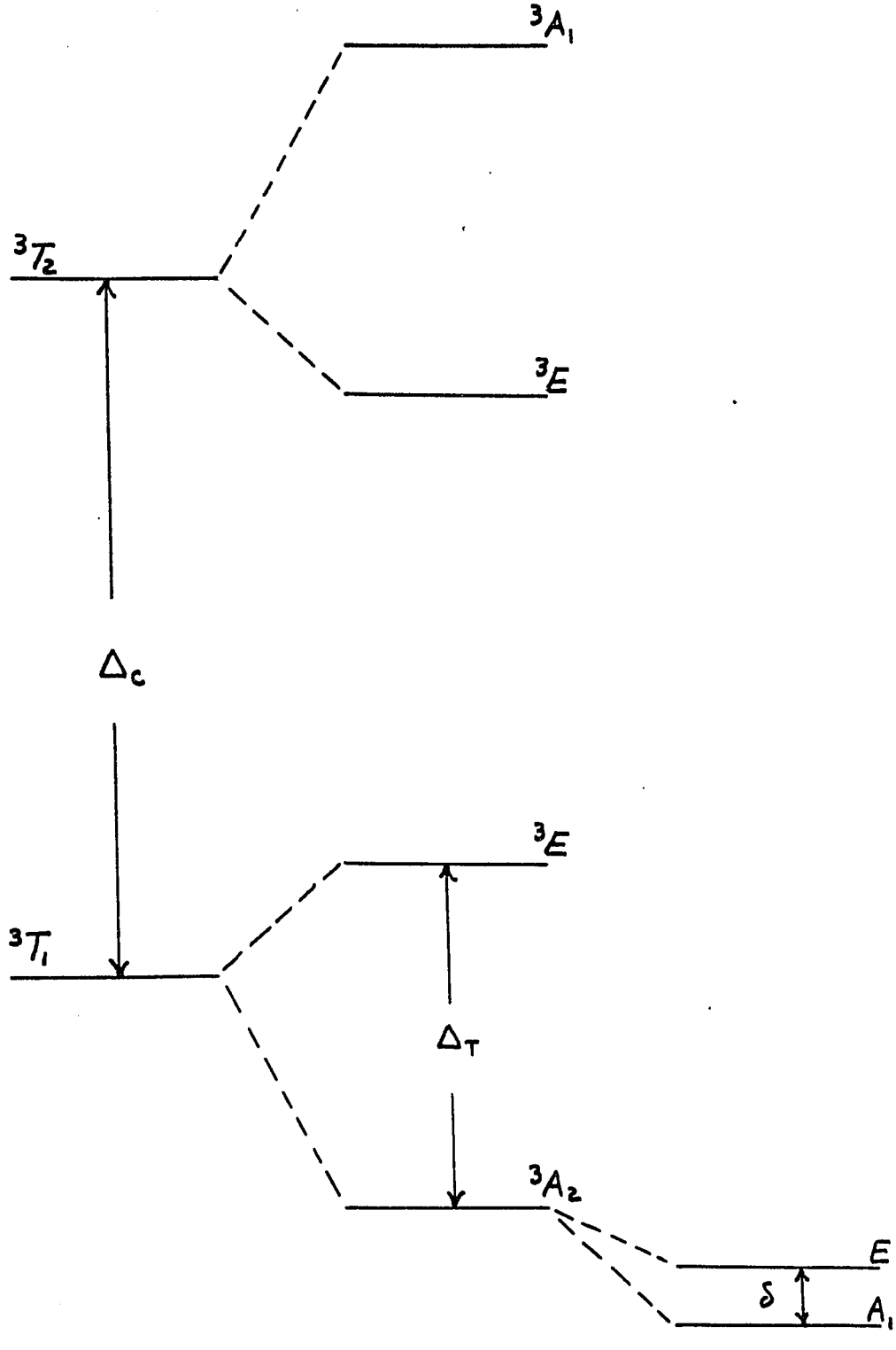


Figure 5

in $\mathcal{H}$, and $m_H^{(2)}$ are those which a quadratic in $\mathcal{H}$. For $\mathcal{H} = \mathcal{H}_x$ the off diagonal terms of Eq. (3) becomes quadratic through a second order perturbation since $(M_S=0|E|M_S=0)$ and $(M_S = \pm 1|E|M_S = \pm 1)$ are separated by the zero field splitting.

If Eqs. (3,4) are substituted into Eq. (5) we obtain the expressions

$$\chi_\perp = 2N\beta^2 \frac{g_\perp^2}{\delta}(1-e^{-\delta/kT})(1+2e^{-\delta/kT})^{-1}$$

$$+ 2N\beta^2\left\{\left[\frac{\gamma^2}{\Delta_C} + \frac{\alpha^2}{\Delta_T}\left(1 - \frac{10\alpha^2\lambda^2}{\Delta_T^2}\right)\right]\right. \tag{6}$$

$$\left. + 2\left[\frac{\gamma^2}{\Delta_C} + \frac{\alpha^2}{\Delta_T}\left(1-(3\alpha^2+2\alpha-4)\frac{\lambda^2}{\Delta_T^2}\right)\right]e^{-\delta/kT}\right\}(1+2e^{-\delta/kT})^{-1}$$

$$\chi_{||} = 2N\beta^2 \frac{g_{||}^2}{kT} e^{-\delta/kT}(1+2e^{-\delta/kT})^{-1}$$

$$+ 2N\beta^2\left\{\left[\frac{2\gamma^2}{\Delta_C} + \frac{2(\alpha+2)^2\alpha^2\lambda^2}{\Delta_T^3}\right]\right. \tag{7}$$

$$\left. + 2\left[\frac{2\gamma^2}{\Delta_C} + \frac{(\alpha+2)^2\alpha^2\lambda^2}{\Delta_T^3}\right]e^{-\delta/kT}\right\}(1+2e^{-\delta/kT})^{-1}$$

These expressions for the susceptibility are valid only when the temperature is low enough so that the population of the ^3E state may be neglected.

