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# MICROWAVE SPECTRUM OF THE WATER MOLECULE

DESMOND WALTER POSENER

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Desmond Walter Posener

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ABSTRACT

## MICROWAVE SPECTRUM OF THE WATER MOLECULE

by

DESMOND WALTER POSENER

Submitted to the Department of Physics on May 4, 1953,  
in partial fulfillment of the requirements for the  
degree of Doctor of Philosophy.

Centrifugal distortion theory applicable to the water molecule and its isotopic modifications has been rederived, apparently eliminating misprints and errors now present in the literature. Using infrared data with this theory, rotational constants and distortion parameters have been calculated for the molecules  $H_2O$ ,  $D_2O$  and  $HDO$ , and the resulting theoretical transition frequencies compared with those observed in the microwave region.

Theoretically calculated parameters have also been used to obtain Q-branch frequencies in  $HDO$ ; while the frequencies computed directly are considerably different from those observed, a simple method is available for relating the two sets with very good accuracy. Analysis of the method leads to the inference that the theoretical distortion corrections are very nearly the true ones, and that reasonable agreement (by which is meant the best available by convenient methods of computation) with experiment can be obtained by a simple (and small) variation of the effective moments alone. The resulting parameters also account satisfactorily for the known  $|\Delta J| = 1$  transitions in  $HDO$ , whose frequencies are still better explained by a further small change in the theoretical effective moments together with a rather large variation of another distortion constant. The detailed discussion of the procedure used indicates the consistency of the results is good.

For this type of molecule centrifugal distortion effects are so large that approximate methods of calculation have only a limited usefulness; the validity of the Hillger-Strandberg-Kivelson-Wilson approximation for the calculation of Q-branch frequencies in  $HDO$  is discussed in detail.

The results for HDO give the following effective reciprocal moments of inertia:  $a = 7.0396 \pm 0.0005 \times 10^5$  Mc/sec,  $b = 2.7360 \pm 0.0005 \times 10^5$  Mc/sec,  $c = 1.9186 \pm 0.0005 \times 10^5$  Mc/sec, with  $\kappa = -0.6841 \pm 0.0002$ .

New transitions observed in the microwave spectra of  $D_2O$  and HDO are:  $D_2O$   $2_{20} \rightarrow 3_{13}$ ,  $10,919.39 \pm 0.05$  Mc/sec; HDO  $8_{45} \rightarrow 8_{44}$ ,  $24,844.77 \pm 0.05$  Mc/sec; HDO  $10_{56} \rightarrow 10_{55}$ ,  $8,836.95 \pm 0.1$  Mc/sec; HDO  $11_{57} \rightarrow 11_{56}$ ,  $22,581.1 \pm 0.2$  Mc/sec. A line previously reported, at  $26,880.38 \pm 0.05$  Mc/sec, is identified as the  $6_{24} \rightarrow 7_{17}$  transition of HDO.

Thesis Supervisor: M.W.P.Strandberg

Title: Associate Professor of Physics

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It is a pleasure to express my sincere gratitude to Professor M.W.P.Strandberg for his valuable guidance and counsel.

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The help of Miss H.Paul in carrying out some of the calculations is also gratefully acknowledged.

I wish to thank Mr.S.Weisbaum and Dr.Y.Beers, of New York University, for communicating to me some of their results prior to publication.

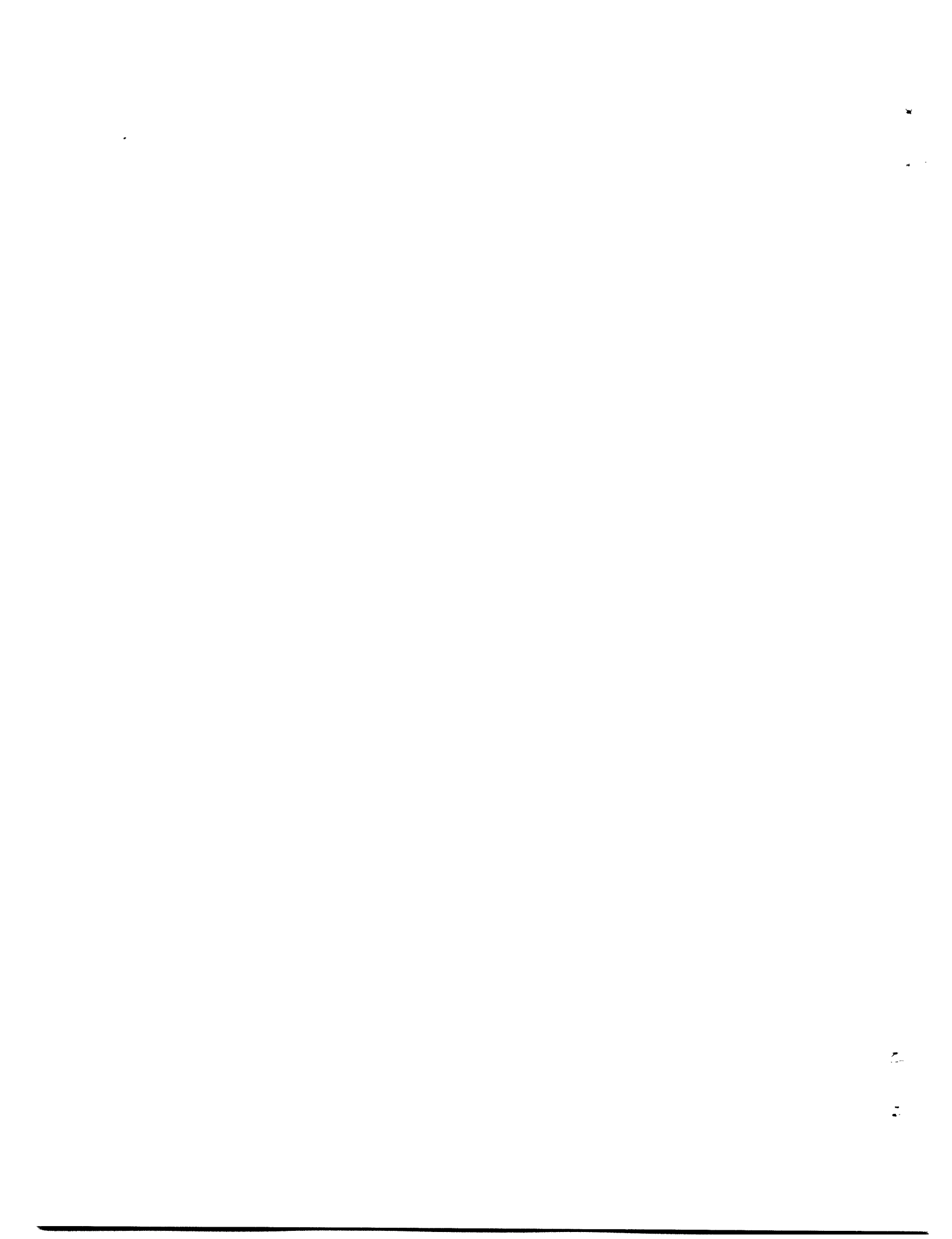
I am also very pleased to acknowledge the grant of a Studentship from the Australian Commonwealth Scientific and Industrial Research Organization, whose financial assistance made this research possible.

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1. p. 6. Last line should read:  $\tan 2\theta = \frac{2I_{x'y'}}{I_{x'x'} - I_{y'y'}}$

2. p. 20. In Eq. (II. 85), last symbol should read:  $K_{33}^0$

3. p. 26. Last line of Eq. (II. 110) should read:

$$k_{SS'S''} = k_{S'S''S} = k_{S''SS'} \\
 = k_{S''S'S} = k_{S'S'S''} = k_{SS'S''} = \frac{1}{6} \left( \frac{\hbar}{\omega_S} \frac{\hbar}{\omega_{S'}} \frac{\hbar}{\omega_{S''}} \right)^{1/2} k_{SS'S''}^0$$

4. p. 35. Fourth line from bottom should read:

$$N_{\mathbf{g}} = \sum_{\mathbf{g}'} I_{\mathbf{g}\mathbf{g}'}^0 \omega_{\mathbf{g}'}$$

5. p. 83. Eq. (VI. 13) should read:

$$\Delta v_{JK} = \frac{\partial v_{JK}}{\partial \left( \frac{a-c}{2} \right)} \Delta \left( \frac{a-c}{2} \right) + \frac{\partial v_{JK}}{\partial \kappa} \Delta \kappa. \quad (\text{VI. 13})$$

6. p. 88. In Table VI. 13, delete "O" in heading of second column.

7. p. 89. In Table VI. 15, for observed value of c, delete 1.91863695 and insert 1.92871409.

8. p. 127. In Eq. (D. 4), read:  $G - F = -\frac{1}{2}(\kappa - 3)$ .

9. p. 156. Reference 26 should read:

26. D. W. Posener, M. I. T. Research Laboratory of Electronics Quarterly Progress Report, July 15, (1952), p. 28; October 15, (1952), p. 20; January 15, (1953), p. 14.

10. p. 156. Insert at foot of page:

\*Denotes that these papers are discussed in Appendix F.

February 10, 1954



## I

INTRODUCTION

The rotational spectrum of water\* has probably been more thoroughly investigated than that of any other asymmetric molecule; many examinations of the infrared spectrum have been carried out, and some are still in progress.

One of the interesting effects observable in the water spectrum arises from the fact that the molecule is so light that vibration and rotation cause comparatively large distortion to the equilibrium structure, and this has to be taken into account in any detailed description of the spectrum.

The theory of centrifugal distortion in asymmetric molecules has been discussed by a number of authors, but very little comparison with experiment has been carried out because of the fact (fortunate, or unfortunate, depending on the point of view!) that most molecules are so heavy that the effects of distortion in their spectra are almost entirely negligible.

With its high resolution, microwave spectroscopy offers the possibility of making a detailed check on the theory. Furthermore, the water molecule is a natural subject to investigate because the distortion effects are so large. This thesis is a contribution to study along these lines.

Microwave lines of water have been observed sporadically ever since microwave spectroscopy became a practical proposition in 1946. King, Hainer and Cross<sup>16</sup> have tabulated

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\* We usually use the word "water" in the generic sense to mean  $H_2O$  and its isotopic modifications.

predicted positions of many microwave lines, mainly based on rigid rotor calculations; their work is still valid as indicating possible microwave transitions, though the predictions are not always accurate in the microwave sense.

One line due to  $\text{H}_2\text{O}$  is known, with the possibility that one more might be detected in the foreseeable future. No  $\text{D}_2\text{O}$  lines had been identified prior to this work. The isotope  $\text{HDO}$ , with its low symmetry, affords a richer spectrum, with which the interpretive part of this thesis will be mainly concerned. Since a considerable number of lines is required for analysis, one of the objects of the present work was to increase our knowledge of the spectrum, preferably by systematic methods, rather than by hit-or-miss searching; this aim was achieved.

In our discussion we will make frequent references to the theory, of which sufficient is given in Chapters II and III. Although there is nothing basically new here, it is convenient for reference in a consistent notation, and, more important, is apparently free of the numerous errors and misprints to be found in the original literature.

So-called "theoretical parameters", obtained by putting numbers (obtained from infrared analysis) into the theoretical expressions, are given in Appendices B and C. Many of the intermediate quantities computed are also shown, for ease in checking or extending this work. Unless otherwise stated, the numerical results are quoted to the number of

significant figures actually used in computing, since rounding-off errors are readily propagated; it is not meant to imply that all these figures are meaningful!

The microwave spectra of  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  are discussed briefly in Chapters IV and V, respectively. We are still in no position to relate these systematically to one another, or to the spectrum of  $\text{HDO}$ .

Chapter VI, concerned with the microwave spectrum of  $\text{HDO}$ , contains the major contribution of this work. New lines in the spectrum are described, and correlation of the observed frequencies with theoretical predictions is discussed in detail. A critical study of methods of fitting molecular parameters to experimental data is given.

The experimental part of the work, mainly concerned with identification of various transitions, is discussed in Appendix E.

II

GEOMETRY, NORMAL COORDINATES, AND POTENTIAL FUNCTIONS

OF

THE MOLECULES  $H_2O$ ,  $D_2O$ ,  $HDO$ \*

1. Equilibrium Geometry

Throughout this work we assume that the equilibrium structures and potential functions of the three molecules  $H_2O$ ,  $D_2O$  and  $HDO$  are the same, to a sufficient degree of approximation.

We consider the non-linear molecule  $XYZ$ , with the  $X$  and  $Z$  atoms either identical (as in  $H_2O$  and  $D_2O$ ) or isotopic (as in  $HDO$ ), and make the following assignments:

	$H_2O$	$HDO$	$D_2O$
X (3)	H	D	D
Y (1)	O	O	O
Z (2)	H	H	D

Since three points define a plane, the molecule remains planar at all times, even when vibrating, so we need consider only a two-dimensional geometry at this stage.

First let us choose the coordinate system  $x'$ ,  $y'$  such

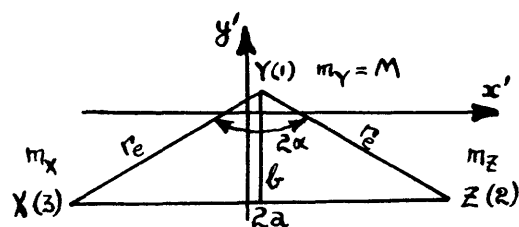


Fig. 1

that the equilibrium position of the molecule is as shown, with the center of mass at the origin. Let  $M$  be the mass of the oxygen atom ( $Y$ ),  $m_H$  and  $m_D$

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\* See references 5, 21, 25, 28, 29, 30.



the masses of the hydrogen and deuterium atoms, respectively, and  $m$  the mass of each of two identical atoms (as in  $\text{H}_2\text{O}$  or  $\text{D}_2\text{O}$ ). Then we have:

$$\begin{aligned} m_1 &= m_Y = M \\ m_2 &= m_Z \quad (= m_{\text{H}} \text{ for HDO; } = m \text{ for H}_2\text{O, D}_2\text{O}) \\ m_3 &= m_X \quad (= m_{\text{D}} \text{ for HDO; } = m \text{ for H}_2\text{O, D}_2\text{O}) . \end{aligned} \quad (\text{II.1})$$

Now define

$$\begin{aligned} \sigma &= m_X + m_Z \quad (= 2m \text{ for H}_2\text{O, D}_2\text{O}) \\ \Sigma &= m_X + m_Y + m_Z = M + \sigma \quad (= M + 2m \text{ for H}_2\text{O, D}_2\text{O}) \\ \mu &= \frac{m_Y(m_X + m_Z)}{m_X + m_Y + m_Z} = \frac{M\sigma}{\Sigma} \quad (= \frac{2mM}{2m+M} \text{ for H}_2\text{O, D}_2\text{O}) \\ \delta &= m_X - m_Z \quad (\geq 0) \quad (= 0 \text{ for H}_2\text{O, D}_2\text{O}) . \end{aligned} \quad (\text{II.2})$$

In terms of the dimensions of the molecule (Fig. 1), we have

$$\begin{aligned} x_1' - x_3' &= a = x_2' - x_1' \\ x_2' - x_3' &= 2a \\ y_1' - y_2' &= b = y_1' - y_3' , \end{aligned} \quad (\text{II.3})$$

with

$$\begin{aligned} a &= r_e \sin \alpha \\ b &= r_e \cos \alpha . \end{aligned} \quad (\text{II.4})$$

Since the center of mass lies at the origin, we have

$$\sum_i m_i x_i' = 0 = \sum_i m_i y_i' ,$$

from which we readily find

	HDO	H <sub>2</sub> O, D <sub>2</sub> O
$x'_1$	$\frac{\delta a}{\Sigma}$	0
$x'_2$	$\frac{(2m_X + M)a}{\Sigma}$	a
$x'_3$	$-\frac{(2m_Z + M)a}{\Sigma}$	-a
$y'_1$	$\frac{\sigma b}{\Sigma}$	$\frac{\mu}{M} b$
$y'_2$	$-\frac{Mb}{\Sigma}$	$-\frac{\mu}{2m} b$
$y'_3$	$-\frac{Mb}{\Sigma}$	$-\frac{\mu}{2m} b$

(II.5)

so the equilibrium moments of inertia are given by

	HDO	H <sub>2</sub> O, D <sub>2</sub> O
$I_{x'x'}$	$\mu b^2$	$\mu b^2 = \mu r_e^2 \cos^2 \alpha$
$I_{y'y'}$	$(\mu + \frac{4m_X m_Z}{\Sigma}) a^2$	$2ma^2 = 2mr_e^2 \sin^2 \alpha$ (II.6)
$I_{x'y'}$	$\frac{M\delta ab}{\Sigma}$	0

Let  $x, y$  be principal axes ( $x', y'$  are, of course, already principal axes for H<sub>2</sub>O and D<sub>2</sub>O); then the equilibrium principal moments are given by the well-known transformation

$$\begin{aligned}
 I_{xx}^e &= I_{x'x'} \cos^2 \theta + I_{y'y'} \sin^2 \theta - 2I_{x'y'} \sin \theta \cos \theta \\
 I_{yy}^e &= I_{x'x'} \sin^2 \theta + I_{y'y'} \cos^2 \theta + 2I_{x'y'} \sin \theta \cos \theta
 \end{aligned}
 \tag{II.7}$$

$$\tan 2\theta = \frac{2I_{x'y'}}{I_{x'x'} - I_{y'y'}}$$

In this coordinate system, which, for the molecules considered, amounts to a III<sup>r</sup> representation\*, the equilibrium positions of the nuclei are given by

	HDO	H <sub>2</sub> O, D <sub>2</sub> O	
$x_1^e$	$\Sigma^{-1}(\delta a \cos \theta + \sigma b \sin \theta)$	0	
$x_2^e$	$\Sigma^{-1}[(2m_X + M)a \cos \theta - Mb \sin \theta]$	a	
$x_3^e$	$-\Sigma^{-1}[(2m_Z + M)a \cos \theta + Mb \sin \theta]$	-a	
$y_1^e$	$-\Sigma^{-1}(\delta a \sin \theta - \sigma b \cos \theta)$	$\frac{\mu}{M}b$	(II.8)
$y_2^e$	$-\Sigma^{-1}[(2m_X + M)a \sin \theta + Mb \cos \theta]$	$-\frac{\mu}{2m}b$	
$y_3^e$	$\Sigma^{-1}[(2m_Z + M)a \sin \theta - Mb \cos \theta]$	$-\frac{\mu}{2m}b$	

and we also have, with

$$\begin{aligned} x_{1j} &= x_1^e - x_j^e \\ y_{1j} &= y_1^e - y_j^e, \end{aligned} \quad (\text{II.8a})$$

	HDO	H <sub>2</sub> O, D <sub>2</sub> O	
$x_{12}$	$-a \cos \theta + b \sin \theta$	-a	
$x_{13}$	$a \cos \theta + b \sin \theta$	a	
$x_{23}$	$2a \cos \theta$	2a	
$y_{12}$	$a \sin \theta + b \cos \theta$	b	(II.9)
$y_{13}$	$-a \sin \theta + b \cos \theta$	b	
$y_{23}$	$-2a \sin \theta$	0	

## 2. The Normal Coordinate Problem

Let us assume the kinetic energy, T, and the harmonic portion of the potential energy, V<sub>0</sub>, can be written in matrix

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\* See Appendix C; we will find that  $I_{xx}^e < I_{yy}^e < I_{zz}^e$ .

form\* as

$$2T = \tilde{\mathbf{u}} \mathbf{p} \dot{\mathbf{u}} , \quad (\text{II.10})$$

$$2V_0 = \tilde{\mathbf{u}} \mathbf{K} \mathbf{u} , \quad (\text{II.11})$$

where, for the molecules under consideration,  $\mathbf{p}$  and  $\mathbf{K}$  are certain  $3 \times 3$  matrices which will be determined specifically later, and  $\mathbf{u}$  is a vector whose components are usually written as

$$\mathbf{u} = \begin{bmatrix} u \\ v \\ w \end{bmatrix} . \quad (\text{II.12})$$

The normal coordinate problem consists in the simultaneous diagonalization of  $\mathbf{p}$  and  $\mathbf{K}$  so as to express the quadratic forms (10) and (11) as simple sums of squares. This may be carried out by well-known methods\*\*, and we find it convenient to use the following one.