Susceptibility in the Temperature Range 77° to 295°K

For the temperature between 77 and 295°K the expressions for the susceptibility have a simpler form if the exponentials are expanded in powers of δ/kT. The results of such an expansion are

$$\chi_{||} = \frac{2}{3}N\beta^2\left\{g_{||}^2\left[k(T+\delta/3k)\right]^{-1} + \frac{6\gamma^2}{\Delta_C} + \frac{4(\alpha+2)^2\alpha^2\lambda^2}{\Delta_T^3}\right\} \tag{8}$$

$$\chi_{\perp} = \frac{2}{3} N\beta^2 \left\{ g_{\perp}^2 \left[k(T - \delta/6k) \right]^{-1} + \frac{3\gamma^2}{\Delta_C} + \frac{3\alpha^2}{\Delta_T} \left[1 - (4\alpha^2 + \alpha - 2) \frac{4}{3} \frac{\lambda^2}{\Delta_T^2} \right] \right\}.$$

Note that the susceptibilities should follow a Curie-Weiss Temperature dependence.

Measurements of the susceptibility have been made by Brumage (1a,5), and the data as a function of temperature are listed in Table V. In the analysis of the data it is assumed that $\delta = 8.3$ cm^{-1}, a value which is consistent with the data from optical spectra (6) and electron spin resonance (2,8,9,10). Figure 6 shows the behavior of $\chi_{\parallel}$ and $\chi_{\perp}$ as a function of $(T + \theta_{\parallel,\perp})^{-1}$. The straight line characteristic of the data indicates that the expanded forms of $\chi_{\parallel}$ and $\chi_{\perp}$, Eq. (8), are suitable in the analysis.

Since the concentration of V^{+++} in the sample is not accurately known, only the ratio of the slopes may be determined from the data. But $g_{\parallel}$ has been measured by electron spin resonance techniques (9,10), and we use the value reported in the literature, $g_{\parallel} = 1.915 \pm 0.002$, to determine

$$g_{\perp} = 1.725 \pm 0.010. \tag{9}$$

The difference in intercept of $\chi_{\parallel}$ and $\chi_{\perp}$ at $T = \infty$ is sensitive to Δ_T, the $^3A_2$ - ^3E separation due to the trigonal component of the crystal field. From the susceptibility data we obtain

$$\Delta_T = 1200 \pm 200 \text{ cm}^{-1}. \tag{10}$$

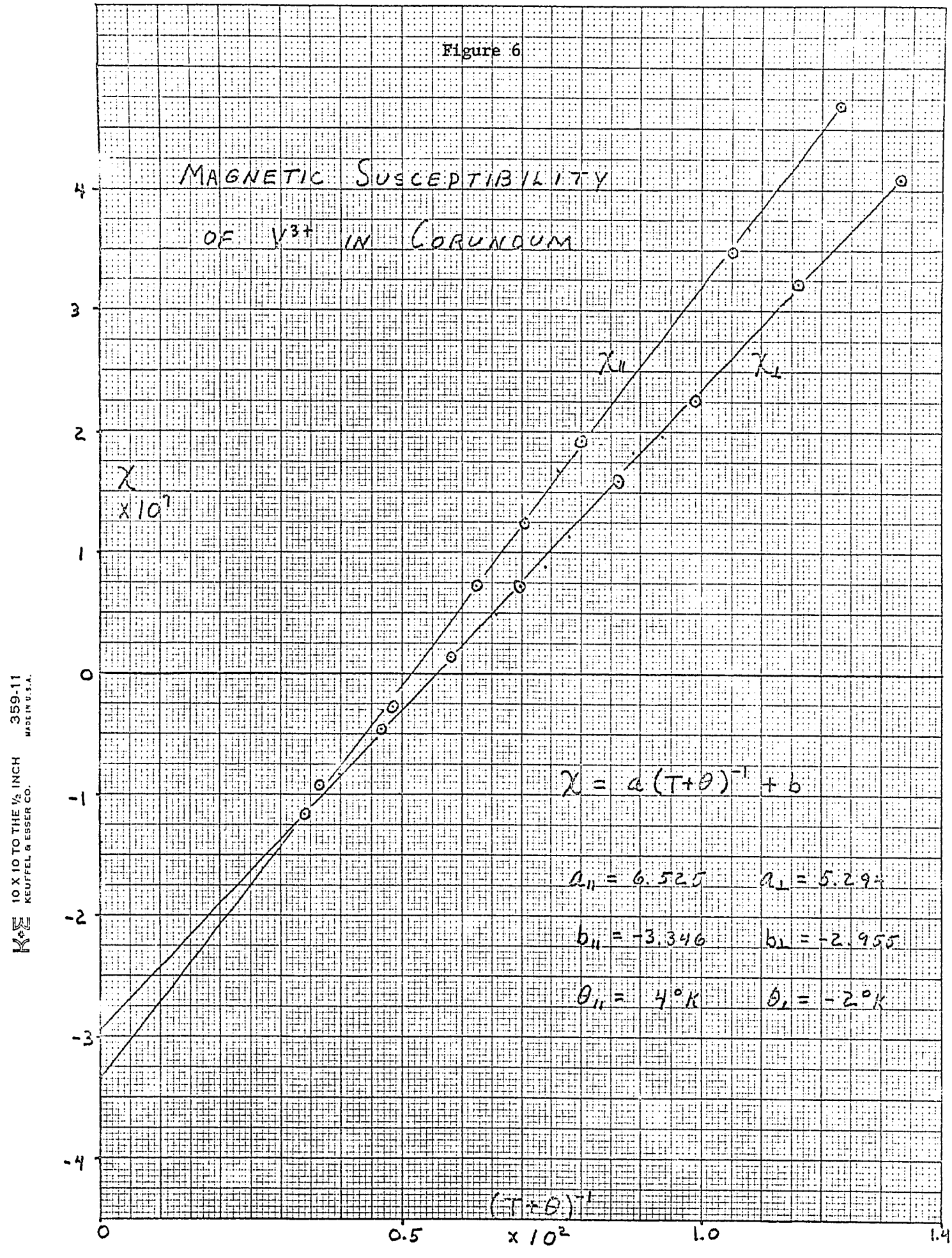
Since we use the difference in $\chi_{\parallel}$ and $\chi_{\perp}$, the diamagnetic portion due to Al_2O_3 and V^{+++} is eliminated from the calculation. Also $g_{\perp}$ depends upon λ and Δ_T, Eq. (3), and from Eq. (9) we find

TABLE V

MAGNETIC SUSCEPTIBILITIES (per gram sample) OF V^{+++}-DOPED CORUNDUM

$T^{o}K$	$\chi_{\parallel}$ (x 10^{7} cgs-emu)	$T^{o}K$	$\chi_{\perp}$ (x 10^{7} cgs-emu)
77.3	4.70	77.3	4.08
88.0	3.68	88.0	3.23
91.0	3.49	103	2.26
121	1.92	109	1.96
127	1.68	118	1.60
138	1.25	130	1.11
145	1.04	137	0.89
155	0.75	145	0.72
156	0.73	154	0.49
202	-0.26	174	0.15
272	-0.93	217	-0.46
290	-1.14	253	-0.84
296	-1.16	296	-1.17

Figure 6



10 X 10 TO THE ½ INCH 359-11
KEUFFEL & ESSER CO. MADE IN U.S.A.

$$\Delta_T \sim 1100 \text{ cm}^{-1} \qquad (11)$$
$$\lambda \sim 90 \text{ cm}^{-1}$$

It is interesting to note that the two methods of determining Δ_T are consistent.

The two parameters λ and Δ_T have also been determined from electron spin resonance absorption and from the optical spectra but the results are not completely consistent. McClure (3) reported $\Delta_T = 960 \text{ cm}^{-1}$, but Zverev and Prokhorov (10) found the low values $\Delta_T = 280 \text{ cm}^{-1}$ and $\lambda = 38 \text{ cm}^{-1}$. Our results are consistent with McClures, but differ significant from those of Zverev and Prokhorov. We feel that the electron spin resonance data has not been interpreted correctly and a more careful analysis (for example inclusion of higher order terms in $g_{\parallel}$) would yield larger values for the parameters under consideration.

It is interesting to compare the free ion and crystal values for and the L-multiplet separations, page 27, reference (4). For the free ion

$$\Delta E(^3F;\ ^3P) \sim 12{,}200 \text{ cm}^{-1} \qquad (12)$$
$$\lambda \sim 104 \text{ cm}^{-1}$$

and in the crystal we find

$$\Delta E(^3F;\ ^3P) \sim 9000 \text{ cm}^{-1} \qquad (13)$$
$$\lambda \sim 90 \text{ cm}^{-1}.$$

Apparently the crystal field has a larger effect percentage-wise in changes of ΔE than in λ. Possibly the "tail" of the electronic wavefunction is more drastically altered by the surrounding ligands than that part in the ion core. Since λ varies as $\frac{1}{r^3}$, it would be less sensitive to changes in the "tail" of the function than would be the elec-

tronic energy.

The Low Temperature Susceptibility

The zero magnetic field splitting, δ , of $^3A_2$ is quite sensitive to λ and Δ_T. The optical spectra reported by Price (6), intensity measurements of ESR absorption (9), pulsed magnetic field resonance experiments (2) indicate that $\delta \sim 8\ cm^{-1}$; and the λ and Δ_T determined from the susceptibility measurements reported in the last section indicate that $\delta \sim 8.6\ cm^{-1}$, but so far no direct measurement of δ has been made.

The temperature dependent term of $\chi_{||}$ increases as T decreases, goes through a maximum, and then approaches zero as $T \rightarrow 0$. The temperature at which the maximum occurs may be found by differentiating the first term of Eq. (6) and setting it equal to zero:

$$\frac{\partial \chi_{||}}{\partial T} = 0 \tag{14}$$

when

$$\frac{\delta}{k\,T} - 2\,e^{-\delta/kT} = 1. \tag{15}$$

This equation is satisfied when

$$\frac{\delta}{k\,T} = 1.463_0 \tag{16}$$

or

$$\delta = (1.016_8)\ T\ \frac{cm\text{-}1}{^oK} \tag{17}$$

Since the location of the maximum is dependent only on δ , this is a direct way of determining the zero field splitting. At present Brumage (1a) is extending his measurements to low temperatures, and the results of this experiment should supplement the data already available.

APPENDIX I

THE STRUCTURE OF CD_2HCOH AND CH_2DCOH

The general expression for the moments of inertia of the molecule, Chapter I, Eq. (1-6), are

$$(I_{CM})_{xx} = (I_{CF})_{xx} + (I_{CT})_{xx} + \frac{M_T M_F}{M}\left[(\eta_z)^2 + (\eta_y + \sigma_y)^2 \right]$$

$$(I_{CM})_{yy} = (I_{CF})_{yy} + (I_{CT})_{yy} + \frac{M_T M_F}{M}\left[\eta_z^2 + \sigma_x^2 \right]$$

$$(I_{CM})_{zz} = (I_{CF})_{zz} + (I_{CT})_{zz} + \frac{M_T M_F}{M}\left[(\eta_y + \sigma_y)^2 + \sigma_x^2 \right]$$

$$(I_{CM})_{xy} = (I_{CF})_{xy} + (I_{CT})_{xy} + \frac{M_T M_F}{M}\left[\sigma_x (\eta_y + \sigma_y) \right]$$

$$(I_{CM})_{xz} = (I_{CF})_{xz} + (I_{CT})_{xz} + \frac{M_T M_F}{M}\left[\sigma_x \eta_z \right]$$

$$(I_{CM})_{yz} = (I_{CF})_{yz} + (I_{CT})_{yz} + \frac{M_T M_F}{M}\left[(\eta_y + \sigma_y) \eta_z \right].$$

These expressions are also applicable to C_6H_5COH.

The molecular structure of acetaldehyde has been determined by Kilb, Lin and Wilson (4), and will be assumed to be applicable to CH_2DCOH and CHD_2COH. In this formulation C-COH is considered to be the frame and has the same inertia properties for both molecules.