Let  $\mu_1 (= \mu_1, \mu_2, \mu_3)$  be the characteristic numbers of  $\mathbf{p}$ , and let  $\mathbf{A}$  be the normalized modal matrix of  $\mathbf{p}$  such that

$$\tilde{\mathbf{A}} \mathbf{p} \mathbf{A} = \boldsymbol{\lambda} , \quad (\text{II.13})$$

where

$$\boldsymbol{\lambda} = \begin{bmatrix} \mu_1 & 0 & 0 \\ 0 & \mu_2 & 0 \\ 0 & 0 & \mu_3 \end{bmatrix} . \quad (\text{II.14})$$

Now let

$$\mathbf{y} = \mathbf{A}^{-1} \mathbf{u} , \quad (\text{II.15})$$

so that

$$2T = \tilde{\mathbf{u}} \mathbf{p} \dot{\mathbf{u}} = \tilde{\mathbf{y}} \tilde{\mathbf{A}} \mathbf{p} \mathbf{A} \dot{\mathbf{y}} = \tilde{\mathbf{y}} \boldsymbol{\lambda} \dot{\mathbf{y}} . \quad (\text{II.16})$$

\* We use the tilde  $\sim$  to indicate the transposed matrix.

\*\* See, for example, reference 9, Sections 1.17, 1.25, 2.12.

Since  $2T \geq 0$  always,  $\mathbf{M}$  is positive definite, and the  $\mu_i$  will all be positive.

Now let

$$\mathbf{M} = \begin{bmatrix} \mu_1^{-\frac{1}{2}} & 0 & 0 \\ 0 & \mu_2^{-\frac{1}{2}} & 0 \\ 0 & 0 & \mu_3^{-\frac{1}{2}} \end{bmatrix}, \quad \mathbf{M}^{-1} = \begin{bmatrix} \mu_1^{\frac{1}{2}} & 0 & 0 \\ 0 & \mu_2^{\frac{1}{2}} & 0 \\ 0 & 0 & \mu_3^{\frac{1}{2}} \end{bmatrix}, \quad (\text{II.17})$$

and define

$$\mathbf{z} = \mathbf{M}^{-1} \mathbf{y}. \quad (\text{II.18})$$

Since  $\mathbf{M}^{-1} \mathbf{M}^{-1} = \boldsymbol{\lambda}$ , we now have

$$2T = \tilde{\mathbf{y}} \mathbf{M}^{-1} \mathbf{M}^{-1} \mathbf{y} = \tilde{\mathbf{y}} \widetilde{\mathbf{M}^{-1} \mathbf{M}^{-1}} \mathbf{y} = \widetilde{\mathbf{M}^{-1} \mathbf{y}} \mathbf{M}^{-1} \mathbf{y} = \tilde{\mathbf{z}} \mathbf{z}. \quad (\text{II.19})$$

Further,

$$2V_0 = \tilde{\mathbf{u}} \mathbf{K} \mathbf{u} = \tilde{\mathbf{y}} \tilde{\mathbf{A}} \mathbf{K} \mathbf{A} \mathbf{y} = \tilde{\mathbf{z}} \tilde{\mathbf{M}} \tilde{\mathbf{A}} \mathbf{K} \mathbf{A} \mathbf{M} \mathbf{z} = \tilde{\mathbf{z}} \mathbf{B} \mathbf{z}, \quad (\text{II.20})$$

where

$$\mathbf{B} = \tilde{\mathbf{M}} \tilde{\mathbf{A}} \mathbf{K} \mathbf{A} \mathbf{M}. \quad (\text{II.21})$$

Now let  $\omega_i^2$  ( $= \omega_1^2, \omega_2^2, \omega_3^2$ ) be the characteristic numbers of  $\mathbf{B}$ , and let  $\mathbf{R}$  be the (orthogonal) normalized modal matrix of  $\mathbf{B}$ , so that

$$\tilde{\mathbf{R}} \mathbf{B} \mathbf{R} = \mathbf{R}^{-1} \mathbf{B} \mathbf{R} = \boldsymbol{\omega} = \begin{bmatrix} \omega_1^2 & 0 & 0 \\ 0 & \omega_2^2 & 0 \\ 0 & 0 & \omega_3^2 \end{bmatrix}, \quad (\text{II.22})$$

and let

$$\mathbf{Q} = \mathbf{R}^{-1} \mathbf{z}. \quad (\text{II.23})$$

Then

$$2V_0 = \tilde{\mathbf{z}} \mathbf{B} \mathbf{z} = \tilde{\mathbf{Q}} \tilde{\mathbf{R}} \mathbf{B} \mathbf{R} \mathbf{Q} = \tilde{\mathbf{Q}} \boldsymbol{\omega} \mathbf{Q}, \quad (\text{II.24})$$

and

$$2T = \tilde{\mathbf{z}} \dot{\mathbf{z}} = \tilde{\mathbf{Q}} \tilde{\mathbf{R}} \dot{\mathbf{R}} \dot{\mathbf{Q}} = \tilde{\mathbf{Q}} \dot{\mathbf{Q}} . \quad (\text{II.25})$$

Hence the transformation

$$\mathbf{Q} = \mathbf{R}^{-1} \mathbf{z} = \mathbf{R}^{-1} \mathbf{H}^{-1} \mathbf{y} = \mathbf{R}^{-1} \mathbf{H}^{-1} \mathbf{A}^{-1} \mathbf{u} = \mathbf{P}^{-1} \mathbf{u} , \quad (\text{II.26})$$

with

$$\mathbf{P}^{-1} = \mathbf{R}^{-1} \mathbf{H}^{-1} \mathbf{A}^{-1} , \quad (\text{II.27})$$

or,

$$\mathbf{u} = \mathbf{P} \mathbf{Q} , \quad (\text{II.28})$$

with

$$\mathbf{P} = \mathbf{A} \mathbf{H} \mathbf{R} , \quad (\text{II.29})$$

simultaneously reduces the forms (10) and (11) to the forms

$$2T = \tilde{\mathbf{Q}} \dot{\mathbf{Q}} = \dot{Q}_1^2 + \dot{Q}_2^2 + \dot{Q}_3^2 , \quad (\text{II.30})$$

$$2V_0 = \tilde{\mathbf{Q}} \boldsymbol{\omega} \mathbf{Q} = \omega_1^2 Q_1^2 + \omega_2^2 Q_2^2 + \omega_3^2 Q_3^2 . \quad (\text{II.31})$$

If the Lagrange equations of motion are now set up, using (30) and (31) for the kinetic and potential energies, it will be readily seen that they describe simple harmonic motion:

$$\frac{d}{dt} \left( \frac{\partial T}{\partial \dot{Q}_1} \right) + \frac{\partial V}{\partial Q_1} = 0 ,$$

or

$$\ddot{Q}_1 + \omega_1^2 Q_1 = 0 ,$$

which describes simple harmonic motion of angular frequency  $\omega_1$ . Thus the normal coordinate problem reduces to finding the coordinates  $Q_1$  for which the motion of the system can be described, in general, as a superposition of simple harmonic

motions.

Here the  $Q_i$  are the normal coordinates of the system, and the  $\omega_i$  are the normal angular frequencies

$$\omega_i = 2\pi\nu_i . \quad (\text{II.32})$$

### 3. Coordinate Transformations and the Kinetic Energy Matrix

In the vibrating molecule, let the instantaneous coordinates of the  $i$ -th particle be  $(x_i, y_i)$ , and let  $\delta x_i, \delta y_i$  be the "displacement coordinates" defined by

$$x_i = x_i^e + \delta x_i \quad y_i = y_i^e + \delta y_i . \quad (\text{II.33})$$

Since the molecule vibrates about the center of mass, which remains fixed, we have

$$\sum_i m_i x_i = 0 = \sum_i m_i y_i , \quad (\text{II.34})$$

and, in first approximation, the internal angular momentum is zero since there are no torques acting:

$$M(x_1^e \delta y_1 - y_1^e \delta x_1) + m_Z(x_2^e \delta y_2 - y_2^e \delta x_2) + m_X(x_3^e \delta y_3 - y_3^e \delta x_3) = 0 \quad (\text{II.35})$$

If we now define a convenient set of "intermediate coordinates"  $u, v, w$  by the relations

	HDO	H <sub>2</sub> O, D <sub>2</sub> O	
u	$\delta x_1 - \frac{1}{\sigma}(m_Z \delta x_2 + m_X \delta x_3)$	$\delta x_1 - \frac{1}{2}(\delta x_2 + \delta x_3)$	(II.36)
v	$\delta y_1 - \frac{1}{\sigma}(m_Z \delta y_2 + m_X \delta y_3)$	$\delta y_1 - \frac{1}{2}(\delta y_2 + \delta y_3)$	
w	$\delta x_2 - \delta x_3$	$\delta x_2 - \delta x_3$	

then the conditions (34) and (35) enable us to solve for the  $\delta x_1$  etc. in terms of the  $u$ ,  $v$  and  $w$ . In matrix notation, with  $\mathbf{u}$  defined as in (12), if we write

$$\mathbf{x} = \mathbf{F}\mathbf{u} \quad , \quad (\text{II.37})$$

where

$$\mathbf{x} = \begin{bmatrix} \delta x_1 \\ \delta x_2 \\ \delta x_3 \\ \delta y_1 \\ \delta y_2 \\ \delta y_3 \end{bmatrix} \quad , \quad (\text{II.38})$$

the transformation matrix  $\mathbf{F}$  is given by

$$\mathbf{F} = \begin{bmatrix} \mathbf{F}^{(x)} \\ \mathbf{F}^{(y)} \end{bmatrix} \quad , \quad (\text{II.39})$$

where

$$\mathbf{F}^{(x)} = \begin{bmatrix} \frac{\mu}{M} & 0 & 0 \\ -\frac{q\mu}{qX} & 0 & \frac{m_X}{qX} \\ -\frac{q\mu}{qZ} & 0 & -\frac{m_Z}{qZ} \end{bmatrix} \quad , \quad (\text{II.40})$$

and

$$\mathbf{F}^{(y)} = \begin{bmatrix} 0 & \frac{\mu}{M} & 0 \\ \frac{My_1^e}{m_Z x_{23}} & -\frac{\mu x_{13}}{m_Z x_{23}} & \frac{m_X y_{23}}{\sigma x_{23}} \\ -\frac{My_1^e}{m_X x_{23}} & \frac{\mu x_{12}}{m_X x_{23}} & -\frac{m_Z y_{23}}{\sigma x_{23}} \end{bmatrix} \quad (\text{II.41})$$

Now, the kinetic energy of the vibrating molecule is given by

$$2T = \sum_i m_i (\dot{x}_i^2 + \dot{y}_i^2) \quad , \quad (\text{II.42})$$



and since

$$\dot{x}_1 = \delta \dot{x}_1, \quad \dot{y}_1 = \delta \dot{y}_1, \quad (\text{II.43})$$

we can use (37) to express the kinetic energy in terms of the intermediate coordinates  $\mathbf{u}$ . After some algebra, we find --  
cf. (10) --

$$2T = \tilde{\mathbf{u}} \mathbf{p} \dot{\mathbf{u}}, \quad (\text{II.44})$$

where

$$\mathbf{p} = \tilde{\mathbf{p}} = \begin{bmatrix} \mu \left(1 + \frac{M \Sigma (y_1^e)^2}{m_X m_Z x_{23}^2}\right) & - \frac{\sigma M^2 x_1^e y_1^e}{m_X m_Z x_{23}^2} & \frac{M y_1^e y_{23}}{x_{23}^2} \\ - \frac{\sigma M^2 x_1^e y_1^e}{m_X m_Z x_{23}^2} & \frac{\mu^2 \Sigma I_{yy}^e}{m_X m_Z M x_{23}^2} & - \frac{M x_1^e y_{23}}{x_{23}^2} \\ \frac{M y_1^e y_{23}}{x_{23}^2} & - \frac{M x_1^e y_{23}}{x_{23}^2} & \frac{4 m_X m_Z a^2}{\sigma x_{23}^2} \end{bmatrix}. \quad (\text{II.45})$$

The displacement coordinates  $\mathbf{x}$  are related to the normal coordinates  $\mathbf{Q}$  through the transformations (37) and (28):

$$\mathbf{x} = \mathbf{F} \mathbf{u} = \mathbf{F} \mathbf{P} \mathbf{Q} = \mathbf{U} \mathbf{Q}, \quad (\text{II.46})$$

where

$$\mathbf{U} = \mathbf{F} \mathbf{P} = \begin{bmatrix} \mathbf{F}^{(x)} \mathbf{P} \\ \mathbf{F}^{(y)} \mathbf{P} \end{bmatrix} = \begin{bmatrix} \mathbf{U}^{(x)} \\ \mathbf{U}^{(y)} \end{bmatrix}. \quad (\text{II.47})$$

Now let us write\*

$$\begin{aligned} \delta x_1 &= m_1^{-\frac{1}{2}} \sum_s L_{1s}^{(x)} Q_s, \\ \delta y_1 &= m_1^{-\frac{1}{2}} \sum_s L_{1s}^{(y)} Q_s, \end{aligned} \quad (\text{II.48})$$

---

\* The literature normally uses an italic "L" where we have "L"; for typing purposes we find it convenient to use the present notation.

or,

$$\begin{aligned}\delta \mathbf{x} &= \mathbf{m}^{-1} \mathbf{L}^{(x)} \mathbf{q} = \mathbf{U}^{(x)} \mathbf{q} , \\ \delta \mathbf{y} &= \mathbf{m}^{-1} \mathbf{L}^{(y)} \mathbf{q} = \mathbf{U}^{(y)} \mathbf{q} ,\end{aligned}\quad (\text{II.49})$$

where

$$\mathbf{m} = \begin{bmatrix} m_1^{\frac{1}{2}} & 0 & 0 \\ 0 & m_2^{\frac{1}{2}} & 0 \\ 0 & 0 & m_3^{\frac{1}{2}} \end{bmatrix} = \begin{bmatrix} M^{\frac{1}{2}} & 0 & 0 \\ 0 & m_Z^{\frac{1}{2}} & 0 \\ 0 & 0 & m_X^{\frac{1}{2}} \end{bmatrix} , \quad (\text{II.50})$$

and

$$\begin{aligned}\mathbf{L}^{(x)} &= \mathbf{m} \mathbf{U}^{(x)} , \\ \mathbf{L}^{(y)} &= \mathbf{m} \mathbf{U}^{(y)} .\end{aligned}\quad (\text{II.51})$$

#### 4. Potential Function

It is desirable to express the potential energy as a function of the displacements of the nuclei from their equilibrium positions, since in this form it should be practically independent of isotopic modifications of the molecule.

Of the two types of coordinate systems which are suitable for this -- central-force and valence-force -- we choose the central-force one, where the coordinates are the changes in the distances between each pair of nuclei.

Let

$$s_{1j} = \left[ (x_1 - x_j)^2 + (y_1 - y_j)^2 \right]^{\frac{1}{2}} \quad (\text{II.52})$$

be the distance between the  $i$ -th and  $j$ -th particles, with

$$s_{1j}^e = \left[ (x_1^e - x_j^e)^2 + (y_1^e - y_j^e)^2 \right]^{\frac{1}{2}} = (x_{1j}^2 + y_{1j}^2)^{\frac{1}{2}} , \quad (\text{II.53})$$

which is the equilibrium distance. Also let

$$r_{1j} = s_{1j} - s_{1j}^e \quad (\text{II.54})$$

be the relative displacement from equilibrium; the  $r_{1j}$  are thus the required coordinates. With

$$\delta x_{1j} = \delta x_1 - \delta x_j, \quad (\text{II.55})$$

we have

$$\begin{aligned} s_{1j}^2 &= (x_1 - x_j)^2 + (y_1 - y_j)^2 \\ &= (x_{1j}^2 + y_{1j}^2) + 2(x_{1j} \delta x_{1j} + y_{1j} \delta y_{1j}) + (\delta x_{1j})^2 + (\delta y_{1j})^2 \\ &\approx (s_{1j}^e)^2 + 2(x_{1j} \delta x_{1j} + y_{1j} \delta y_{1j}), \quad \text{to first order,} \end{aligned}$$

so that

$$s_{1j} \approx s_{1j}^e + \frac{1}{s_{1j}^e} (x_{1j} \delta x_{1j} + y_{1j} \delta y_{1j}),$$

and

$$r_{1j} = s_{1j} - s_{1j}^e \approx \frac{1}{s_{1j}^e} (x_{1j} \delta x_{1j} + y_{1j} \delta y_{1j}). \quad (\text{II.56})$$

We will denote the set of coordinates  $r_{1j}$  by  $\mathbf{r}$ :

$$\mathbf{r} = \begin{bmatrix} r_1 \\ r_2 \\ r_3 \end{bmatrix} = \begin{bmatrix} r_{12} \\ r_{13} \\ r_{23} \end{bmatrix}. \quad (\text{II.57})$$

From (56), using the  $\delta x_{1j}$  and  $\delta y_{1j}$  calculated by means of (37), and the  $x_{1j}$  and  $y_{1j}$  given by (9), together with the obvious relations

$$s_{12}^e = r_e = s_{13}^e, \quad s_{23}^e = 2a, \quad (\text{II.58})$$

we can calculate the components of  $\mathbf{r}$  in terms of the intermediate coordinates  $\mathbf{u}$ ; we write

$$\mathbf{r} = \mathbf{T} \mathbf{u} , \quad (\text{II.59})$$

with

$$\mathbf{T} = \begin{bmatrix} \frac{1}{r_e} \left( x_{12} - \frac{M y_1^e y_{12}}{m_Z x_{23}} \right) & \frac{\mu y_{12}}{r_e} \left( \frac{1}{M} + \frac{x_{13}}{m_Z x_{23}} \right) & - \frac{m_X}{\sigma r_e} \left( x_{12} + \frac{y_{12} y_{23}}{x_{23}} \right) \\ \frac{1}{r_e} \left( x_{13} + \frac{M y_1^e y_{13}}{m_X x_{23}} \right) & \frac{\mu y_{13}}{r_e} \left( \frac{1}{M} - \frac{x_{12}}{m_X x_{23}} \right) & \frac{m_Z}{\sigma r_e} \left( x_{13} + \frac{y_{13} y_{23}}{x_{23}} \right) \\ \frac{M \sigma y_1^e y_{23}}{2 m_X m_Z a x_{23}} & - \frac{M \sigma x_1^e y_{23}}{2 m_X m_Z a x_{23}} & \frac{2a}{x_{23}} \end{bmatrix} \quad (\text{II.60})$$

Using (28), we can also write  $\mathbf{r}$  in terms of the normal coordinates:

$$\mathbf{r} = \mathbf{T} \mathbf{u} = \mathbf{T} \mathbf{P} \mathbf{Q} = \mathbf{S} \mathbf{Q} , \quad (\text{II.61})$$

where

$$\mathbf{S} = \mathbf{T} \mathbf{P} . \quad (\text{II.62})$$

We can now get down to the business of handling the potential function. In terms of the  $r_{ij}$ , the harmonic, or quadratic, portion of the potential energy function may be written in the central-force form

$$2V_0 = \sum_{i=1}^3 \sum_{\substack{k=1 \\ j>1 \\ l>k}}^3 K_{ijkl} r_{ij} r_{kl} , \quad (\text{II.63})$$

with

$$\begin{aligned} K_{1213} &= K_{1312} \\ K_{1223} &= K_{2312} \\ K_{1323} &= K_{2313} . \end{aligned} \quad (\text{II.64})$$

For the type of molecule under consideration, the

potential is invariant to interchange of the nuclei 2 and 3 (i.e. invariant under the symmetry operation  $\sigma_v$ , which refers to reflection in the  $x', y'$ -plane); this interchange results in the exchange of  $r_{12}$  and  $r_{13}$ , so we must have:

$$\begin{aligned} K_{1212} &= K_{1313} \\ K_{1223} &= K_{1323} . \end{aligned} \quad (\text{II.65})$$

Thus we can write:

$$2V_0 = K_{1212}(r_{12}^2 + r_{13}^2) + K_{2323}r_{23}^2 + 2K_{1213}r_{12}r_{13} + 2K_{1223}(r_{12} + r_{13})r_{23} \quad (\text{II.66})$$

or,

$$2V_0 = K'_{11}(r_1^2 + r_2^2) + K'_{33}r_3^2 + 2K'_{12}r_1r_2 + 2K'_{13}(r_1 + r_2)r_3 , \quad (\text{II.67})$$

i.e.

$$2V_0 = \mathbf{r}'\mathbf{K}'\mathbf{r}' , \quad (\text{II.68})$$

where

$$\mathbf{K}' = \begin{bmatrix} K'_{11} & K'_{12} & K'_{13} \\ K'_{12} & K'_{11} & K'_{13} \\ K'_{13} & K'_{13} & K'_{33} \end{bmatrix} = \begin{bmatrix} K_{1212} & K_{1213} & K_{1223} \\ K_{1213} & K_{1212} & K_{1223} \\ K_{1223} & K_{1223} & K_{2323} \end{bmatrix} . \quad (\text{II.69})$$

In terms of the intermediate coordinates  $\mathbf{u}$ , we have from (59),

$$2V_0 = \mathbf{r}'\mathbf{K}'\mathbf{r}' = \mathbf{\tilde{u}}\mathbf{\tilde{T}}\mathbf{K}'\mathbf{T}\mathbf{u} = \mathbf{\tilde{u}}\mathbf{K}\mathbf{u} , \quad (\text{II.70})$$

where

$$\mathbf{K} = \mathbf{\tilde{T}}\mathbf{K}'\mathbf{T} . \quad (\text{II.71})$$

We now have the harmonic portion of the potential energy in the required form (10).

The cubic portion of the potential may be written

$$V_1 = \sum_{i \leq j \leq k} K_{ijk} r_i r_j r_k . \quad (\text{II.72})$$

In this work we are interested in the analogous expression in terms of the normal coordinates:

$$V_1 = \sum_{s \leq s' \leq s''} k'_{ss's''} Q_s Q_{s'} Q_{s''} , \quad (\text{II.73})$$

where the  $k'_{ss's''}$  will be functions of the  $K_{ijk}$  and the transformation coefficients  $S_{ij}$ , since  $\mathbf{r} = \mathbf{S} \mathbf{Q}$ . For purposes of computation, we find it convenient to express the relations between the  $K_{ijk}$  and the  $k'_{ss's''}$  in the following way: let

$$\mathbf{k} = \begin{bmatrix} K_{111} & K_{112} & K_{113} \\ K_{122} & K_{222} & K_{223} \\ K_{133} & K_{233} & K_{333} \\ 0 & 0 & K_{123} \end{bmatrix} , \quad \mathbf{k}' = \begin{bmatrix} k'_{111} & k'_{112} & k'_{113} \\ k'_{122} & k'_{222} & k'_{223} \\ k'_{133} & k'_{233} & k'_{333} \\ 0 & 0 & k'_{123} \end{bmatrix} , \quad (\text{II.74})$$

and

$$\mathbf{S}' = \begin{bmatrix} s_{11}^2 & s_{12}^2 & s_{13}^2 \\ s_{21}^2 & s_{22}^2 & s_{23}^2 \\ s_{31}^2 & s_{32}^2 & s_{33}^2 \\ s_{11}s_{21} & s_{12}s_{22} & s_{13}s_{23} \end{bmatrix} , \quad (\text{II.75})$$

$$\mathbf{S}'' = \begin{bmatrix} 2S_{11}S_{12} & 2S_{11}S_{13} & 2S_{12}S_{13} \\ 2S_{21}S_{22} & 2S_{21}S_{23} & 2S_{22}S_{23} \\ 2S_{31}S_{32} & 2S_{31}S_{33} & 2S_{32}S_{33} \\ S_{11}S_{22} + S_{12}S_{21} & S_{11}S_{23} + S_{13}S_{21} & S_{12}S_{23} + S_{13}S_{22} \end{bmatrix} \quad (\text{II.76})$$

Now let

$$\begin{aligned} \alpha &= \mathbf{kS} \\ \beta &= \tilde{\mathbf{S}}' \alpha = \tilde{\mathbf{S}}' \mathbf{kS} \\ \gamma &= \tilde{\alpha} \mathbf{S}'' = \tilde{\mathbf{S}} \tilde{\mathbf{k}} \mathbf{S}'' \end{aligned} \quad (\text{II.77})$$

Then it may be verified that

$$\mathbf{k}' = \begin{bmatrix} \beta_{11} & \beta_{12} + \gamma_{11} & \beta_{13} + \gamma_{12} \\ \beta_{21} + \gamma_{21} & \beta_{22} & \beta_{23} + \gamma_{23} \\ \beta_{31} + \gamma_{32} & \beta_{32} + \gamma_{33} & \beta_{33} \\ 0 & 0 & \gamma_{13} + \gamma_{22} + \gamma_{31} \end{bmatrix} \quad (\text{II.78})$$

From the symmetry of the molecules we are dealing with, as discussed on pp 16-17, it is easily seen that we must have

$$\begin{aligned} K_{111} &= K_{222} \\ K_{112} &= K_{122} \\ K_{113} &= K_{223} \\ K_{133} &= K_{233} \end{aligned} \quad (\text{II.79})$$

A discussion of the method of determining the potential constants from observed infrared data will be postponed until Section 6.

### 5. Specialization to H<sub>2</sub>O Type Molecules

For this type of molecule (described by the point group C<sub>2v</sub>, with orthorhombic symmetry), we have

$$\mathbf{u} = \begin{bmatrix} \delta x_1 - \frac{1}{2}(\delta x_2 + \delta x_3) \\ \delta y_1 - \frac{1}{2}(\delta y_2 + \delta y_3) \\ \delta x_2 - \delta x_3 \end{bmatrix}, \quad (\text{II.80})$$

$$\mathbf{F}^{(x)} = \begin{bmatrix} \frac{\mu}{M} & 0 & 0 \\ -\frac{\mu}{2m} & 0 & \frac{1}{2} \\ -\frac{\mu}{2m} & 0 & -\frac{1}{2} \end{bmatrix}, \quad \mathbf{F}^{(y)} = \begin{bmatrix} 0 & \frac{\mu}{M} & 0 \\ \frac{\mu}{2m} \cot \alpha & -\frac{\mu}{2m} & 0 \\ -\frac{\mu}{2m} \cot \alpha & -\frac{\mu}{2m} & 0 \end{bmatrix}. \quad (\text{II.81})$$

We define

$$\mu' = \mu \left(1 + \frac{\mu b^2}{2ma^2}\right) = \frac{\mu I_{zz}^e}{I_{yy}^e}, \quad (\text{II.82})$$

then

$$\mathbf{p} = \begin{bmatrix} \mu' & 0 & 0 \\ 0 & \mu & 0 \\ 0 & 0 & \frac{\mu}{2m} \end{bmatrix}, \quad (\text{II.83})$$

and

$$\mathbf{T} = \begin{bmatrix} -\frac{\mu'}{\mu} \sin \alpha & \cos \alpha & \frac{1}{2} \sin \alpha \\ \frac{\mu'}{\mu} \sin \alpha & \cos \alpha & \frac{1}{2} \sin \alpha \\ 0 & 0 & 1 \end{bmatrix}, \quad (\text{II.84})$$

so from (71),

$$\mathbf{K} = \begin{bmatrix} 2(K'_{11} - K'_{12})T_{11}^2 & 0 & 0 \\ 0 & 2(K'_{11} + K'_{12})T_{12}^2 & 2(K'_{11} + K'_{12})T_{12}T_{13} \\ & & + 2K'_{13}T_{12} \\ 0 & 2(K'_{11} + K'_{12})T_{12}T_{13} & 2(K'_{11} + K'_{12})T_{13}^2 \\ & + 2K'_{13}T_{12} & + 4K'_{13}T_{13} + K_{33} \end{bmatrix}, \quad (\text{II.85})$$



or,

$$\mathbf{K} = \begin{bmatrix} k_3' & 0 & 0 \\ 0 & k_2' & \frac{1}{2}k_4' \\ 0 & \frac{1}{2}k_4' & k_1' \end{bmatrix}. \quad (\text{II.86})$$

Also,

$$\boldsymbol{\lambda} = \boldsymbol{\mu}, \quad \mathbf{A} = \mathbf{I}, \quad \mathbf{y} = \mathbf{u}, \quad (\text{II.87})$$

where  $\mathbf{I}$  is the identity matrix, and

$$\mathbf{z} = \begin{bmatrix} \mu^{\frac{1}{2}} u \\ \mu^{\frac{1}{2}} v \\ \left(\frac{\mu}{2}\right)^{\frac{1}{2}} w \end{bmatrix}. \quad (\text{II.88})$$

Thus,

$$\begin{aligned} \mathbf{B} = \mathbf{MKM} &= \begin{bmatrix} \mu^{-1} k_3' & 0 & 0 \\ 0 & \mu^{-1} k_2' & \frac{1}{2} \left(\frac{\mu}{2}\right)^{-\frac{1}{2}} k_4' \\ 0 & \frac{1}{2} \left(\frac{\mu}{2}\right)^{-\frac{1}{2}} k_4' & \left(\frac{\mu}{2}\right)^{-1} k_1' \end{bmatrix} \\ &= \begin{bmatrix} k_3 & 0 & 0 \\ 0 & k_2 & \frac{1}{2}k_4 \\ 0 & \frac{1}{2}k_4 & k_1 \end{bmatrix}. \end{aligned} \quad (\text{II.89})$$

If we choose

$$\mathbf{R} = \begin{bmatrix} 0 & 0 & 1 \\ \sin \gamma & \cos \gamma & 0 \\ \cos \gamma & -\sin \gamma & 0 \end{bmatrix}, \quad (\text{II.90})$$

then,

$$\mathbf{e} = \mathbf{RBR} = \begin{bmatrix} k_1 \cos^2 \gamma + k_2 \sin^2 \gamma & (k_2 - k_1) \sin \gamma \cos \gamma & 0 \\ + k_4 \sin \gamma \cos \gamma & + \frac{1}{2}(k_4 \cos^2 \gamma - \sin^2 \gamma) & 0 \\ (k_2 - k_1) \sin \gamma \cos \gamma & k_1 \sin^2 \gamma + k_2 \cos^2 \gamma & 0 \\ + \frac{1}{2}(k_4 \cos^2 \gamma - \sin^2 \gamma) & - k_4 \sin \gamma \cos \gamma & 0 \\ 0 & 0 & k_3 \end{bmatrix}, \quad (\text{II.91})$$

and

$$\mathbf{e} = \begin{bmatrix} \omega_1^2 & 0 & 0 \\ 0 & \omega_2^2 & 0 \\ 0 & 0 & \omega_3^2 \end{bmatrix}, \quad (\text{II.92})$$

provided

$$(k_2 - k_1) \sin \gamma \cos \gamma + \frac{1}{2} k_4 (\cos^2 \gamma - \sin^2 \gamma) = 0, \quad (\text{II.93})$$

i.e. if

$$\tan 2\gamma = \frac{k_4}{k_1 - k_2}, \quad (\text{II.94})$$

(see also equations 106 and 107). Then

$$\begin{aligned} \omega_1^2 &= k_1 \cos^2 \gamma + k_2 \sin^2 \gamma + k_4 \sin \gamma \cos \gamma \\ \omega_2^2 &= k_1 \sin^2 \gamma + k_2 \cos^2 \gamma - k_4 \sin \gamma \cos \gamma \\ \omega_3^2 &= k_3. \end{aligned} \quad (\text{II.95})$$