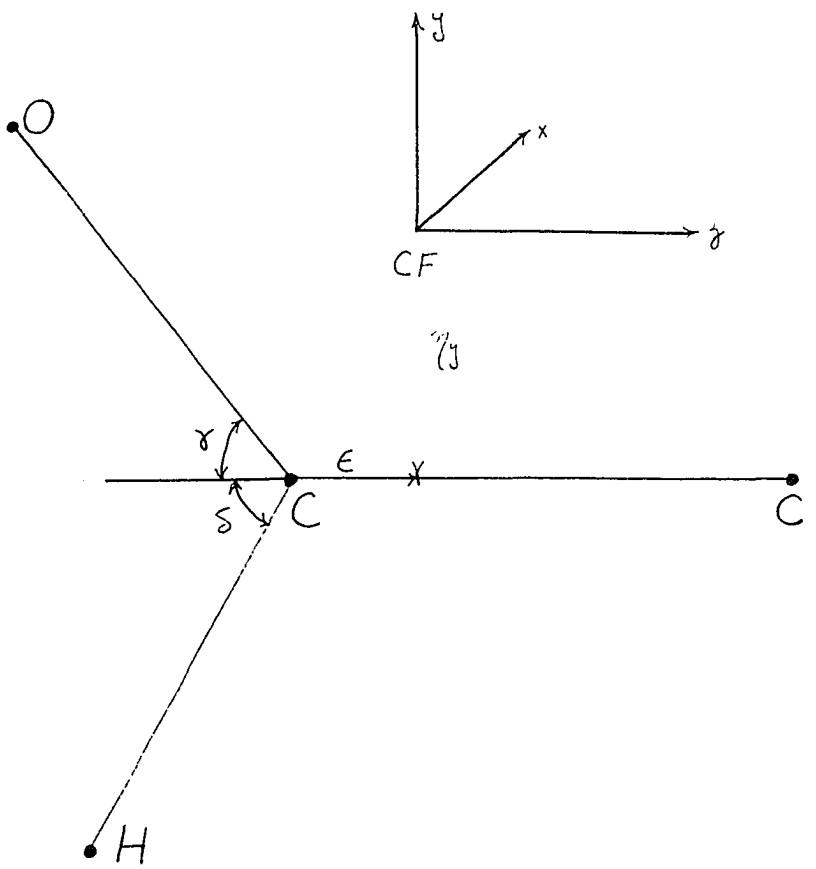


Figure 7

CO = 1.206 Å

CH = 1.114 Å

C-C = 1.501 Å

$\gamma = 56^\circ\ 5'$

$\delta = 62^\circ 31'$

These values for the structural parameters give the results

$$(I_{CF})_{xx} = 45.283 \text{ amu Å}^2$$

$$(I_{CF})_{yy} = 33.601 \text{ amu } \mathring{A}^2$$

$$(I_{CF})_{zz} = 11.682 \text{ amu } \mathring{A}^2$$

$$(I_{CF})_{yz} = -12.904 \text{ amu } \mathring{A}^2$$

$$(I_{CF})_{xy} = (I_{CF})_{xz} = 0$$

$$\eta_y = -3.6935 \times 10^{-1} \mathring{A}$$

$$\epsilon = 1.6197 \times 10^{-1} \mathring{A}$$

For the top it is assumed that all three atoms lie in a plane perpendicular to the C-C axis.

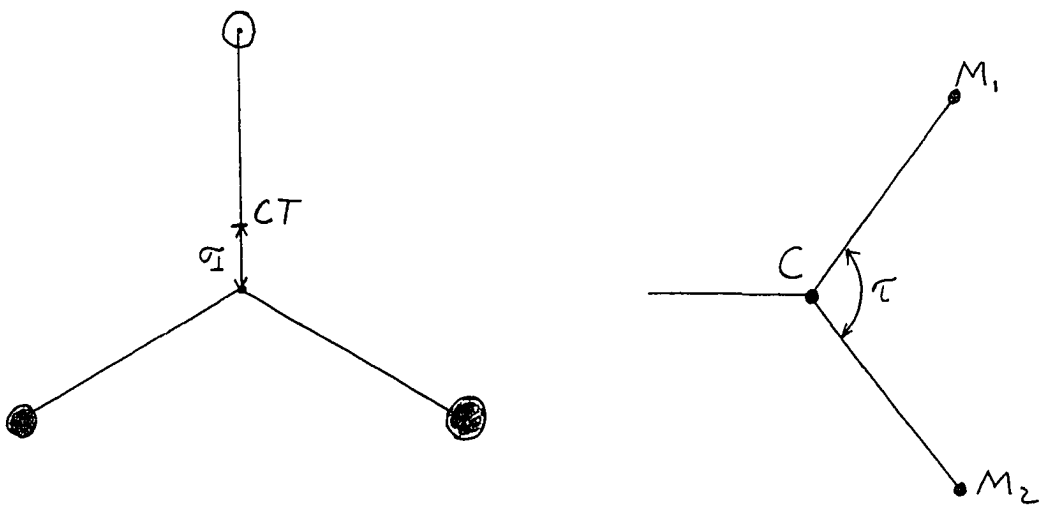


Figure 8

CH_2DCOH	CD_2HCOH
CH = CD = 1.087 Å	CH = CD = 1.087
τ = 108° 24'	τ = 108° 24'
$(I_{CT})_{xx} = 2.3498 - 7.827 \times 10^{-1} \sin^2\alpha$	$(I_{CT})_{xx} = 1.8803 + 1.2516 \sin^2\alpha$
$(I_{CT})_{yy} = 1.5671 + 7.827 \times 10^{-1} \sin^2\alpha$	$(I_{CT})_{yy} = 3.1318 - 1.2516 \sin^2\alpha$
$(I_{CT})_{zz} = 3.9169$	$(I_{CT})_{zz} = 5.0121$
$(I_{CT})_{xy} = 7.827 \times 10^{-1} \sin\alpha \cos\alpha$	$(I_{CT})_{xy} = 1.2516 \sin\alpha \cos\alpha$