Also,

$$\mathbf{P} = \mathbf{MR} = \begin{bmatrix} 0 & 0 & \mu'^{-\frac{1}{2}} \\ \mu'^{-\frac{1}{2}} \sin \gamma & \mu'^{-\frac{1}{2}} \cos \gamma & 0 \\ \left(\frac{m}{2}\right)^{-\frac{1}{2}} \cos \gamma & - \left(\frac{m}{2}\right)^{-\frac{1}{2}} \sin \gamma & 0 \end{bmatrix} \quad (\text{II.96})$$

and

$$\mathbf{U}^{(x)} = \mathbf{F}^{(x)} \mathbf{P} = \begin{bmatrix} 0 & 0 & \frac{\mu}{M} \mu'^{-\frac{1}{2}} \\ \frac{1}{2} \left(\frac{m}{2}\right)^{-\frac{1}{2}} \cos \gamma & - \frac{1}{2} \left(\frac{m}{2}\right)^{-\frac{1}{2}} \sin \gamma & - \frac{\mu}{2m} \mu'^{-\frac{1}{2}} \\ - \frac{1}{2} \left(\frac{m}{2}\right)^{-\frac{1}{2}} \cos \gamma & \frac{1}{2} \left(\frac{m}{2}\right)^{-\frac{1}{2}} \sin \gamma & - \frac{\mu}{2m} \mu'^{-\frac{1}{2}} \end{bmatrix} \quad (\text{II.97})$$

$$\mathbf{U}^{(y)} = \mathbf{F}^{(y)} \mathbf{P} = \begin{bmatrix} \frac{\mu}{M} \sin \gamma & \frac{\mu}{M} \cos \gamma & 0 \\ -\frac{\mu}{2m} \sin \gamma & -\frac{\mu}{2m} \cos \gamma & \frac{\mu}{2m} \mu'^{-\frac{1}{2}} \cot \alpha \\ -\frac{\mu}{2m} \sin \gamma & -\frac{\mu}{2m} \cos \gamma & -\frac{\mu}{2m} \mu'^{-\frac{1}{2}} \cot \alpha \end{bmatrix} \quad (\text{II.98})$$

$$\mathbf{L}^{(x)} = \mathbf{mU}^{(x)} = \begin{bmatrix} 0 & 0 & \frac{\mu}{M} \mu'^{-\frac{1}{2}} \\ 2^{-\frac{1}{2}} \cos \gamma & -2^{-\frac{1}{2}} \sin \gamma & -\frac{\mu}{2m} \mu'^{-\frac{1}{2}} \\ -2^{-\frac{1}{2}} \cos \gamma & 2^{-\frac{1}{2}} \sin \gamma & -\frac{\mu}{2m} \mu'^{-\frac{1}{2}} \end{bmatrix} \quad (\text{II.99})$$

$$\mathbf{L}^{(y)} = \mathbf{mU}^{(y)} = \begin{bmatrix} \left(\frac{\mu}{M}\right)^{\frac{1}{2}} \sin \gamma & \left(\frac{\mu}{M}\right)^{\frac{1}{2}} \cos \gamma & 0 \\ -\frac{1}{2} \left(\frac{\mu}{M}\right)^{\frac{1}{2}} \sin \gamma & -\frac{1}{2} \left(\frac{\mu}{M}\right)^{\frac{1}{2}} \cos \gamma & \frac{\mu}{2m} \mu'^{-\frac{1}{2}} \cot \alpha \\ -\frac{1}{2} \left(\frac{\mu}{M}\right)^{\frac{1}{2}} \sin \gamma & -\frac{1}{2} \left(\frac{\mu}{M}\right)^{\frac{1}{2}} \cos \gamma & -\frac{\mu}{2m} \mu'^{-\frac{1}{2}} \cot \alpha \end{bmatrix} \quad (\text{II.100})$$

$$\mathbf{S} = \mathbf{FP} = \begin{bmatrix} \mu^{-\frac{1}{2}} \sin \gamma \cos \alpha & \mu^{-\frac{1}{2}} \cos \gamma \cos \alpha & -\frac{\mu'^{\frac{1}{2}}}{\mu} \sin \alpha \\ +\frac{1}{2} \left(\frac{m}{2}\right)^{-\frac{1}{2}} \cos \gamma \sin \alpha & -\frac{1}{2} \left(\frac{m}{2}\right)^{-\frac{1}{2}} \sin \gamma \sin \alpha & 0 \\ \mu^{-\frac{1}{2}} \sin \gamma \cos \alpha & \mu^{-\frac{1}{2}} \cos \gamma \cos \alpha & \frac{\mu'^{\frac{1}{2}}}{\mu} \sin \alpha \\ +\frac{1}{2} \left(\frac{m}{2}\right)^{-\frac{1}{2}} \cos \gamma \sin \alpha & -\frac{1}{2} \left(\frac{m}{2}\right)^{-\frac{1}{2}} \sin \gamma \sin \alpha & 0 \\ \left(\frac{m}{2}\right)^{-\frac{1}{2}} \cos \gamma & -\left(\frac{m}{2}\right)^{-\frac{1}{2}} \sin \gamma & 0 \end{bmatrix} \quad (\text{II.101})$$

$$\mathbf{S}^{-1} = \begin{bmatrix} \frac{1}{2} \mu^{\frac{1}{2}} \sin \gamma \sec \alpha & \frac{1}{2} \mu^{\frac{1}{2}} \sin \gamma \sec \alpha & -\frac{1}{2} \mu^{\frac{1}{2}} \sin \gamma \tan \alpha \\ & & +\left(\frac{m}{2}\right)^{\frac{1}{2}} \cos \gamma \\ \frac{1}{2} \mu^{\frac{1}{2}} \cos \gamma \sec \alpha & \frac{1}{2} \mu^{\frac{1}{2}} \cos \gamma \sec \alpha & -\frac{1}{2} \mu^{\frac{1}{2}} \cos \gamma \tan \alpha \\ & & -\left(\frac{m}{2}\right)^{\frac{1}{2}} \sin \gamma \\ -\frac{1}{2} \frac{\mu}{\mu'^{\frac{1}{2}}} \operatorname{cosec} \alpha & \frac{1}{2} \frac{\mu}{\mu'^{\frac{1}{2}}} \operatorname{cosec} \alpha & 0 \end{bmatrix} \quad (\text{II.102})$$

## 6. Determination of Potential Constants from Observed Data

The constants in the harmonic portion of the potential energy can be determined from the normal frequencies, provided the latter are known for two isotopic species (e.g. H<sub>2</sub>O and D<sub>2</sub>O) since there are four independent constants involved, and only three normal frequencies for each molecule. The normal frequencies are, of course, determined by analysis of the vibrational spectra, and we do not attempt to do this here but merely use results given by other workers.

Thus, Darling and Dennison<sup>5</sup> have given the normal frequencies for H<sub>2</sub>O and D<sub>2</sub>O, and we base our calculations on their work.

From the relations (95) it is readily shown that

$$\begin{aligned}
 k_1' &= \frac{1}{2} \frac{[\mu(\omega_1^2 + \omega_2^2)]^{(H)} - [\mu(\omega_1^2 + \omega_2^2)]^{(D)}}{(\mu/m)^{(H)} - (\mu/m)^{(D)}} \\
 k_2' &= \frac{[m(\omega_1^2 + \omega_2^2)]^{(H)} - [m(\omega_1^2 + \omega_2^2)]^{(D)}}{(m/\mu)^{(H)} - (m/\mu)^{(D)}} \\
 k_3'' &= \left(\frac{\mu}{m}\right)^2 k_3' = \frac{\mu^2}{m^2} \omega_3^2 \\
 k_4' &= + 2 \left[ \frac{m\mu}{2} (k_1 k_2 - \omega_1^2 \omega_2^2) \right]^{\frac{1}{2}}
 \end{aligned}
 \tag{II.103}$$

where the k's refer to equations (86) and (89), and the superscripts (H), (D) mean the terms concerned are to have the appropriate values for H<sub>2</sub>O and D<sub>2</sub>O, respectively.

Knowing the k's, one can easily work back to the K's of equations (66) through (69) by means of the relations

$$\begin{aligned}
K_{1212} &= K'_{11} = \frac{1}{4}(k'_2 \sec^2 \alpha + k''_3 \operatorname{cosec}^2 \alpha) \\
K_{1213} &= K'_{12} = \frac{1}{4}(k'_2 \sec^2 \alpha - k''_3 \operatorname{cosec}^2 \alpha) \\
K_{1223} &= K'_{13} = \frac{1}{4}(k'_4 - k'_2 \tan \alpha) \sec \alpha \\
K_{2323} &= K'_{33} = k'_1 - \frac{1}{2}k'_4 \tan \alpha + \frac{1}{4}k'_2 \tan^2 \alpha .
\end{aligned} \tag{II.104}$$

One may also calculate the transformation coefficients of  $\mathbf{R}$  (equation 90) by means of the relations

$$\begin{aligned}
\sin \gamma &= + \left( \frac{\omega_1^2 - k_1}{\omega_1^2 - \omega_2^2} \right)^{\frac{1}{2}} \\
\cos \gamma &= + \left( \frac{\omega_1^2 - k_2}{\omega_1^2 - \omega_2^2} \right)^{\frac{1}{2}} ,
\end{aligned} \tag{II.105}$$

which in turn can be derived from the alternative formulae

$$\begin{aligned}
\sin \gamma &= + 2^{-\frac{1}{2}} (1-x^{\frac{1}{2}})^{\frac{1}{2}} \\
\cos \gamma &= + 2^{-\frac{1}{2}} (1+x^{\frac{1}{2}})^{\frac{1}{2}} ,
\end{aligned} \tag{II.106}$$

where

$$x = \frac{(k_1 - k_2)^2}{k_4 + (k_1 - k_2)^2} = \left( \frac{k_1 - k_2}{\omega_1^2 - \omega_2^2} \right)^2 . \tag{II.107}$$

The cubic potential constants appearing in (72) may be calculated in the following manner. In the notation of equation (III.42) we write

$$V_1 = \sum_{ss's''} k_{ss's''} q_s q_{s'} q_{s''} , \tag{II.108}$$

where the relations between the  $q_s$  and our normal coordinates  $Q_s$  are given by

$$q_s = \left(\frac{\omega_s}{\hbar}\right)^{\frac{1}{2}} Q_s, \quad (\text{II.109})$$

and those between the  $k_{ss's''}$  and the  $k'_{ss's''}$  of (73) are

$$\begin{aligned} k_{sss} &= \left(\frac{\hbar}{\omega_s}\right)^{3/2} k'_{sss} \\ k_{sss'} &= k_{ss's} = k_{s'ss} = \frac{1}{3} \frac{\hbar}{\omega_s} \left(\frac{\hbar}{\omega_{s'}}\right)^{\frac{1}{2}} k'_{sss'} \\ k_{ss's''} &= k_{s's''s} = k_{s''ss'} \\ &= k_{s's's} = k_{s'ss} = k_{ss's} = \frac{1}{6} \left(\frac{\hbar}{\omega_s} \frac{\hbar}{\omega_{s'}} \frac{\hbar}{\omega_{s''}}\right)^{\frac{1}{2}} k'_{ss's''}, \end{aligned} \quad (\text{II.110})$$

where  $s < s' < s''$ , and the second of these equations holds also when  $s$  and  $s'$  are interchanged.

Quantities simply related to the  $k_{ss's''}$  are given for  $\text{H}_2\text{O}$  by Darling and Dennison, and from these the  $k'_{ss's''}$  can be obtained as the coefficients in (73). By applying the analysis (74) through (78) in reverse -- i.e. using the inverse transformation matrix  $\mathbf{S}^{-1}$  throughout in place of  $\mathbf{S}$  -- the  $K_{ijk}$  of (72) may be calculated.

## 7. Nature of the Normal Vibrations

One can get a good picture of the normal vibrations by examining the matrix  $\mathbf{S}^{-1}$ , since  $\mathbf{Q} = \mathbf{S}^{-1}\mathbf{r}$  shows the relation between the central-force coordinates and the normal coordinates.

For  $\text{H}_2\text{O}$  ( $\text{D}_2\text{O}$  will be very similar), we see from Appendix B, Section 2, that  $Q_1$  is formed primarily from equal contributions from  $r_{12}$  and  $r_{13}$ , so that  $\omega_1$  represents a stretching vibration along the two O-H bonds in which both

hydrogen atoms are moving symmetrically in phase;  $\omega_1$  is thus associated with a symmetrical stretching vibration. Likewise,  $\omega_3$  corresponds to O-H bond stretching in which the two motions are exactly out of phase, so this is an antisymmetrical stretching vibration. The frequency  $\omega_2$  corresponds to a bending of the molecule.

The corresponding matrix for HDO is (roughly)

$$\mathbf{s}^{-1} = \begin{bmatrix} 0.0188 & 1.6597 & 0.0832 \\ 1.2863 & 1.2722 & -1.6425 \\ -1.2087 & 0.1202 & -0.0566 \end{bmatrix} \times 10^{-12} \text{ g}^{\frac{1}{2}},$$

so the main contribution to  $Q_1$  is from  $r_2 = r_{13}$ , and the frequency  $\omega_1$  corresponds primarily to a stretching of the O-D bond. Similarly, the frequency  $\omega_3$  arises almost entirely from the O-H bond stretching. The frequency  $\omega_2$  is again due to a bending vibration.

The displacement coordinates  $\mathbf{x}$  (which are referred to the principal axes coordinate system) may be expressed in terms of the normal coordinates by means of the matrices  $\mathbf{U}$ , and the columns of  $\mathbf{U}$  give the (relative) displacements of each nucleus for a particular normal vibration. Using the components of  $\mathbf{U}$  one can then make geometrical diagrams showing the relative amplitudes and directions of motion of each nucleus. A set of such diagrams for HDO, based on the calculations presented here, follows\*. They are self-

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\* For  $\text{H}_2\text{O}$ ,  $\text{D}_2\text{O}$ , see references 5, 7, 28.

explanatory, but note should be made of the  $\omega_2$  bending vibration, which is clearly shown to consist mainly of motion of the light atoms in a direction almost perpendicular to their bonds with oxygen; accordingly, one might suppose that a valence-force potential would be more appropriate than the central-force type used here.



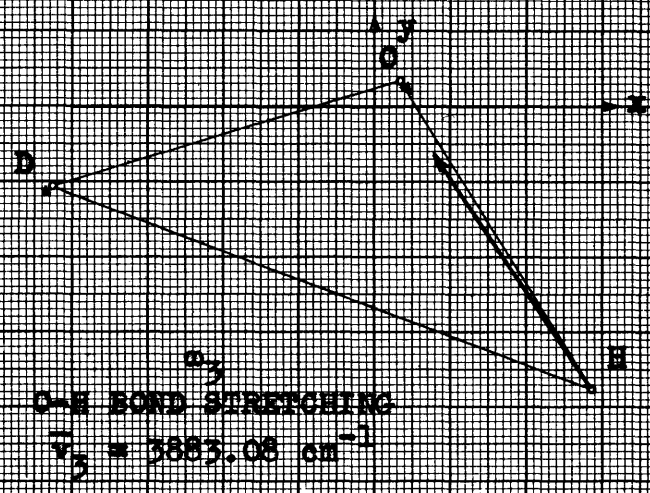
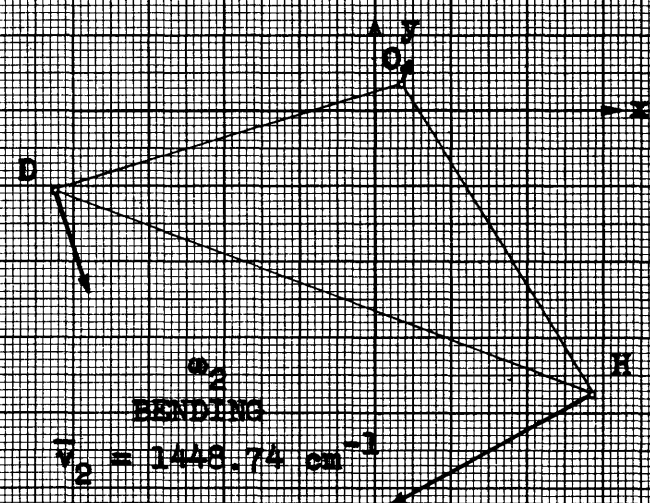
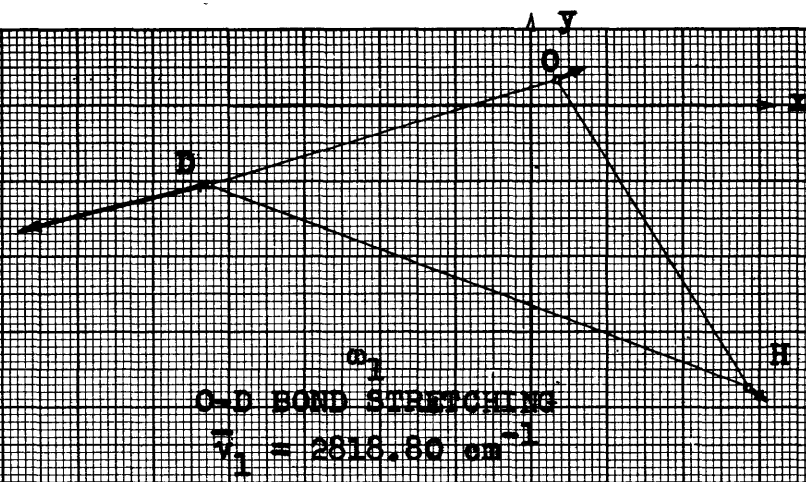


Figure 2

Normal Vibrations of the HDO Molecule

## III

VIBRATION - ROTATION ENERGY OF MOLECULESABRIDGED THEORY

The notation and methods of this Chapter are based on those of Nielsen\*, though we find it convenient to deviate slightly from his work.

Our aim is to treat primarily the rotation problem, including vibrational interaction, to the extent that the theory may be applied to molecules considered in this thesis, so we neglect certain aspects of the general theory.

1. The Classical Problem

Let

$$\mathbf{r}_1 = \mathbf{r}_1^e + \delta\mathbf{r}_1 \quad (\text{III.1})$$

be the instantaneous position vector of the  $i$ -th nucleus, of mass  $m_i$ , in the molecule; here  $\mathbf{r}_1^e$  denotes the equilibrium position vector, and  $\delta\mathbf{r}_1$  is the vector representing the displacement from equilibrium.

We neglect all effects due to the finite masses of the electrons in the molecule.

The components  $g_1$  of  $\mathbf{r}_1$  are to be measured in a coordinate system ( $g = x, y, z$ ) fixed in the molecule, and thus in general rotating with angular velocity  $\omega$  about a space-fixed system whose origin coincides with the origin of the molecule-fixed (gyrating) system. Accordingly, we are also

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\* References 24, 25.

neglecting effects due to translation of the molecule with respect to the observer; such effects are not of interest here.

In the gyrating system, the  $i$ -th particle has a velocity  $\dot{\mathbf{g}}_i$ ; because of the rotation, however, an observer in the fixed system sees a velocity  $\dot{\mathbf{g}}_i + (\boldsymbol{\omega} \times \mathbf{g}_i)$ , and the kinetic energy  $T$  of the nuclei of the molecule is therefore given by

$$2T = \sum_i m_i [\dot{\mathbf{g}}_i + (\boldsymbol{\omega} \times \mathbf{g}_i)]^2. \quad (\text{III.2})$$

Since

$$\dot{\mathbf{g}}_i \cdot (\boldsymbol{\omega} \times \mathbf{g}_i) = (\boldsymbol{\omega} \times \mathbf{g}_i) \cdot \dot{\mathbf{g}}_i = \boldsymbol{\omega} \cdot (\mathbf{g}_i \times \dot{\mathbf{g}}_i),$$

expansion of (2) gives

$$2T = \sum m_i \dot{\mathbf{g}}_i^2 + \sum m_i (\boldsymbol{\omega} \times \mathbf{g}_i) \cdot (\boldsymbol{\omega} \times \mathbf{g}_i) + 2\boldsymbol{\omega} \cdot \sum m_i (\mathbf{g}_i \times \dot{\mathbf{g}}_i). \quad (\text{III.3})$$

The first term represents the vibrational energy, the second the pure rotational energy, and the third the energy of interaction between rotation and vibration.

It is convenient to place certain restrictions on the gyrating coordinate system. Firstly, we choose the origin to lie at the center of mass of the nuclei. Secondly, we let the axes  $g$  coincide with the principal axes of the molecule when all nuclei are in their equilibrium positions. Thirdly, we observe that in the equilibrium condition there is no internal angular momentum of the molecule. The first and last of these restrictions are expressed in the relations

$$\sum m_i \mathbf{g}_i = 0, \quad (\text{III.4})$$

$$\sum m_i (\mathbf{g}_i^e \times \dot{\mathbf{g}}_i) = 0, \quad (\text{III.5})$$

and these are equivalent to (II.34) and (II.35) of the previous Chapter. We also note that

$$\dot{\mathbf{g}}_1 = \delta \dot{\mathbf{g}}_1, \quad (\text{III.6})$$

since  $\dot{\mathbf{g}}_1^e = 0$ .

The rotational energy term in (3) may be written

$$\sum_1 m_1 (\boldsymbol{\omega} \times \mathbf{g}_1) \cdot (\boldsymbol{\omega} \times \mathbf{g}_1) = \sum_{g,g'} I_{gg'} \omega_g \omega_{g'}, \quad (g, g' = x, y, z) \quad (\text{III.7})$$

where

$$I_{gg'} = \sum_1 m_1 (\mathbf{g}_1^2 \delta_{gg'} - g_1 g_1'), \quad (\text{III.8})$$

and  $\delta_{gg'}$  is the Kronecker delta.

Using (5) and (6), the interaction energy term in (3) becomes

$$\begin{aligned} 2\boldsymbol{\omega} \cdot \sum_1 m_1 (\mathbf{g}_1 \times \dot{\mathbf{g}}_1) &= 2\boldsymbol{\omega} \cdot \sum_1 m_1 [(\mathbf{g}_1^e \times \delta \mathbf{g}_1) + (\delta \mathbf{g}_1 \times \delta \dot{\mathbf{g}}_1)] \\ &= 2\boldsymbol{\omega} \cdot \sum_1 m_1 (\delta \mathbf{g}_1 \times \delta \dot{\mathbf{g}}_1) = 2\boldsymbol{\omega} \cdot \mathbf{M} \\ &= 2 \sum_g M_g \omega_g, \end{aligned} \quad (\text{III.9})$$

with

$$\mathbf{M} = \sum_1 m_1 (\delta \mathbf{g}_1 \times \delta \dot{\mathbf{g}}_1), \quad (\text{III.10})$$

and

$$M_g = \sum_{1g'} \sum_{1g''} m_1 \epsilon_{gg'g''} \delta g_1' \delta \dot{g}_1''. \quad (\text{III.11})$$

Here

$$\epsilon_{gg'g''} = \begin{cases} +1 & \text{if } gg'g'' \text{ is an even permutation of } x, y, z \\ -1 & \text{if } gg'g'' \text{ is an odd permutation of } x, y, z \\ 0 & \text{otherwise.} \end{cases} \quad (\text{III.12})$$

Finally, let us write the vibrational energy as

$$\frac{1}{2} \sum_1 m_1 \dot{\mathbf{g}}_1^2 = \frac{1}{2} \sum_s \dot{Q}_s^2, \quad (\text{III.13})$$

where the  $Q_s$  are the normal coordinates of the molecule, and

let the equation

$$\delta g_1 = m_1^{-\frac{1}{2}} \sum_s L_{1s}^{(g)} Q_s \quad (\text{III.14})$$

define the transformation coefficients\*  $L_{1s}^{(g)}$ . It follows from (13) that

$$\sum_g \sum_s L_{1s}^{(g)} L_{1s'}^{(g)} = \delta_{ss'}. \quad (\text{III.15})$$

In terms of the normal coordinates, we may now write (11) in the form

$$M_g = - \sum_s A_s^{(g)} \dot{Q}_s, \quad (\text{III.16})$$

where

$$\begin{aligned} A_s^{(g)} &= \sum_{1s'} \sum_{g'} \sum_{g''} \sum_{s''} \epsilon_{gg'g''} L_{1s'}^{(g')} L_{1s''}^{(g'')} Q_{s'} \\ &= \sum_{s'} (\sum_{g'} \sum_{g''} \sum_{s''} \epsilon_{gg'g''} L_{1s'}^{(g')} L_{1s''}^{(g'')} Q_{s'}) \\ &= \sum_{s'} \zeta_{ss'}^{(g)} Q_{s'}, \end{aligned} \quad (\text{III.17})$$

with

$$\zeta_{ss'}^{(g)} = - \zeta_{s's}^{(g)} = \sum_g \sum_{g'} \sum_{g''} \epsilon_{gg'g''} L_{1s}^{(g')} L_{1s'}^{(g'')} \quad (\text{III.18})$$

The kinetic energy (3) now becomes

$$2T = \sum_s \dot{Q}_s^2 + \sum_{gg'} I_{gg'} \omega_g \omega_{g'} + 2 \sum_g M_g \omega_g. \quad (\text{III.19})$$

The momenta  $p_s$ ,  $P_g$ , conjugate to  $Q_s$  and  $\omega_g$ , are given by

$$p_s = \frac{\partial T}{\partial \dot{Q}_s}, \quad P_g = \frac{\partial T}{\partial \omega_g}, \quad (\text{III.20})$$

hence

$$p_s = \dot{Q}_s - \sum_g A_s^{(g)} \omega_g, \quad (\text{III.21})$$

$$P_g = \sum_{g'} I_{gg'} \omega_{g'} + M_g = \sum_{g'} I_{gg'} \omega_{g'} - \sum_s A_s^{(g)} \dot{Q}_s. \quad (\text{III.22})$$

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\* These are, of course, the same coefficients as discussed in equations (II.48) through (II.51).

Thus (19) becomes

$$2T = \sum_s \dot{Q}_s^2 - 2 \sum_g \sum_s A_s^{(g)} \dot{Q}_s \omega_g + \sum_{g g'} I_{g g'} \omega_g \omega_{g'} ,$$

or, on rearranging,

$$\begin{aligned} 2T &= \sum_s (\dot{Q}_s - \sum_g A_s^{(g)} \omega_g) \dot{Q}_s + \sum_{g g'} (\sum_s I_{g g'} \omega_{g'} - \sum_s A_s^{(g)} \dot{Q}_s) \omega_g \\ &= \sum_s p_s \dot{Q}_s + \sum_g P_g \omega_g . \end{aligned} \quad (\text{III.23})$$

If we use (21) to replace  $\dot{Q}_s$  by  $p_s + \sum_g A_s^{(g)} \omega_g$ , then (23) becomes

$$\begin{aligned} 2T &= \sum_s p_s^2 + \sum_g \sum_s p_s A_s^{(g)} \omega_g + \sum_g P_g \omega_g \\ &= \sum_s p_s^2 + \sum_g (\sum_s p_s A_s^{(g)} + P_g) \omega_g \\ &= \sum_s p_s^2 + \sum_g (P_g - p_g) \omega_g \\ &= \sum_s p_s^2 + \sum_g N_g \omega_g , \end{aligned} \quad (\text{III.24})$$

where, using (17),

$$\boxed{p_g = - \sum_s p_s A_s^{(g)} = \sum_{s s'} \zeta_{s s'}^{(g)} Q_s p_{s'}}, \quad (\text{III.25})$$

and  $p_g$  is the  $g$ -th component of internal (vibrational) angular momentum.

Here,

$$\begin{aligned} N_g &= P_g - p_g \\ &= \sum_{g'} I_{g g'} \omega_{g'} - \sum_s A_s^{(g)} \dot{Q}_s + \sum_s p_s A_s^{(g)} \\ &= \sum_{g'} I_{g g'} \omega_{g'} - \sum_s (\sum_{g'} A_s^{(g')} \omega_{g'}) A_s^{(g)} \\ &= \sum_{g'} I'_{g g'} \omega_{g'} , \end{aligned} \quad (\text{III.26})$$

with

$$I'_{gg'} = I_{gg'} - \sum_s A_s^{(g)} A_s^{(g')} . \quad (\text{III.27})$$

Then,

$$\begin{aligned} I'_{gg'} &= \sum_1 m_1 (\mathfrak{g}_1^2 \delta_{gg'} - \mathfrak{g}_1 \mathfrak{g}'_1) - \sum_s \sum_{s'} \sum_{s''} \zeta_{ss'}^{(g)} \zeta_{ss''}^{(g')} Q_s Q_{s''} \\ &= I_{gg'}^e + \sum_s a_s^{(gg')} Q_s + \sum_s \sum_{s'} \left[ A_{ss'}^{(gg')} - \sum_{s''} \zeta_{ss''}^{(g)} \zeta_{s's''}^{(g')} \right] Q_s Q_{s'} \\ &= I'_{g'g} , \end{aligned} \quad (\text{III.28})$$

where

$$a_s^{(gg')} = a_s^{(g'g)} = \sum_1 m_1^{\frac{1}{2}} \left[ 2\delta_{gg'} \sum_{s'} \mathfrak{g}'_1 e_{1s}^{(g'')} - (\mathfrak{g}_1 e_{1s}^{(g')} + \mathfrak{g}'_1 e_{1s}^{(g)}) \right] \quad (\text{III.29})$$

$$A_{ss'}^{(gg')} = \sum_1 \left[ \delta_{gg'} \sum_{s''} L_{1s}^{(g'')} L_{1s'}^{(g'')} - L_{1s}^{(g)} L_{1s'}^{(g')} \right] , \quad (\text{III.30})$$

or, from (15),

$$A_{ss'}^{(gg')} = \delta_{ss'} \delta_{gg'} - \sum_1 L_{1s}^{(g)} L_{1s'}^{(g')} . \quad (\text{III.31})$$

In (28),  $I_{gg'}^e$  is the equilibrium value of the moment of inertia about the  $gg'$ -axes; in (29),  $\mathfrak{g}_1^e$ ,  $\mathfrak{g}'_1^e$  and  $\mathfrak{g}''_1^e$  are the equilibrium coordinates of the  $i$ -th particle on the axes  $g$ ,  $g'$  and  $g''$ , respectively.

From (26) we have

$$N_g = \sum_{g'} I'_{gg'} \omega_{g'} ,$$

so we may write

$$\omega_g = \sum_{g'} \mu_{gg'} N_{g'} \quad (\text{III.32})$$

for the inverse transformation. Then (24) can be written

$$\begin{aligned}
2T &= \sum_{\mathbf{s}} p_{\mathbf{s}}^2 + \sum_{\mathbf{g}} N_{\mathbf{g}} \omega_{\mathbf{g}} \\
&= \sum_{\mathbf{s}} p_{\mathbf{s}}^2 + \sum_{\mathbf{g}\mathbf{g}'} \mu_{\mathbf{g}\mathbf{g}'} N_{\mathbf{g}} N_{\mathbf{g}'} . \quad (\text{III.33})
\end{aligned}$$

Now let us expand the  $\mu_{\mathbf{g}\mathbf{g}'}$  to terms of the second order in  $Q_{\mathbf{s}}$ ; after some algebra, we find, to this approximation, that

$$\mu_{\mathbf{g}\mathbf{g}'} \approx \frac{1}{I_{\mathbf{g}\mathbf{g}}^e I_{\mathbf{g}'\mathbf{g}'}^e} (I_{\mathbf{g}\mathbf{g}}^e \delta_{\mathbf{g}\mathbf{g}'} - \sum_{\mathbf{s}} a_{\mathbf{s}}^{(\mathbf{g}\mathbf{g}')} Q_{\mathbf{s}} - \sum_{\mathbf{s}\mathbf{s}'} G_{\mathbf{s}\mathbf{s}'}^{(\mathbf{g}\mathbf{g}')} Q_{\mathbf{s}} Q_{\mathbf{s}'}), \quad (\text{III.34})$$

with

$$G_{\mathbf{s}\mathbf{s}'}^{(\mathbf{g}\mathbf{g}')} = A_{\mathbf{s}\mathbf{s}'}^{(\mathbf{g}\mathbf{g}')} - \sum_{\mathbf{s}''} \zeta_{\mathbf{s}\mathbf{s}''}^{(\mathbf{g})} \zeta_{\mathbf{s}'\mathbf{s}''}^{(\mathbf{g}')} - \sum_{\mathbf{g}''} \frac{a_{\mathbf{s}}^{(\mathbf{g}\mathbf{g}'')} a_{\mathbf{s}'}^{(\mathbf{g}'\mathbf{g}'')}}{I_{\mathbf{g}''\mathbf{g}''}^e}. \quad (\text{III.35})$$

Substituting in (33), using the relation

$$N_{\mathbf{g}} = P_{\mathbf{g}} - p_{\mathbf{g}},$$

we have

$$2T = \sum_{\mathbf{s}} p_{\mathbf{s}}^2 + \sum_{\mathbf{g}\mathbf{g}'} \mu_{\mathbf{g}\mathbf{g}'} (P_{\mathbf{g}} - p_{\mathbf{g}}) (P_{\mathbf{g}'} - p_{\mathbf{g}'}), \quad (\text{III.36})$$

and, expanding to the same order of approximation,

$$\begin{aligned}
2T &\approx \sum_{\mathbf{s}} p_{\mathbf{s}}^2 + \sum_{\mathbf{g}} \frac{P_{\mathbf{g}}^2}{I_{\mathbf{g}\mathbf{g}}^e} - 2 \sum_{\mathbf{g}} \frac{P_{\mathbf{g}} p_{\mathbf{g}}}{I_{\mathbf{g}\mathbf{g}}^e} + \sum_{\mathbf{g}} \frac{p_{\mathbf{g}}^2}{I_{\mathbf{g}\mathbf{g}}^e} \\
&\quad - \sum_{\mathbf{g}\mathbf{g}'} \sum_{\mathbf{s}} \frac{P_{\mathbf{g}} P_{\mathbf{g}'}}{I_{\mathbf{g}\mathbf{g}}^e I_{\mathbf{g}'\mathbf{g}'}^e} a_{\mathbf{s}}^{(\mathbf{g}\mathbf{g}')} Q_{\mathbf{s}} + 2 \sum_{\mathbf{g}\mathbf{g}'} \sum_{\mathbf{s}} \frac{P_{\mathbf{g}} p_{\mathbf{g}'}}{I_{\mathbf{g}\mathbf{g}}^e I_{\mathbf{g}'\mathbf{g}'}^e} a_{\mathbf{s}}^{(\mathbf{g}\mathbf{g}')} Q_{\mathbf{s}} \\
&\quad - \sum_{\mathbf{g}\mathbf{g}'} \sum_{\mathbf{s}\mathbf{s}'} \frac{P_{\mathbf{g}} P_{\mathbf{g}'}}{I_{\mathbf{g}\mathbf{g}}^e I_{\mathbf{g}'\mathbf{g}'}^e} G_{\mathbf{s}\mathbf{s}'}^{(\mathbf{g}\mathbf{g}')} Q_{\mathbf{s}} Q_{\mathbf{s}'} . \quad (\text{III.37})
\end{aligned}$$

The potential energy may be written



$$V = \frac{1}{2} \sum_s \omega_s^2 Q_s^2 + \sum k'_{ss's'} Q_s Q_{s'} Q_{s'} + \sum k'_{ss's''s'''} Q_s Q_{s'} Q_{s''} Q_{s'''} \quad (s \leq s' \leq s'' \leq s''') , \quad (\text{III.38})$$

where the  $k'_{ss's''}$  and  $k'_{ss's''s'''}$  are the cubic and quartic anharmonic potential constants, respectively, and

$$\omega_s = 2\pi\nu_s , \quad (\text{III.39})$$

where the  $\nu_s$  are the normal frequencies (in c/sec).

Thus, to the order of approximation which we are considering, the classical Hamiltonian becomes:

$$\begin{aligned} H \approx & \frac{1}{2} \sum_s p_s^2 + \frac{1}{2} \sum_s \frac{p_s^2}{I_e} - \sum_s \frac{p_s p_g}{I_e} + \frac{1}{2} \sum_s \frac{p_g^2}{I_{gg}} \\ & - \frac{1}{2} \sum_{gg'} \sum_s \frac{p_g p_{g'}}{I_e I_e} a_{ss'}^{(gg')} Q_s + \sum_{gg'} \sum_s \frac{p_g p_{g'}}{I_e I_e} a_{ss'}^{(gg')} Q_s \\ & - \frac{1}{2} \sum_{gg'} \sum_{ss'} \frac{p_g p_{g'}}{I_{gg} I_{g'g'}} G_{ss'}^{(gg')} Q_s Q_{s'} + \frac{1}{2} \sum_s \omega_s^2 Q_s^2 \\ & + \sum k'_{ss's''} Q_s Q_{s'} Q_{s''} + \sum k'_{ss's''s'''} Q_s Q_{s'} Q_{s''} Q_{s'''} \end{aligned} \quad (\text{III.40})$$

where the summation over the last two terms is restricted by the condition  $s \leq s' \leq s'' \leq s'''$ . The  $p_g$  are given by (25) in terms of the normal coordinates  $Q_s$  and their conjugate momenta  $p_s$ .

## 2. The Energy Matrix

The quantum-mechanical Hamiltonian can be obtained from (40) if the quantities  $p_s$ ,  $P_g$ ,  $p_g$ ,  $Q_s$  are regarded as operators. The interaction between vibration and rotation may be considered small enough to allow us to neglect the non-commutability of  $P_g$  with  $p_g$ ; products such as  $P_g P_{g'}$  have to be symmetrized in order that the Hamiltonian be Hermitian, but this is automatically achieved by the double summation over  $g$  and  $g'$  appearing in (40). We need to symmetrize explicitly only the product  $p_{g'} Q_s$ , and replace it by  $\frac{1}{2}(p_{g'} Q_s + Q_s p_{g'})$ ;  $p_g$  itself contains the factor  $Q_s p_{s'}$ , which does not need to be symmetrized since its coefficient  $a_{ss'}^{(g)}$  vanishes when  $s' = s$ .