CH_2DCOH	CD_2HCOH
$(I_{CT})_{xz} = (I_{CT})_{yz} = 0$	$(I_{CT})_{xz} = (I_{CT})_{yz} = 0$
$\sigma_\perp = 2.5421 \times 10^{-1}$ Å	$\sigma_\perp = -2.0341 \times 10^{-1}$ Å
$\eta_z = 1.7201$ Å	$\eta_z = 1.7201$ Å
$\frac{M_T M_F}{M} = 3.6703$ amu	$\frac{M_T M_F}{M} = 4.4865$ amu
$I'_x = I'_y = 1.6049$ amu Å^2	$I'_x = I'_y = -1.5698$ Å amu
$I'_z = 4.1541$ amu Å^2	$I'_z = 5.1978$ amu Å^2
$\eta = -8.296 \times 10^{-2}$	$\eta = 6.485 \times 10^{-2}$

The numerical values for the terms in Eq. (3-1) are

CDH_2COH	CD_2HCOH
$(I_{CM})^{(o)}_{xx} = 59.2306$ amu Å^2	$(I_{CM})^{(o)}_{xx} = 61.2359$ amu Å^2
$(I_{CM})^{(1)}_{xx} = -6.8921 \times 10^{-1}$	$(I_{CM})^{(1)}_{xx} = 6.7145 \times 10^{-1}$
$(I_{CM})^{(2)}_{xx} = -1.01983$	$(I_{CM})^{(2)}_{xx} = 1.0660$
$(I_{CM})^{(o)}_{yy} = 46.0284$	$(I_{CM})^{(o)}_{yy} = 50.0081$
$(I_{CM})^{(2)}_{yy} = 1.01983$	$(I_{CM})^{(2)}_{yy} = -1.0660$
$(I_{CM})^{(o)}_{zz} = 16.3365$	$(I_{CM})^{(o)}_{zz} = 17.4915$
$(I_{CM})^{(1)}_{zz} = -6.8921 \times 10^{-1}$	$(I_{CM})^{(1)}_{zz} = 6.7145 \times 10^{-1}$
$(I_{CM})^{(o)}_{xy} = -1.01983$	$(I_{CM})^{(o)}_{xy} = 1.0660$
$(I_{CM})^{(1)}_{xy} = 3.44605 \times 10^{-1}$	$(I_{CM})^{(1)}_{xy} = -3.3708 \times 10^{-1}$
$(I_{CM})^{(o)}_{xz} = -1.60490$	$(I_{CM})^{(o)}_{xz} = 1.5698$
$(I_{CM})^{(o)}_{yz} = -15.2362$	$(I_{CM})^{(o)}_{yz} = -15.7548$
$(I_{CM})^{(1)}_{yz} = 1.60490$	$(I_{CM})^{(1)}_{yz} = -1.5698$

Also for Eq. (3-2) the results are

$I^{(o)}_{xx} = 59.231$ amu Å^2	$I^{(o)}_{xx} = 61.2359$ amu Å^2

CDH_2COH	CD_2HCOH
$I_{xx}^{(1)} = -6.8921 \times 10^{-1}$	$I_{xx}^{(1)} = 6.7415 \times 10^{-1}$
$I_{xx}^{(2)} = -1.6399$	$I_{xx}^{(2)} = 5.9184 \times 10^{-1}$
$I_{yy}^{(o)} = 45.408$	$I_{yy}^{(o)} = 49.5340$
$I_{yy}^{(2)} = 1.6399$	$I_{yy}^{(2)} = -5.9184 \times 10^{-1}$
$I_{zz}^{(o)} = 12.154$	$I_{zz}^{(o)} = 12.2719$
$I_{zz}^{(1)} = 0$	$I_{zz}^{(1)} = 0$
$I_{zz}^{(2)} = 2.8587 \times 10^{-2}$	$I_{zz}^{(2)} = 2.1859 \times 10^{-2}$
$I_{xy}^{(o)} = 3.4460 \times 10^{-1}$	$I_{xy}^{(o)} = 5.9184 \times 10^{-1}$
$I_{xy}^{(1)} = -1.6399$	$I_{xy}^{(1)} = -3.3708 \times 10^{-1}$
$I_{xz}^{(o)} = 0$	$I_{xz}^{(o)} = 0$
$I_{xz}^{(1)} = -1.3314 \times 10^{-1}$	$I_{xz}^{(1)} = -1.0180 \times 10^{-1}$
$I_{yz}^{(o)} = -15.103$	$I_{yz}^{(o)} = -15.6530$
$I_{yz}^{(1)} = 0$	$I_{yz}^{(1)} = 0$
$I_{yz}^{(2)} = -1.3314 \times 10^{-1}$	$I_{yz}^{(2)} = -1.0180 \times 10^{-1}$

For the rotational constants of Eq. (3-3) the results are

CH_2DCOH	CD_2HCOH
$\mu_{xx}^{(o)} = 8.44158$ (amu $\mathring{A}^2)^{-1}(10^3)$	$\mu_{xx}^{(o)} = 8.16514$ (amu $\mathring{A}^2)^{-1}(10^3)$
$\mu_{xx}^{(1)} = 9.8227 \times 10^{-1}$	$\mu_{xx}^{(1)} = -8.9891 \times 10^{-2}$
$\mu_{xx}^{(2)} = 2.4938 \times 10^{-1}$	$\mu_{xx}^{(2)} = -7.5942 \times 10^{-2}$
$\mu_{yy}^{(o)} = 18.7686$	$\mu_{yy}^{(o)} = 16.9100$
$\mu_{yy}^{(2)} = -9.1894 \times 10^{-1}$	$\mu_{yy}^{(2)} = 4.7258 \times 10^{-1}$
$\mu_{zz}^{(o)} = 70.1219$	$\mu_{zz}^{(o)} = 68.2549$
$\mu_{zz}^{(2)} = -1.3733$	$\mu_{zz}^{(2)} = 9.6090 \times 10^{-1}$
$\mu_{xy}^{(o)} = 1.0920 \times 10^{-1}$	$\mu_{xy}^{(o)} = -9.3082 \times 10^{-2}$