Accordingly, we may write\*

$$H = H_0 + H'$$

$$H_0 = \frac{1}{2} \sum_s (p_s^2 + \omega_s^2 Q_s^2) + \frac{1}{2} \sum_g \frac{P_g^2}{I_{gg}}$$

$$H' = H^{(1)} + H^{(2)}$$

(III.41)

$$H^{(1)} = \sum k'_{ss's''} Q_s Q_{s'} Q_{s''} - \sum_g \frac{P_g p_g}{I_{gg}} - \frac{1}{2} \sum_{gg'} \sum_s \frac{P_g P_{g'}}{I_{gg} I_{g'g'}} a_s^{(gg')} Q_s$$

$$+ \frac{1}{2} \sum_{gg'} \frac{P_g}{I_{gg} I_{g'g'}} a_s^{(gg')} (p_{g'} Q_s + Q_s p_{g'})$$

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\* One may proceed in a more sophisticated manner, and first obtain a general Hamiltonian; Darling and Dennison<sup>5</sup> give, without derivation, the form

$$H^{(2)} = \frac{1}{2} \sum_{\mathbf{g}} \frac{p_{\mathbf{g}}^2}{I_{\mathbf{e}}^{\mathbf{g}\mathbf{g}}} - \frac{1}{2} \sum_{\mathbf{g}\mathbf{g}'} \sum_{\mathbf{s}\mathbf{s}'} \frac{P_{\mathbf{g}} P_{\mathbf{g}'}}{I_{\mathbf{e}}^{\mathbf{g}\mathbf{g}} I_{\mathbf{e}}^{\mathbf{g}'\mathbf{g}'}} G_{\mathbf{s}\mathbf{s}'}^{(\mathbf{g}\mathbf{g}')} Q_{\mathbf{s}} Q_{\mathbf{s}'} + \sum k'_{\mathbf{s}\mathbf{s}'\mathbf{s}''\mathbf{s}'''} Q_{\mathbf{s}} Q_{\mathbf{s}'} Q_{\mathbf{s}''} Q_{\mathbf{s}'''} .$$

The reasons for the separation of  $H^{(1)}$  and  $H^{(2)}$  will appear shortly.

In (41) we have not taken into account the possibility of degeneracies occurring between the normal frequencies  $\omega_{\mathbf{g}}$  because this complication does not arise in the ground states of the molecules  $\text{H}_2\text{O}$ ,  $\text{HDO}$ ,  $\text{D}_2\text{O}$ .

It is now convenient to replace  $Q_{\mathbf{g}}$  and  $p_{\mathbf{g}}$  by the dimensionless coordinates

$$q_{\mathbf{g}} = \left(\frac{\omega_{\mathbf{g}}}{\hbar}\right)^{\frac{1}{2}} Q_{\mathbf{g}} , \quad (\text{III.42})$$

and their conjugate momenta\*

$$p'_{\mathbf{g}} = \left(\frac{\hbar}{\omega_{\mathbf{g}}}\right)^{\frac{1}{2}} p_{\mathbf{g}} , \quad (\text{III.43})$$

then to redefine a dimensionless  $p_{\mathbf{g}}$  by the relation

$$p_{\mathbf{g}}(\text{new}) = \frac{p'_{\mathbf{g}}}{\hbar} = (\hbar\omega_{\mathbf{g}})^{-\frac{1}{2}} p_{\mathbf{g}}(\text{old}) . \quad (\text{III.44})$$

We also introduce new potential constants  $k_{\mathbf{s}\mathbf{s}'\mathbf{s}''}$  and  $k_{\mathbf{s}\mathbf{s}'\mathbf{s}''\mathbf{s}'''}$ , where the  $k_{\mathbf{s}\mathbf{s}'\mathbf{s}''}$  are discussed in Section II.6, and the  $k_{\mathbf{s}\mathbf{s}'\mathbf{s}''\mathbf{s}'''}$  can be treated in a similar manner.

With these changes, the components of the Hamiltonian

$$H = \frac{1}{2} \sum_{\mathbf{g}\mathbf{g}'} \mu^{-1/4} (P_{\mathbf{g}} - p_{\mathbf{g}}) \mu_{\mathbf{g}\mathbf{g}'} \mu^{-1/2} (P_{\mathbf{g}'} - p_{\mathbf{g}'}) \mu^{1/4} + \frac{1}{2} \sum_{\mathbf{g}} \mu^{1/4} p_{\mathbf{g}} \mu^{-1/2} p_{\mathbf{g}} \mu^{1/4} + V ,$$

where  $\mu^{-1}$  is the determinant of the  $I'_{\mathbf{g}\mathbf{g}'}$  given in (28). It may be verified, however, that to this order of approximation, the resulting operator symmetrization is equivalent to (41).

\* Nielsen<sup>25</sup>, equation (II.44a) and thereafter, continues to use  $p_{\mathbf{g}}$ , but with the meaning of our  $p'_{\mathbf{g}}$ .

may be written

$$\begin{aligned}
 H_0 &= \frac{1}{2} \hbar \sum_s \omega_s (p_s^2 + q_s^2) + \frac{1}{2} \sum_g \frac{P_g^2}{I_{gg}} \\
 H^{(1)} &= \sum_{ss's''} k_{ss's''} q_s q_{s'} q_{s''} - \sum_g \frac{P_g P_g}{I_{gg}} \\
 &\quad - \frac{1}{2} \hbar^{\frac{1}{2}} \sum_{gg'} \sum_s \frac{P_g P_{g'}}{I_{gg} I_{g'g'}} \frac{a_s^{(gg')}}{\omega_s^{\frac{1}{2}}} q_s \\
 &\quad + \frac{1}{2} \hbar^{\frac{1}{2}} \sum_{gg'} \sum_s \frac{P_g}{I_{gg} I_{g'g'}} \frac{a_s^{(gg')}}{\omega_s^{\frac{1}{2}}} (p_{g'} q_s + q_s p_{g'}) \\
 H^{(2)} &= \frac{1}{2} \sum_g \frac{p_g^2}{I_{gg}} - \frac{1}{2} \hbar \sum_{gg'} \sum_{ss'} \frac{P_g P_{g'}}{I_{gg} I_{g'g'}} \frac{G_{ss'}^{(gg')}}{\omega_s^{\frac{1}{2}} \omega_{s'}^{\frac{1}{2}}} q_s q_{s'} \\
 &\quad + \sum_{ss's''} \sum_{s''s'''} k_{ss's''s'''} q_s q_{s'} q_{s''} q_{s'''}
 \end{aligned} \tag{III.45}$$

with

$$p_g = \hbar \sum_{ss'} \left( \frac{\omega_{s'}}{\omega_s} \right)^{\frac{1}{2}} \zeta_{ss'}^{(g)} q_s p_{s'} \tag{III.46}$$

The two terms of  $H_0$  belong to the harmonic oscillator and rigid rotor, respectively. Corrections for anharmonicity, Coriolis interaction, and centrifugal distortion are included in  $H^{(1)}$ , which we will regard as a small perturbation on  $H_0$ .

In order to calculate matrix elements of  $H$  we will choose the usual representation in which  $H_0$  is diagonal in the vibrational quantum numbers  $v_s$  and in the rotational quantum numbers  $J$  and  $M$ . In this representation, the harmonic

oscillator matrix elements of  $q_s$  and  $p_s$  are given by\*

$$\boxed{(v_s | q_s | v_s + 1) = i(v_s | p_s | v_s + 1) = \left[ \frac{1}{2}(v_s + 1) \right]^{\frac{1}{2}}} \quad (\text{III.47})$$

where  $i = \sqrt{-1}$ , while the matrix elements of  $P_g$  are\*\*

$$\boxed{\begin{aligned} (K | P_y | K+1) &= -i(K | P_x | K+1) = \frac{1}{2} \hbar \left[ J(J+1) - K(K+1) \right]^{\frac{1}{2}} \\ (K | P_z | K) &= \hbar K \end{aligned}} \quad (\text{III.48})$$

We note that  $q_s$  and  $p_s$  are diagonal in  $J, K, M$  and  $v_s$ , (for  $s' \neq s$ ), while  $P_g$  is diagonal in  $J, M, v_s$ .

### 3. Vibrational Diagonalization

First let us diagonalize the vibrational dependence by conventional perturbation theory\*\*\*. We remove matrix elements connecting different states  $v, v'$  (where  $v$  denotes the set  $v_1, v_2, \dots$  describing a particular vibrational state) and bring them into each  $v$  submatrix. The resulting matrix, though diagonal in  $v$ , will still be off-diagonal in  $K$ . We thus have

$$(v | H | v) = (v | H_0 | v) + (v | H' | v) + \sum_{v'} \frac{|(v | H' | v')|^2}{W(v) - W(v')} \quad (\text{III.49})$$

where

$$W(v) = \sum_s (v_s + \frac{1}{2}) \hbar \omega_s, \quad (\text{III.50})$$

\* For brevity, we will not list conjugate matrix elements.

\*\* We use the same phase factor as King, Hainer and Cross<sup>15</sup>; this paper is hereafter referred to as KHC I.

\*\*\* The literature usually applies a contact transformation to diagonalize the Hamiltonian, but for present purposes it appears simpler to use the straightforward method.

and we have neglected rotational corrections which are small compared to the energy differences between vibrational states.

We may now investigate the Hamiltonian (45). The zeroth-order part,  $H_0$ , gives the usual harmonic oscillator energies, though the rotational term is still not diagonal in  $K$ :

$$(v|H_0|v) = \sum_s (v_s + \frac{1}{2}) \hbar \omega_s + \frac{1}{2} \sum_s \frac{P_s^2}{I_s \omega_s} . \quad (\text{III.51})$$

In  $H^{(1)}$ , all terms except the second are odd in  $q_s$ ,  $p_s$ , hence give no first order correction, but may contribute in second order; the second term has no diagonal matrix elements since  $s' \neq s$  in (46).

The last of these terms in  $H^{(1)}$  is a correction to the second (Coriolis) term, which is itself small (vanishing in the limit of the rigid rotor or non-rotating oscillator). For the ground vibrational state ( $v = 0$ ), with which we are primarily concerned here, this term can be neglected, so we will not carry it through in the calculations.

However, this Coriolis correction term, as well as the cubic potential term in  $k_{s's''}$ , may connect higher vibrational states by resonance; the second order perturbation term gives some denominators  $W(v) - W(v')$  of the form  $\omega_s - \omega_{s'}$ ,  $2\omega_s - \omega_{s'}$ , etc., so that if  $\omega_s \approx \omega_{s'}$ ,  $2\omega_s \approx \omega_{s'}$ , etc., portions of the matrix must be diagonalized by solution of the appropriate secular equations rather than by conventional perturbation theory. Other similar resonances may occur, and the matrix must be examined carefully for each individual case. Types of such resonance do occur both in  $H_2O$

and HDO. Fortunately, however, the ground state is not affected by any of these interactions\*, so we will not have to consider the effect further here.

Inspection of  $H^{(2)}$  shows that the terms are even in  $q_s$ ,  $p_s$ , so matrix elements diagonal in  $v$  can occur, giving first order contributions to the energy. As before, resonances may occur, but again they will not affect the ground state, so will be neglected here. We will neglect the term in  $p_g^2$  and the quartic anharmonic terms, since, being independent of the angular momentum operators  $P_g$ , they will appear only as vibrational corrections.

Thus, in the following, we will consider the perturbation

$$\begin{aligned}
 H'' = & \sum_s \sum_{s'} \sum_{s''} k_{ss's''} q_s q_{s'} q_{s''} - \sum_g \frac{P_g p_g}{I_g e} \\
 & - \frac{1}{2} \hbar^{\frac{1}{2}} \sum_{gg'} \frac{P_g P_{g'}}{I_g e I_{g'} e} \sum_s \frac{a_s^{(gg')}}{\omega_s^{\frac{1}{2}}} q_s \\
 & - \frac{1}{2} \hbar \sum_{gg'} \frac{P_g P_{g'}}{I_g e I_{g'} e} \sum_{ss'} \frac{q_{ss'}^{(gg')}}{\omega_s^{\frac{1}{2}} \omega_{s'}^{\frac{1}{2}}} q_s q_{s'} . \quad (\text{III.52})
 \end{aligned}$$

We will start by computing the first order corrections, i.e. the diagonal elements of the last term in (52).

The diagonal matrix elements of  $q_s q_{s'}$  are

$$(v_s | q_s q_{s'} | v_s) = (v_s + \frac{1}{2}) \delta_{ss'} , \quad (\text{III.53})$$

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\*Because resonance effects occur for denominators of the type  $\omega_{s'} - \omega_s$ , hence with matrix elements of the type

$(v_s v_{s'} | v_s - 1 v_{s'} + 1)$ : for the ground state the matrix elements  $(v_s | v_s - 1)$  etc. do not exist.

so that

$$(\nu | H'' | \nu) = -\frac{1}{2}\hbar \sum_{gg'} \frac{P_g P_{g'}}{I_{gg} I_{g'g'}} \sum_s (\nu_s + \frac{1}{2}) \frac{a_{ss}^{(gg')}}{\omega_s} . \quad (\text{III.54})$$

For the second order terms, let us write

$$H''_1 = \sum_{s'} \sum_{s''} \sum_{s'''} k_{ss's''} a_s a_{s'} a_{s''} ,$$

$$H''_2 = - \sum_g \frac{P_g P_g}{I_{gg}} = -\hbar \sum_g \frac{P_g}{I_{gg}} \sum_{ss'} \left(\frac{\omega_{s'}}{\omega_s}\right)^{\frac{1}{2}} \zeta_{ss'}^{(g)} a_s p_{s'} ,$$

$$H''_3 = -\frac{1}{2}\hbar \sum_{gg'} \frac{P_g P_{g'}}{I_{gg} I_{g'g'}} \sum_s \frac{a_s^{(gg')}}{\omega_s} a_s .$$

The matrix elements of  $H''_3$  are

$$(\nu_s | H''_3 | \nu_{s+1}) = -\frac{1}{2}\hbar^{\frac{1}{2}} \sum_{gg'} \frac{P_g P_{g'}}{I_{gg} I_{g'g'}} \frac{a_s^{(gg')}}{\omega_s} \left[\frac{1}{2}(\nu_s + 1)\right]^{\frac{1}{2}} . \quad (\text{III.55})$$

For  $H''_2$  we have

$$\begin{aligned} (\nu_s \nu_{s'} | a_s p_{s'} | \nu_{s+1} \nu_{s'+1}) &= -\frac{1}{2}i \left[ (\nu_s + 1)(\nu_{s'} + 1) \right]^{\frac{1}{2}} , \\ (\nu_s \nu_{s'} | a_s p_{s'} | \nu_{s+1} \nu_{s'-1}) &= \frac{1}{2}i \left[ (\nu_s + 1)\nu_{s'} \right]^{\frac{1}{2}} , \end{aligned}$$

so the matrix elements of  $p_g$  become

$$\begin{aligned} (\nu_s \nu_{s'} | p_g | \nu_{s+1} \nu_{s'+1}) &= \frac{1}{2}\hbar^{\frac{1}{2}} \zeta_{ss'}^{(g)} (\omega_s - \omega_{s'}) \left[ \frac{(\nu_s + 1)(\nu_{s'} + 1)}{\omega_s \omega_{s'}} \right]^{\frac{1}{2}} , \\ (\nu_s \nu_{s'} | p_g | \nu_{s+1} \nu_{s'-1}) &= \frac{1}{2}\hbar^{\frac{1}{2}} \zeta_{ss'}^{(g)} (\omega_s + \omega_{s'}) \left[ \frac{(\nu_s + 1)\nu_{s'}}{\omega_s \omega_{s'}} \right]^{\frac{1}{2}} , \end{aligned} \quad (\text{III.56})$$

hence,



$$(v_s v_{s'} | H_2'' | v_{s+1} v_{s'+1}) = \frac{1}{2} 1 \hbar \sum_g \frac{P_g}{I e^{g g}} \zeta_{s s'}^{(g)} (\omega_s - \omega_{s'}) \left[ \frac{(v_s + 1)(v_{s'} + 1)}{\omega_s \omega_{s'}} \right]^{\frac{1}{2}} \quad (\text{III.57})$$

$$(v_s v_{s'} | H_2'' | v_{s+1} v_{s'-1}) = \frac{1}{2} 1 \hbar \sum_g \frac{P_g}{I e^{g g}} \zeta_{s s'}^{(g)} (\omega_s + \omega_{s'}) \left[ \frac{(v_s + 1)v_{s'}}{\omega_s \omega_{s'}} \right]^{\frac{1}{2}} .$$

Finally, for  $H_1''$ , we may write

$$\begin{aligned} \sum_s \sum_{s'} \sum_{s''} k_{s s' s''} q_s q_{s'} q_{s''} &= \sum_s k_{s s s} q_s^3 + 3 \sum_s \sum_{s'} k_{s s' s} q_s q_{s'}^2 \\ &+ \sum_s \sum_{s'} \sum_{s''} k_{s s' s''} q_s q_{s'} q_{s''} , \end{aligned} \quad (\text{III.58})$$

where  $\sum_{s'}$  means a summation over values of  $s'$  different from  $s$ , and  $\sum_{s''}$  means that in this summation  $s''$  is to take only values different from  $s$  and from  $s'$ . Now,

$$(v_s | q_s^3 | v_{s+3}) = \left[ \frac{1}{8} (v_s + 1)(v_s + 2)(v_s + 3) \right]^{\frac{1}{2}}$$

$$(v_s | q_s^3 | v_{s+1}) = \frac{3}{2} (v_s + 1) \left[ \frac{1}{2} (v_s + 1) \right]^{\frac{1}{2}}$$

$$(v_s v_{s'} | q_s q_{s'}^2 | v_{s+1} v_{s'+1}) = \left[ \frac{1}{8} (v_s + 1)(v_{s'} + 1)(v_{s'} + 2) \right]^{\frac{1}{2}}$$

$$(v_s v_{s'} | q_s q_{s'}^2 | v_{s+1} v_{s'}) = (v_{s'} + \frac{1}{2}) \left[ \frac{1}{2} (v_s + 1) \right]^{\frac{1}{2}}$$

$$(v_s v_{s'} | q_s q_{s'}^2 | v_{s+1} v_{s'-2}) = \left[ \frac{1}{8} (v_s + 1) v_{s'} (v_{s'} - 1) \right]^{\frac{1}{2}}$$

$$(v_s v_{s'} v_{s''} | q_s q_{s'} q_{s''} | v_{s+1} v_{s'+1} v_{s''+1}) = \left[ \frac{1}{8} (v_s + 1)(v_{s'} + 1)(v_{s''} + 1) \right]^{\frac{1}{2}}$$

$$(v_s v_{s'} v_{s''} | q_s q_{s'} q_{s''} | v_{s+1} v_{s'+1} v_{s''-1}) = \left[ \frac{1}{8} (v_s + 1)(v_{s'} + 1) v_{s''} \right]^{\frac{1}{2}}$$

$$(v_s v_{s'} v_{s''} | q_s q_{s'} q_{s''} | v_{s+1} v_{s'-1} v_{s''+1}) = \left[ \frac{1}{8} (v_s + 1) v_{s'} (v_{s''} + 1) \right]^{\frac{1}{2}}$$

$$(v_s v_{s'} v_{s''} | q_s q_{s'} q_{s''} | v_{s+1} v_{s'-1} v_{s''-1}) = \left[ \frac{1}{8} (v_s + 1) v_{s'} v_{s''} \right]^{\frac{1}{2}} .$$

The matrix elements of  $H_1''$  are then obvious, except perhaps for the  $(v_s | v_{s+1})$  terms; for these we have

$$(v_s | k_{sss} q_s^3 + 3 \sum_{s'} k_{ss's'} q_s q_{s'}^2 | v_{s+1}) = \left[ \frac{3}{2} k_{sss}(v_s+1) + 3 \sum_{s'} k_{ss's'}(v_{s'}+\frac{1}{2}) \right] \left[ \frac{1}{2}(v_s+1) \right]^{\frac{1}{2}}.$$

Thus the off-diagonal matrix elements of (52) -- excluding the last term -- are

$$\begin{aligned} (v_s | v_{s+3}) &: k_{sss} \left[ \frac{1}{8}(v_s+1)(v_s+2)(v_s+3) \right]^{\frac{1}{2}} \\ (v_s | v_{s+1}) &: \left[ \frac{3}{2}(v_s+1)k_{sss} + 3 \sum_{s'} k_{ss's'}(v_{s'}+\frac{1}{2}) \right. \\ &\quad \left. - \frac{1}{2} \hbar \sum_{gg'} \frac{P_g P_{g'}}{I_g I_{g'}} \frac{a_s^{(gg')}}{\omega_s} \right] \left[ \frac{1}{2}(v_s+1) \right]^{\frac{1}{2}} \\ (v_s v_{s'} | v_{s+1} v_{s'+1}) &: \frac{1}{2} \hbar \sum_g \frac{P_g}{I_g} \zeta_{ss'}^{(g)}(\omega_s - \omega_{s'}) \left[ \frac{(v_s+1)(v_{s'}+1)}{\omega_s \omega_{s'}} \right]^{\frac{1}{2}} \\ (v_s v_{s'} | v_{s+1} v_{s'-1}) &: \frac{1}{2} \hbar \sum_g \frac{P_g}{I_g} \zeta_{ss'}^{(g)}(\omega_s + \omega_{s'}) \left[ \frac{(v_s+1)v_{s'}}{\omega_s \omega_{s'}} \right]^{\frac{1}{2}} \\ (v_s v_{s'} | v_{s+1} v_{s'+2}) &: 3 k_{ss's'} \left[ \frac{1}{2}(v_s+1)(v_{s'}+1)(v_{s'}+2) \right]^{\frac{1}{2}} \\ (v_s v_{s'} | v_{s+1} v_{s'-2}) &: 3 k_{ss's'} \left[ \frac{1}{2}(v_s+1)v_{s'}(v_{s'}-1) \right]^{\frac{1}{2}} \\ (v_s v_{s'} v_{s''} | v_{s+1} v_{s'+1} v_{s''+1}) &: k_{ss's''} \left[ \frac{1}{8}(v_s+1)(v_{s'}+1)(v_{s''}+1) \right]^{\frac{1}{2}} \\ (v_s v_{s'} v_{s''} | v_{s+1} v_{s'+1} v_{s''-1}) &: k_{ss's''} \left[ \frac{1}{8}(v_s+1)(v_{s'}+1)v_{s''} \right]^{\frac{1}{2}} \\ (v_s v_{s'} v_{s''} | v_{s+1} v_{s'-1} v_{s''+1}) &: k_{ss's''} \left[ \frac{1}{8}(v_s+1)v_{s'}(v_{s''}+1) \right]^{\frac{1}{2}} \\ (v_s v_{s'} v_{s''} | v_{s+1} v_{s'-1} v_{s''-1}) &: k_{ss's''} \left[ \frac{1}{8}(v_s+1)v_{s'}v_{s''} \right]^{\frac{1}{2}}. \end{aligned} \tag{III.59}$$

From (59) we get for the second order contributions

$$\begin{aligned}
 \sum_{\mathbf{v}'} \frac{|(\mathbf{v}|\mathbf{v}')|^2}{W(\mathbf{v})-W(\mathbf{v}')} &= H_{\mathbf{v}}'' - \frac{1}{8} \sum_{\mathbf{g}\mathbf{g}'} \sum_{\mathbf{g}''\mathbf{g}'''} \frac{P_{\mathbf{g}} P_{\mathbf{g}'} P_{\mathbf{g}''} P_{\mathbf{g}'''}}{I_{\mathbf{g}\mathbf{g}}^e I_{\mathbf{g}'\mathbf{g}'}^e I_{\mathbf{g}''\mathbf{g}''}^e I_{\mathbf{g}'''\mathbf{g}'''}^e} \sum_{\mathbf{s}} \frac{a_{\mathbf{s}}^{(\mathbf{g}\mathbf{g}')} a_{\mathbf{s}}^{(\mathbf{g}''\mathbf{g}''')}}{\omega_{\mathbf{s}}^2} \\
 &+ \frac{3}{2} \hbar^{-1/2} \sum_{\mathbf{g}\mathbf{g}'} \frac{P_{\mathbf{g}} P_{\mathbf{g}'}}{I_{\mathbf{g}\mathbf{g}}^e I_{\mathbf{g}'\mathbf{g}'}^e} \sum_{\mathbf{s}\mathbf{s}'} (v_{\mathbf{s}} + \frac{1}{2}) k_{\mathbf{s}\mathbf{s}\mathbf{s}'} \frac{a_{\mathbf{s}'}^{(\mathbf{g}\mathbf{g}')}}{\omega_{\mathbf{s}'}^{3/2}} \\
 &+ \frac{1}{2} \hbar \sum_{\mathbf{g}\mathbf{g}'} \frac{P_{\mathbf{g}} P_{\mathbf{g}'}}{I_{\mathbf{g}\mathbf{g}}^e I_{\mathbf{g}'\mathbf{g}'}^e} \sum_{\mathbf{s}\mathbf{s}'} (v_{\mathbf{s}} + \frac{1}{2}) \frac{\zeta_{\mathbf{s}\mathbf{s}'}^{(\mathbf{g})} \zeta_{\mathbf{s}\mathbf{s}'}^{(\mathbf{g}')}}{\omega_{\mathbf{s}}} \frac{3\omega_{\mathbf{s}}^2 + \omega_{\mathbf{s}'}^2}{\omega_{\mathbf{s}}^2 - \omega_{\mathbf{s}'}^2}, \\
 &\hspace{15em} \text{(III.60)}
 \end{aligned}$$

where  $H_{\mathbf{v}}''$  includes all the purely vibrational terms, which have not been calculated explicitly here. If we now add in (51) and (54), the vibrational diagonalization of the Hamiltonian gives finally

$$\begin{aligned}
 (\mathbf{v}|H|\mathbf{v}) &= E_{\mathbf{v}} + \frac{1}{2} \sum_{\mathbf{g}} \frac{P_{\mathbf{g}}^2}{I_{\mathbf{g}\mathbf{g}}^e} - \frac{1}{2} \hbar \sum_{\mathbf{g}\mathbf{g}'} \frac{P_{\mathbf{g}} P_{\mathbf{g}'}}{I_{\mathbf{g}\mathbf{g}}^e I_{\mathbf{g}'\mathbf{g}'}^e} \sum_{\mathbf{s}} (v_{\mathbf{s}} + \frac{1}{2}) \frac{1}{\omega_{\mathbf{s}}} \\
 &\times \left[ G_{\mathbf{s}\mathbf{s}}^{(\mathbf{g}\mathbf{g}')} - \sum_{\mathbf{s}'} \zeta_{\mathbf{s}\mathbf{s}'}^{(\mathbf{g})} \zeta_{\mathbf{s}\mathbf{s}'}^{(\mathbf{g}')} \frac{3\omega_{\mathbf{s}}^2 + \omega_{\mathbf{s}'}^2}{\omega_{\mathbf{s}}^2 - \omega_{\mathbf{s}'}^2} - 3\hbar^{-3/2} \omega_{\mathbf{s}} \sum_{\mathbf{s}'} k_{\mathbf{s}\mathbf{s}\mathbf{s}'} \frac{a_{\mathbf{s}'}^{(\mathbf{g}\mathbf{g}')}}{\omega_{\mathbf{s}'}^{3/2}} \right] \\
 &- \frac{1}{8} \sum_{\mathbf{g}\mathbf{g}'} \sum_{\mathbf{g}''\mathbf{g}'''} \frac{P_{\mathbf{g}} P_{\mathbf{g}'} P_{\mathbf{g}''} P_{\mathbf{g}'''}}{I_{\mathbf{g}\mathbf{g}}^e I_{\mathbf{g}'\mathbf{g}'}^e I_{\mathbf{g}''\mathbf{g}''}^e I_{\mathbf{g}'''\mathbf{g}'''}^e} \sum_{\mathbf{s}} \frac{a_{\mathbf{s}}^{(\mathbf{g}\mathbf{g}')} a_{\mathbf{s}}^{(\mathbf{g}''\mathbf{g}''')}}{\omega_{\mathbf{s}}^2} \\
 &= E_{\mathbf{v}} + \frac{1}{2} \sum_{\mathbf{g}} \sum_{\mathbf{g}'} \sigma_{\mathbf{g}\mathbf{g}'}^{\mathbf{v}} \frac{P_{\mathbf{g}} P_{\mathbf{g}'}}{I_{\mathbf{g}\mathbf{g}}^e I_{\mathbf{g}'\mathbf{g}'}^e} + \frac{1}{4} \sum_{\mathbf{g}} \sum_{\mathbf{g}'} \sum_{\mathbf{g}''} \sum_{\mathbf{g}'''} \tau_{\mathbf{g}\mathbf{g}'\mathbf{g}''\mathbf{g}'''} \frac{P_{\mathbf{g}} P_{\mathbf{g}'} P_{\mathbf{g}''} P_{\mathbf{g}'''}}{I_{\mathbf{g}\mathbf{g}}^e I_{\mathbf{g}'\mathbf{g}'}^e I_{\mathbf{g}''\mathbf{g}''}^e I_{\mathbf{g}'''\mathbf{g}'''}^e} \\
 &= E_{\mathbf{v}} + H_{\mathbf{R}}, \hspace{10em} \text{(III.61)}
 \end{aligned}$$

where  $E_{\mathbf{v}}$  is purely vibrational energy, and

$$H_R = \frac{1}{2} \sum_g \sum_{g'} \sigma_{gg'}^v P_g P_{g'} + \frac{1}{4} \sum_g \sum_{g'} \sum_{g''} \sum_{g'''} \tau_{gg'g''g'''} P_g P_{g'} P_{g''} P_{g'''} \quad (\text{III.62})$$

$$\sigma_{gg'}^v = \frac{1}{I_{gg'}^v} = \frac{\delta_{gg'}}{I_{gg'}^e} - \sum_s (v_s + \frac{1}{2}) b_s^{(gg')} \quad (\text{III.63})$$

$$\tau_{gg'g''g'''} = -\frac{1}{2} \frac{1}{I_{gg}^e I_{g'g'}^e I_{g''g''}^e I_{g'''g'''}^e} \sum_s \frac{a_s^{(gg')} a_s^{(g'g'')}}{\omega_s^2} \quad (\text{III.64})$$

$$b_s^{(gg')} = \frac{1}{I_{gg}^e I_{g'g'}^e} \frac{\hbar}{\omega_s} \left[ A_{ss}^{(gg')} - \sum_{g''} \frac{a_s^{(gg'')} a_s^{(g'g'')}}{I_{g''g''}^e} - 4 \sum_{s'} \zeta_{ss'}^{(g)} \zeta_{ss'}^{(g')} \frac{\omega_s^2}{\omega_s^2 - \omega_{s'}^2} - 3 \hbar^{-3/2} \omega_s \sum_{s'} k_{sss'} \frac{a_{s'}^{(gg')}}{\omega_{s'}^{3/2}} \right] \quad (\text{III.65})$$

For the ground vibrational state, when  $v_s = v_{s'} = 0$ , the double summation over the third term in (65) gives

$$b_s^{(gg')}_{(v=0)} = \frac{1}{I_{gg}^e I_{g'g'}^e} \frac{\hbar}{\omega_s} \left[ A_{ss}^{(gg')} - \sum_{g''} \frac{a_s^{(gg'')} a_s^{(g'g'')}}{I_{g''g''}^e} - 2 \sum_{s'} \zeta_{ss'}^{(g)} \zeta_{ss'}^{(g')} \frac{\omega_s}{\omega_s + \omega_{s'}} - 3 \hbar^{-3/2} \omega_s \sum_{s'} k_{sss'} \frac{a_{s'}^{(gg')}}{\omega_{s'}^{3/2}} \right]. \quad (\text{III.66})$$

If  $\omega_s \approx \omega_{s'}$ , a case which is applicable to  $H_2O$ , a Coriolis resonance interaction may occur between vibrational levels, and, apart from other changes, the third term in (65) will require modification.

Equation (63) defines moments of inertia in the  $v$ -th vibrational state\*:

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\* These are usually called "effective moments of inertia", but we will reserve this term for use in the next section.

$$\begin{aligned}
 I_{gg'}^V &= I_{gg}^e \left[ \delta_{gg'} - I_{gg}^e \sum_s (v_s + \frac{1}{2}) b_s^{(gg')} \right]^{-1} \\
 &\approx I_{gg}^e \left[ \delta_{gg'} + I_{gg}^e \sum_s (v_s + \frac{1}{2}) b_s^{(gg')} \right], \quad (\text{III.67})
 \end{aligned}$$

since the  $b_s^{(gg')}$  are small.

We can obtain a useful relation between the  $I_{gg}^V$  of a planar molecule; for this case, with the usual convention

$$I_{aa} \leq I_{bb} \leq I_{cc}, \quad (\text{III.68})$$

we have

$$I_{cc}^e = I_{aa}^e + I_{bb}^e, \quad (\text{III.69})$$

the c-axis being necessarily normal to the plane of the molecule. We now define the "inertia defect"\*

$$\Delta_V = I_{cc}^V - I_{aa}^V - I_{bb}^V. \quad (\text{III.70})$$

It is readily verified from the definitions (18), (29), (30) that, for this case,

$$\begin{aligned}
 A_{ss}^{(cc)} &= A_{ss}^{(aa)} + A_{ss}^{(bb)} \\
 a_s^{(cc)} &= a_s^{(aa)} + a_s^{(bb)} \\
 a_s^{(ac)} &= 0 = a_s^{(bc)} \\
 \zeta_{ss'}^{(a)} &= 0 = \zeta_{ss'}^{(b)},
 \end{aligned}$$

---

\* Our definition follows that of Darling and Dennison<sup>5</sup>, who were the first to introduce the quantity; a number of other writers have used the negative of this.

so, from (67) and (69), it can be easily shown that

$$\Delta_v \approx - \sum_s (v_s + \frac{1}{2}) \frac{\hbar}{\omega_s} \left[ \frac{(a_s^{(cc)})^2}{I_{cc}^e} - \frac{(a_s^{(aa)})^2 + (a_s^{(ab)})^2}{I_{aa}^e} - \frac{(a_s^{(bb)})^2 + (a_s^{(ab)})^2}{I_{bb}^e} + 4 \sum_{s'} (\zeta_{ss'}^{(c)})^2 \frac{\omega_s^2}{\omega_s^2 - \omega_{s'}^2} \right].$$

(III.71)

In particular, for the ground vibrational state,

$$\Delta_0 \approx - \sum_s \frac{\hbar}{2\omega_s} \left[ \frac{(a_s^{(cc)})^2}{I_{cc}^e} - \frac{(a_s^{(aa)})^2 + (a_s^{(ab)})^2}{I_{aa}^e} - \frac{(a_s^{(bb)})^2 + (a_s^{(ab)})^2}{I_{bb}^e} + 2 \sum_{s'} (\zeta_{ss'}^{(c)})^2 \frac{\omega_s}{\omega_s + \omega_{s'}} \right].$$

(III.72)

The great advantage of these last two expressions is that they are independent of the anharmonic potential constants. For the water molecule, our calculations (Appendix C) show the approximation is good to a few percent for this case.