CH_2DCOH	CD_2HCOH
$\mu_{xy}^{(1)} = -4.6721 \times 10^{-1}$	$\mu_{xy}^{(1)} = 1.9929 \times 10^{-1}$
$\mu_{xz}^{(o)} = -1.3569 \times 10^{-1}$	$\mu_{xz}^{(o)} = 1.1827 \times 10^{-1}$
$\mu_{xz}^{(1)} = 4.8811 \times 10^{-1}$	$\mu_{xz}^{(1)} = -3.2193 \times 10^{-1}$
$\mu_{yz}^{(o)} = -23.3230$	$\mu_{yz}^{(o)} = -21.5689$
$\mu_{yz}^{(2)} = 9.9632 \times 10^{-1}$	$\mu_{yz}^{(2)} = -7.0629 \times 10^{-1}$

Also the coefficients of the torsional equation and certain terms of H_{TR}, Eqs. (3-7,16), are

CH_2DCOH	CD_2HCOH
$\mu_T^{(o)} = 1.9228 \times 10^{2}$	$\mu_T^{(o)} = 1.6543 \times 10^{2}$ (amu Å)$^{-1}$
$\mu_T^{(1)} = 6.3873$	$\mu_T^{(1)} = -4.1757$
$\mu_T^{(2)} = -1.6535$	$\mu_T^{(2)} = 6.4511 \times 10^{-1}$
$a_x = 3.2657$	$a_x = -2.3080$
$b_x = 4.9513 \times 10^{-1}$	$b_x = -3.1520 \times 10^{-1}$
$a_y = -23.3230$	$a_y = -21.5689$
$b_y = -5.3163$	$b_y = 3.7084$
$c_y = 1.0385$	$c_y = -6.7818 \times 10^{-1}$
$d_y = 9.1876 \times 10^{-2}$	$d_y = 3.6734 \times 10^{-2}$
$a_z = 70.1219$	$a_z = 68.2549$
$b_z = 3.1937$	$b_z = -2.0878$
$c_z = -1.1898$	$c_z = 9.2504 \times 10^{-1}$
$d_z = -1.0199 \times 10^{-1}$	$d_z = -5.3768 \times 10^{-2}$

APPENDIX II

THE STRUCTURE OF C_6H_5COH

The structure of C_6H_5COH has not been accurately determined by the usual methods of isotopic substitution. It will be assumed that the ring structure has the same values for the parameters as benzene, and then the aldehyde structure is similar to that for acetaldehyde. Usually the splitting of the spectral lines due to internal rotation is not as sensitive to the structure as the actual frequencies of the lines. The benzene ring is considered as the frame and the lighter aldehyde group as the top.

Benzene Ring	Aldehyde Group
C-C: 1.397 Å	C-O: 1.211
C-H: 1.084 Å	C-H: 1.193
	$\gamma = 56^\circ\ 27'$
C-C connecting bond: 1.480	$\delta = 55^\circ\ 54'$
$M_H = 1.008$	
$M_C = 12.01$	
$M_O = 16.00$	

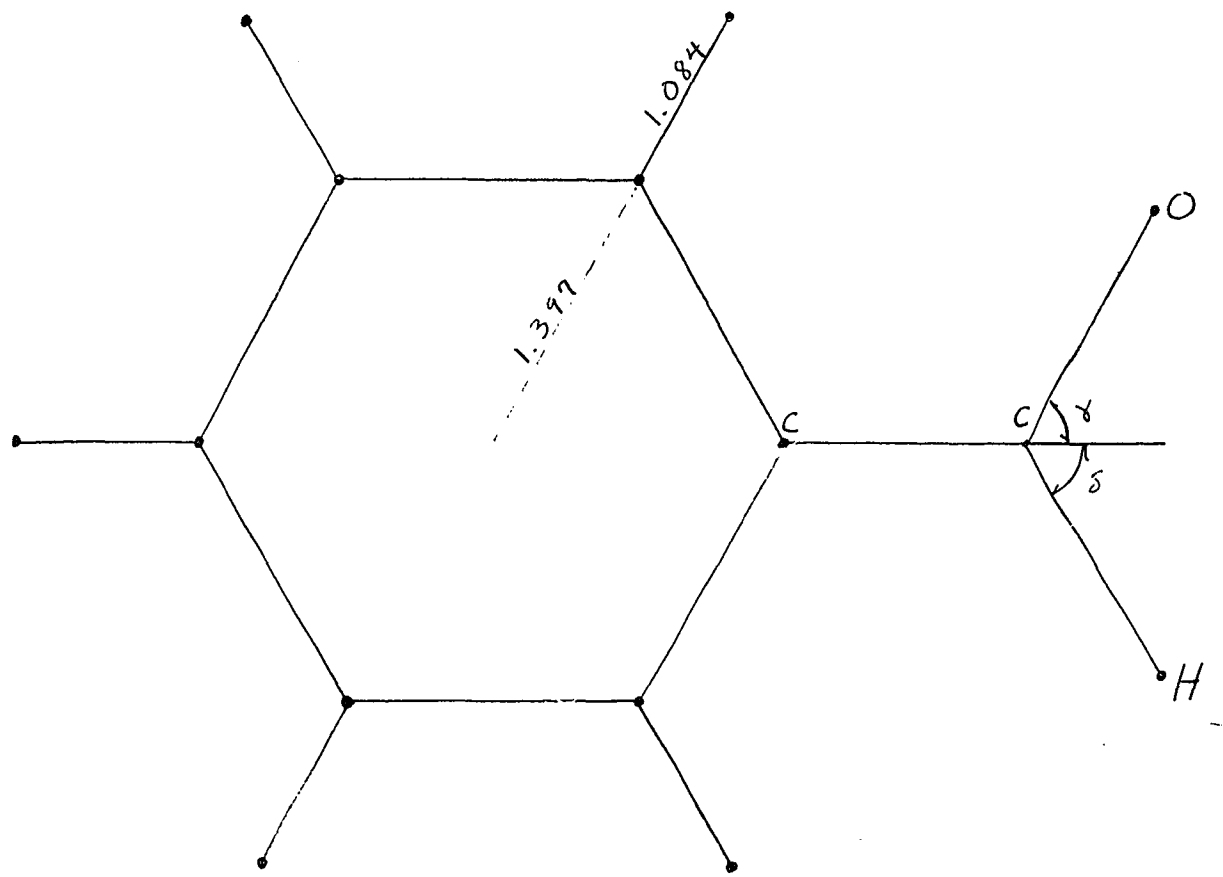


Figure 9

The results for this structure are

$(I_{CF})_{xx} = 259.52$ amu $\mathring{A}^2$

$(I_{CF})_{yy} = 170.59$ amu $\mathring{A}^2$

$(I_{CF})_{zz} = 88.93$ amu $\mathring{A}^2$

$(I_{CF})_{xy} = (I_{CF})_{xz} = (I_{CF})_{yz} = 0$

$(I_{CT})_{zz} = 3.7817$ amu $\mathring{A}^2$

$(I_{CT})_{xx} = 3.7817 \cos^2\alpha$

$(I_{CT})_{yy} = 3.7817 \sin^2\alpha$

$(I_{CT})_{xy} = -3.7817 \sin\alpha \cos\alpha$

$(I_{CT})_{xz} = (I_{CT})_{yz} = 0.$

$\sigma_\perp = 0.8906$ $\mathring{A}$

$\eta_z = 3.186$ $\mathring{A}$

$I'_x = 40.52$ amu $\mathring{A}^2$

$I'_z = 15.11$ amu $\mathring{A}^2$

for $\alpha = 0$

$$(I_{CM})_{xx} = 419.60 \text{ amu } \mathring{A}^2$$
$$(I_{CM})_{yy} = 315.56 \text{ amu } \mathring{A}^2$$
$$(I_{CM})_{zz} = 104.04 \text{ amu } \mathring{A}^2$$
$$(I_{CM})_{yz} = 40.52 \text{ amu } \mathring{A}^2$$
$$(I_{CM})_{xz} = (I_{CM})_{xy} = 0.$$

The effective moments of inertia, Eq. (4-2), are

$I_{xx}^{(o)} = 419.60 \text{ amu } \mathring{A}^2$ $\qquad$ $I_{zz}^{(o)} = 88.93$

$I_{xx}^{(2)} = -123.80$ $\qquad$ $I_{xy}^{(1)} = -123.80$

$I_{yy}^{(o)} = 206.87$ $\qquad$ $I_{xz} = 0$

$I_{yy}^{(2)} = 123.80$ $\qquad$ $I_{yz} = 0.$

For the rotational constants of Eqs. (4-3,19) the results are

$\mu_{xx}^{(o)} = 1.1916 \left(\text{amu } \mathring{A}^2\right)^{-1} (10)^3$ $\qquad$ $\mu_{zz}^{(o)} = 5.6223$

$\mu_{xx}^{(2)} = 5.6197 \times 10^{-1}$ $\qquad$ $\mu_{xy}^{(1)} = -7.1311 \times 10^{-1}$

$\mu_{yy}^{(o)} = 2.4170$ $\qquad$ $\mu_{xz} = 0$

$\mu_{yy}^{(2)} = -1.0197$ $\qquad$ $\mu_{yz} = 0$

$R = 1.2683 \times 10^{-1}$

Also the coefficients of the torsional equation and certain terms of H_{TR}, Eqs. (4-8,19), are

$$\frac{I_x'}{I_z'}\left(\mu_{xx}^{(o)} - \mu_{xy}^{(1)}\right) = 5.1085 \left(\mathring{A}^2 \text{ amu}\right)^{-1} (10^3)$$

$$\frac{I_x'}{I_z'}\mu_{yy}^{(o)} = -6.4824$$

$$\mu_{zz}^{(o)} = 5.6223$$

$$R = 1.2683 \times 10^{-1}$$

$$\mu_T^{(o)} = 5.6099 \times 10 \left(\text{amu } \mathring{A}^2\right)^{-1} (10^3)$$

$$\mu_T^{(2)} = 1.0499 \times \mu_T^{(o)}$$

$$g^{(o)} = 7.7193 \times 10^6 \mathring{A}^6 \text{ (amu)}^3$$

$$g^{(2)} = 9.7908 \times 10^5.$$

APPENDIX III

A Van Vleck transformation has been carried out to fourth order. The result is:

$$H = H_o + H_1$$

$$(n\ell|E|n\ell') = (n\ell|H_1|n\ell') + \sum \frac{(n\ell|H_1|n''\ell'')(n''\ell''|H_1|n\ell')}{E_n - E_{n''}}$$

$$+ \sum \frac{(n\ell|H_1|n''\ell'')(n''\ell''|H_1|n'''\ell''')(n'''\ell'''|H_1|n\ell')}{(E_n - E_{n''})\ (E_n - E_{n'''})}$$

$$- \frac{1}{2}\sum\Bigg[\frac{(n\ell|H_1|n\ell'')(n\ell''|H_1|n'''\ell''')(n'''\ell'''|H_1|n\ell')}{(E_n - E_{n'''})^2}$$

$$+ \frac{(n\ell|H_1|n''''\ell'''')(n'''\ell'''|H_1|n\ell'')(n\ell''|H_1|n\ell')}{(E_n - E_{n'''})^2}\Bigg]$$

$$+ \sum \frac{(n\ell|H_1|n''\ell'')(n''\ell''|H_1|n'''\ell''')(n'''\ell'''|H_1|n''''\ell'''')(n''''\ell''''|H_1|n\ell')}{(E_n - E_{n''})\ (E_n - E_{n'''})\ (E_n - E_{n''''})}$$

$$- \frac{1}{2}\sum\Bigg[\frac{(n\ell|H_1|n''\ell'')(n''\ell''|H_1|n\ell''')(n\ell'''|H_1|n''''\ell'''')(n''''\ell''''|H_1|n\ell')}{(E_n - E_{n''})^2\ (E_n - E_{n''''})}$$

$$+ \frac{(n\ell|H_1|n''\ell'')(n''\ell''|H_1|n\ell''')(n\ell'''|H_1|n''''\ell'''')(n''''\ell''''|H_1|n\ell')}{(E_n - E_{n''})\ (E_n - E_{n''''})^2}\Bigg]$$

$$+\sum \frac{(n\ell|H_1|n\ell''')(n\ell'''|H_1|n''\ell'')(n''\ell''|H_1|n''''\ell'''')(n\ell''''|H_1|n\ell')}{(E_n - E_{n''})^3}$$

$$-\sum\Bigg[\frac{(n\ell|H_1|n\ell''')(n\ell'''|H_1|n''\ell'')(n''\ell''|H_1|n''''\ell'''')(n''''\ell''''|H_1|n\ell')}{(E_n - E_{n''})^2\,(E_n - E_{n''''})}$$

$$+\frac{(n\ell|H_1|n''''\ell'''')(n''''\ell''''|H_1|n''\ell'')(n''\ell''|H_1|n\ell''')(n\ell'''|H_1|n\ell')}{(E_n - E_{n''''})\,(E_n - E_{n''})^2}\Bigg]$$

APPENDIX IV

FORMULATION FOR C_6H_5COH WHEN $s > 100$

The results of Chapter IV are applicable when the barrier height parameter, s, is less than 100. Above this value the solutions of Matheius equation have not been tabulated. In this region it appears best to expand the trigonometric functions, $\sin^{-n}\alpha$, about $\alpha = 0$. Then the zeroeth order torsional functions are the Hermite polynomials, if we use localized functions. This is reasonable since the overlap integrals when the symmetry functions are used is exceptionally small; affecting the ninth digit of the energy for s = 100.

Under these conditions the Hamiltonian has the form

$$H_o = H_T + H_R$$

$$H_T = \mu_T^{(o)} p^2 + V\alpha^2$$

and H_R is the same as Eq. (4-18). Then H_T' and H_{TR} are

$$H_T' = V\left(-\frac{1}{3}\alpha^4 + \frac{2}{45}\alpha^6 - \frac{1}{315}\alpha^8 + \cdots\right)$$

$$+ A\left(\alpha^2 p^2 + p^2\alpha^2\right) + B\left(\alpha^4 p^2 + p^2\alpha^4\right)$$

$$+ C\left(\alpha^6 p^2 + p^2\alpha^6\right)$$

$$H_{TR} = \left(D\alpha^2 + E\alpha^4\right) P_x^2 + \left(F\alpha^2 + G\alpha^4\right) P_y^2$$

$$+ \left(H\alpha + I\alpha^3\right)\left(P_xP_y + P_yP_x\right).$$

$$+\left[J(\alpha p + p\alpha) + K(\alpha^3 p + p\alpha^3)\right] P_x$$

$$+\left[L p + M(\alpha^2 p + p\alpha^2) + N(\alpha^4 p + p\alpha^4)\right] P_y$$

$$+ O\, p\, P_z .$$

The coefficients are related to those used in Chapter IV in the following manner:

$$A = \mu_T^{(2)}$$

$$B = -\left(\tfrac{1}{3}\mu_T^{(2)} + \mu_T^{(4)}\right)$$

$$C = \tfrac{2}{45}\mu_T^{(2)} + \tfrac{2}{3}\mu_T^{(4)} + \mu_T^{(6)}$$

$$D = \mu_{xx}^{(2)}$$

$$E = -\left(\tfrac{1}{3}\ {}^{(2)}_{yy} + \ {}^{(4)}_{yy}\right.$$

$$F = \mu_{yy}^{(2)}$$

$$G = -\left(\tfrac{1}{3}\mu_{yy}^{(2)} + \mu_{yy}^{(4)}\right)$$

$$H = \mu_{xy}^{(1)}$$

$$I = -\left(\tfrac{1}{3}\mu_{xy}^{(1)} + \mu_{xy}^{(3)}\right)$$

$$J = a_x^{(o)}$$

$$K = -\left(\tfrac{1}{6} a_x^{(o)} + a_x^{(2)}\right)$$

$$L = a_y^{(o)}$$

$$M = -\left(\tfrac{1}{2} a_y^{(o)} + a_y^{(2)}\right)$$

$$N = \tfrac{1}{24} a_y^{(o)} + \tfrac{5}{6} a_y^{(2)} + a_y^{(4)}$$

$$O = 2\mu_{zz}^{(o)}$$

where the a_i are the coefficients in Eq. (4-19).

The method of solution is as follows: the eigenfunctions of H_o are the basis for the perturbation calculation. The perturbing Hamiltonian is $H_T' + H_{TR}$ and the off diagonal elements are removed by the Van Vleck transformation. Around s = 100 it is necessary to calculate up to fourth order terms to obtain the coefficients of P_x^2, etc. For $s > 500$ only third order perturbation is necessary. The matrix elements of α^2, p^2, $\alpha^2 p^2$, etc, are most easily determined by matrix multiplication, starting with

$$(n \mid \alpha \mid n+1) = \frac{1}{\sqrt{2\delta}}\ (n+1)^{\frac{1}{2}}$$

$$(n\,|\,\alpha\,|\,n-1) = \frac{1}{\sqrt{2\gamma}}\,(n)^{\frac{1}{2}}$$

$$(n|\frac{\partial}{\partial\alpha}|n+1) = \sqrt{\frac{\gamma}{2}}\;(n+1)^{\frac{1}{2}}$$

$$(n|\frac{\partial}{\partial\alpha}|n-1) = -\sqrt{\frac{\gamma}{2}}\;(n)^{\frac{1}{2}}$$

$$\gamma^2 = \frac{V_2}{\mu_T^{(o)}}\,.$$

Since the basic functions are localized at 0 and π , and the "overlap" integrals are small, it is possible to transform to the principal axes of the molecule in the limit of infinite barrier. This procedure has not been utilized here, but could reduce part of the calculation involved.

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