#### 4. Rotational Diagonalization

Diagonalization of the vibrational dependence leads to the Hamiltonian (62) for the rotational energies. To this order of approximation, there appear no terms cubic in the angular momentum operators, and the calculation of matrix elements from (48) is straightforward, though tedious; we

list some of these in Appendix A. Collecting terms, and simplifying, leads to the following matrix elements of (62):

$$\begin{aligned}
 (K|H_R|K) &= R_0 + R_2 K^2 - D_K K^4 \\
 (K|H_R|K\pm 1) &= [g(J, K\pm 1)]^{\frac{1}{2}} (2K\pm 1) \left[ \frac{1}{2} (B_{yz}^V \pm i B_{zx}^V) \right. \\
 &\quad \left. + (R_8^{(x)} \pm i R_8^{(y)}) J(J+1) + (R_9^{(x)} \pm i R_9^{(y)}) [K^2 + (K\pm 1)^2] \right] \\
 (K|H_R|K\pm 2) &= [g(J, K\pm 1) g(J, K\pm 2)]^{\frac{1}{2}} \left[ (R_4 \pm i R_4') \right. \\
 &\quad \left. - (R_5 \pm i R_5') [K^2 + (K\pm 2)^2] \right] \\
 (K|H_R|K\pm 3) &= [g(J, K\pm 1) g(J, K\pm 2) g(J, K\pm 3)]^{\frac{1}{2}} (2K\pm 3) (R_7^{(y)} \pm i R_7^{(x)}) \\
 (K|H_R|K\pm 4) &= [g(J, K\pm 1) g(J, K\pm 2) g(J, K\pm 3) g(J, K\pm 4)]^{\frac{1}{2}} (R_6 \pm i R_6')
 \end{aligned}
 \tag{III.73}$$

where

$$\begin{aligned}
 R_0 &= \frac{1}{2} (B_{xx}^V + B_{yy}^V) J(J+1) - D_J J^2 (J+1)^2 \\
 R_2 &= B_{zz}^V - \frac{1}{2} (B_{xx}^V + B_{yy}^V) - D_{JK} J(J+1) \\
 R_4 &= \frac{1}{4} (B_{yy}^V - B_{xx}^V) + \delta_J J(J+1) \\
 R_4' &= \frac{1}{2} B_{xy}^V + \delta_J' J(J+1)
 \end{aligned}
 \tag{III.74}$$

$$B_{gg'}^V = \frac{1}{2} \hbar^2 \sigma_{gg'}^{v(\text{eff})} = \frac{\hbar^2}{2I_{gg'}^{v(\text{eff})}}
 \tag{III.75}$$

$$\sigma_{gg'}^{v(\text{eff})} = \sigma_{gg'}^v - D_{gg'}$$

$$g(J, K\pm 1) = J(J+1) - K(K\pm 1)
 \tag{III.76}$$

and

$$\begin{aligned}
D_{xx} &= \frac{\hbar^2}{8} (\tau_{xxxx} + \tau_{yyyy} - 2\tau_{xxyy} + 4\tau_{xyxy} - 12\tau_{yzyz} + 8\tau_{zxzx}) \\
D_{yy} &= \frac{\hbar^2}{8} (\tau_{xxxx} + \tau_{yyyy} - 2\tau_{xxyy} + 4\tau_{xyxy} + 8\tau_{yzyz} - 12\tau_{zxzx}) \\
D_{zz} &= -\frac{3}{4}(D_{xx} + D_{yy}) + \frac{\hbar^2}{8} (5\tau_{yzyz} + 5\tau_{zxzx}) \\
D_{xy} &= \frac{5}{2}\hbar^2 \tau_{yzxz} \\
D_{yz} &= -\frac{5}{8}\hbar^2 (\tau_{yzxx} - \tau_{yzyy} - 2\tau_{xyzx}) \\
D_{zx} &= \frac{5}{8}\hbar^2 (\tau_{zxxx} - \tau_{zxyy} + 2\tau_{xyyz}) \\
D_J &= -\frac{\hbar^4}{32} (3\tau_{xxxx} + 3\tau_{yyyy} + 2\tau_{xxyy} + 4\tau_{xyxy}) \\
D_K &= D_J - \frac{\hbar^4}{4} (\tau_{zzzz} - \tau_{zzxx} - \tau_{yyzz} - 2\tau_{yzyz} - 2\tau_{zxzx}) \\
D_{JK} &= -D_J - D_K - \frac{\hbar^4}{4} \tau_{zzzz} \\
\delta_J &= -\frac{\hbar^4}{16} (\tau_{xxxx} - \tau_{yyyy}) \\
\delta'_J &= \frac{\hbar^4}{8} (\tau_{xxxy} + \tau_{yyxy}) \\
R_5 &= -\frac{\hbar^4}{32} (\tau_{xxxx} - \tau_{yyyy} + 2\tau_{yyzz} - 2\tau_{zzxx} + 4\tau_{yzyz} - 4\tau_{zxzx}) \\
R'_5 &= \frac{\hbar^4}{16} (\tau_{xxxy} + \tau_{yyxy} - 2\tau_{zzxy} - 4\tau_{yzxz}) \\
R_6 &= \frac{\hbar^4}{64} (\tau_{xxxx} + \tau_{yyyy} - 2\tau_{xxyy} - 4\tau_{xyxy}) \\
R'_6 &= -\frac{\hbar^4}{16} (\tau_{xxxy} - \tau_{yyxy}) \\
R_7^{(x)} &= -\frac{\hbar^4}{16} (\tau_{zxxx} - \tau_{zxyy} - 2\tau_{xyyz}) \\
R_7^{(y)} &= -\frac{\hbar^4}{16} (\tau_{zyxx} - \tau_{zyyy} + 2\tau_{xyzx}) \\
R_8^{(x)} &= \frac{\hbar^4}{16} (\tau_{yzxx} + 3\tau_{yzyy} + 2\tau_{xyzx}) \\
R_8^{(y)} &= \frac{\hbar^4}{16} (3\tau_{zxxx} + \tau_{zxyy} + 2\tau_{xyyz}) \\
R_9^{(x)} &= -R_8^{(x)} + \frac{\hbar^4}{8} \tau_{yzzz} \\
R_9^{(y)} &= -R_8^{(y)} + \frac{\hbar^4}{8} \tau_{zxzz}
\end{aligned} \tag{III.77}$$
  

$$\begin{aligned}
R_5 &= -\frac{\hbar^4}{32} (\tau_{xxxx} - \tau_{yyyy} + 2\tau_{yyzz} - 2\tau_{zzxx} + 4\tau_{yzyz} - 4\tau_{zxzx}) \\
R'_5 &= \frac{\hbar^4}{16} (\tau_{xxxy} + \tau_{yyxy} - 2\tau_{zzxy} - 4\tau_{yzxz}) \\
R_6 &= \frac{\hbar^4}{64} (\tau_{xxxx} + \tau_{yyyy} - 2\tau_{xxyy} - 4\tau_{xyxy}) \\
R'_6 &= -\frac{\hbar^4}{16} (\tau_{xxxy} - \tau_{yyxy}) \\
R_7^{(x)} &= -\frac{\hbar^4}{16} (\tau_{zxxx} - \tau_{zxyy} - 2\tau_{xyyz}) \\
R_7^{(y)} &= -\frac{\hbar^4}{16} (\tau_{zyxx} - \tau_{zyyy} + 2\tau_{xyzx}) \\
R_8^{(x)} &= \frac{\hbar^4}{16} (\tau_{yzxx} + 3\tau_{yzyy} + 2\tau_{xyzx}) \\
R_8^{(y)} &= \frac{\hbar^4}{16} (3\tau_{zxxx} + \tau_{zxyy} + 2\tau_{xyyz}) \\
R_9^{(x)} &= -R_8^{(x)} + \frac{\hbar^4}{8} \tau_{yzzz} \\
R_9^{(y)} &= -R_8^{(y)} + \frac{\hbar^4}{8} \tau_{zxzz}
\end{aligned} \tag{III.78}$$



The quantities usually designated by  $R_1$  do not appear in this work, since they arise only in cases where degenerate vibrational modes exist; the quantity  $D_K$  is sometimes denoted by  $-R_3$ .

What we call "effective moments of inertia" are defined in (75); they include modifications arising from centrifugal distortion terms ( $D_{gg'}$ ).

In general, the matrix (73) must be diagonalized numerically to obtain the rotational energy levels. Methods of doing this in the rigid rotor limit have been discussed by KHC I; the necessary extension of their work is given in our Appendix D.

### 5. Specialization to $H_2O$ Type Molecules

Using the matrices  $\mathbf{L}^{(x)}$ ,  $\mathbf{L}^{(y)}$  of (II.99) and (II.100), we can write explicitly the rotation-vibration constants for the non-linear  $XY_2$  type of molecule. We find, rather easily, that

$$\begin{aligned}\zeta_{13}^{(z)} &= I_{zz}^{e-\frac{1}{2}} (I_{xx}^{e\frac{1}{2}} \cos \gamma - I_{yy}^{e\frac{1}{2}} \sin \gamma) , \\ \zeta_{23}^{(z)} &= - I_{zz}^{e-\frac{1}{2}} (I_{xx}^{e\frac{1}{2}} \sin \gamma + I_{yy}^{e\frac{1}{2}} \cos \gamma) ,\end{aligned}\tag{III.79}$$

and, using "vector" forms for the  $a_s^{(gg')}$  defined in (29), for convenience of presentation,

$$a^{(xx)} = \begin{bmatrix} 2I_{xx}^{e\frac{1}{2}} \sin \gamma \\ 2I_{xx}^{e\frac{1}{2}} \cos \gamma \\ 0 \end{bmatrix} \quad a^{(yy)} = \begin{bmatrix} 2I_{yy}^{e\frac{1}{2}} \cos \gamma \\ -2I_{yy}^{e\frac{1}{2}} \sin \gamma \\ 0 \end{bmatrix}$$

$$\begin{aligned}
\mathbf{a}^{(zz)} = \mathbf{a}^{(xx)} + \mathbf{a}^{(yy)} &= \begin{bmatrix} 2(I_{xx}^{e\frac{1}{2}} \sin \gamma + I_{yy}^{e\frac{1}{2}} \cos \gamma) \\ 2(I_{xx}^{e\frac{1}{2}} \cos \gamma - I_{yy}^{e\frac{1}{2}} \sin \gamma) \\ 0 \end{bmatrix} \\
&= \begin{bmatrix} -2I_{zz}^{e\frac{1}{2}} \zeta_{23}^{(z)} \\ 2I_{zz}^{e\frac{1}{2}} \zeta_{13}^{(z)} \\ 0 \end{bmatrix} \\
\mathbf{a}^{(xy)} &= \begin{bmatrix} 0 \\ 0 \\ -2\left(\frac{I_{xx}^e I_{yy}^e}{I_{zz}^e}\right)^{\frac{1}{2}} \end{bmatrix}
\end{aligned} \tag{III.80}$$

From (64) we obtain for the  $\tau_{gg'g''g'''} :$

$$\begin{aligned}
\tau_{xxxx} &= -2(I_{xx}^e)^{-3} \left( \frac{\sin^2 \gamma}{\omega_1^2} + \frac{\cos^2 \gamma}{\omega_2^2} \right) \\
\tau_{yyyy} &= -2(I_{yy}^e)^{-3} \left( \frac{\cos^2 \gamma}{\omega_1^2} + \frac{\sin^2 \gamma}{\omega_2^2} \right) \\
\tau_{zzzz} &= -2(I_{zz}^e)^{-3} \left( \frac{(\zeta_{23}^{(z)})^2}{\omega_1^2} + \frac{(\zeta_{13}^{(z)})^2}{\omega_2^2} \right) \\
\tau_{xyxy} &= -2(I_{xx}^e I_{yy}^e I_{zz}^e)^{-1} \frac{1}{\omega_3^2} \\
\tau_{xxyy} &= -2(I_{xx}^e I_{yy}^e)^{-3/2} \sin \gamma \cos \gamma \frac{\omega_2^2 - \omega_1^2}{\omega_1^2 \omega_2^2} \\
\tau_{xxzz} &= -2(I_{xx}^e I_{zz}^e)^{-3/2} \left( \frac{\zeta_{13}^{(z)} \cos \gamma}{\omega_2^2} - \frac{\zeta_{23}^{(z)} \sin \gamma}{\omega_1^2} \right) \\
\tau_{yyzz} &= 2(I_{yy}^e I_{zz}^e)^{-3/2} \left( \frac{\zeta_{13}^{(z)} \sin \gamma}{\omega_2^2} + \frac{\zeta_{23}^{(z)} \cos \gamma}{\omega_1^2} \right) .
\end{aligned} \tag{III.81}$$

From these, the various distortion coefficients in Section 4 can be readily calculated; it does not seem necessary to give them explicitly here.

The inertia defect of (71) can now be written down; using the relation

$$(\zeta_{13}^{(z)})^2 + (\zeta_{23}^{(z)})^2 = 1, \quad (\text{III.82})$$

we find

$$\Delta_V = 4\hbar \left[ (v_1 + \frac{1}{2}) (\zeta_{13}^{(z)})^2 \frac{\omega_3^2}{\omega_1(\omega_3^2 - \omega_1^2)} + (v_2 + \frac{1}{2}) (\zeta_{23}^{(z)})^2 \frac{\omega_3^2}{\omega_2(\omega_3^2 - \omega_2^2)} - (v_3 + \frac{1}{2}) \left[ (\zeta_{13}^{(z)})^2 \frac{\omega_1^2}{\omega_3(\omega_3^2 - \omega_1^2)} + (\zeta_{23}^{(z)})^2 \frac{\omega_2^2}{\omega_3(\omega_3^2 - \omega_2^2)} \right] \right]. \quad (\text{III.83})$$

For the ground vibrational state, this reduces to

$$\Delta_0 = 2\hbar \left[ \frac{(\zeta_{13}^{(z)})^2 (\omega_1^3 - \omega_3^3)}{\omega_1 \omega_3 (\omega_1^2 - \omega_3^2)} + \frac{(\zeta_{23}^{(z)})^2 (\omega_2^3 - \omega_3^3)}{\omega_2 \omega_3 (\omega_2^2 - \omega_3^2)} \right]. \quad (\text{III.84})$$

The quantities  $A_{ss'}^{(gg')}$ , defined in (30) are found to be

$$\begin{aligned} A_{11}^{(xx)} &= A_{22}^{(yy)} = \sin^2 \gamma \\ A_{22}^{(xx)} &= A_{11}^{(yy)} = \cos^2 \gamma \\ A_{33}^{(xx)} &= I_{xx}^e / I_{zz}^e \\ A_{33}^{(yy)} &= I_{yy}^e / I_{zz}^e \\ A_{11}^{(zz)} &= A_{22}^{(zz)} = A_{33}^{(zz)} = 1. \end{aligned} \quad (\text{III.85})$$

Finally, the  $b_s^{(gg')}$  of (65) may now be calculated:

$$\begin{aligned}
b_1^{(xx)} &= -\frac{3\hbar}{I_{xx}^2} \left[ \frac{\sin^2 \gamma}{\omega_1} + 2 I_{xx}^{e\frac{1}{2}} \left[ \frac{k_{111} \sin \gamma}{(\hbar\omega_1)^{3/2}} + \frac{k_{112} \cos \gamma}{(\hbar\omega_2)^{3/2}} \right] \right] \\
b_2^{(xx)} &= -\frac{3\hbar}{I_{xx}^2} \left[ \frac{\cos^2 \gamma}{\omega_2} + 2 I_{xx}^{e\frac{1}{2}} \left[ \frac{k_{221} \sin \gamma}{(\hbar\omega_1)^{3/2}} + \frac{k_{222} \cos \gamma}{(\hbar\omega_2)^{3/2}} \right] \right] \\
b_3^{(xx)} &= -\frac{3\hbar}{I_{xx}^2} \left[ \frac{1}{\omega_3} \frac{I_{xx}^e}{I_{zz}^e} + 2 I_{xx}^{e\frac{1}{2}} \left[ \frac{k_{331} \sin \gamma}{(\hbar\omega_1)^{3/2}} + \frac{k_{332} \cos \gamma}{(\hbar\omega_2)^{3/2}} \right] \right] \\
b_1^{(yy)} &= -\frac{3\hbar}{I_{yy}^2} \left[ \frac{\cos^2 \gamma}{\omega_1} + 2 I_{yy}^{e\frac{1}{2}} \left[ \frac{k_{111} \cos \gamma}{(\hbar\omega_1)^{3/2}} - \frac{k_{112} \sin \gamma}{(\hbar\omega_2)^{3/2}} \right] \right] \\
b_2^{(yy)} &= -\frac{3\hbar}{I_{yy}^2} \left[ \frac{\sin^2 \gamma}{\omega_2} + 2 I_{yy}^{e\frac{1}{2}} \left[ \frac{k_{221} \cos \gamma}{(\hbar\omega_1)^{3/2}} - \frac{k_{222} \sin \gamma}{(\hbar\omega_2)^{3/2}} \right] \right] \\
b_3^{(yy)} &= -\frac{3\hbar}{I_{yy}^2} \left[ \frac{1}{\omega_3} \frac{I_{yy}^e}{I_{zz}^e} + 2 I_{yy}^{e\frac{1}{2}} \left[ \frac{k_{331} \cos \gamma}{(\hbar\omega_1)^{3/2}} - \frac{k_{332} \sin \gamma}{(\hbar\omega_2)^{3/2}} \right] \right] \\
b_1^{(zz)} &= -\frac{3\hbar}{I_{zz}^2} \left[ \frac{(\zeta_{23}^{(z)})^2}{\omega_1} + (\zeta_{13}^{(z)})^2 \frac{3\omega_1^2 + \omega_3^2}{3\omega_1(\omega_1^2 - \omega_3^2)} \right. \\
&\quad \left. - 2 I_{zz}^{e\frac{1}{2}} \left[ \frac{k_{111} \zeta_{23}^{(z)}}{(\hbar\omega_1)^{3/2}} - \frac{k_{112} \zeta_{13}^{(z)}}{(\hbar\omega_2)^{3/2}} \right] \right] \\
b_2^{(zz)} &= -\frac{3\hbar}{I_{zz}^2} \left[ \frac{(\zeta_{13}^{(z)})^2}{\omega_2} + (\zeta_{23}^{(z)})^2 \frac{3\omega_2^2 + \omega_3^2}{3\omega_2(\omega_2^2 - \omega_3^2)} \right. \\
&\quad \left. - 2 I_{zz}^{e\frac{1}{2}} \left[ \frac{k_{221} \zeta_{23}^{(z)}}{(\hbar\omega_1)^{3/2}} - \frac{k_{222} \zeta_{13}^{(z)}}{(\hbar\omega_2)^{3/2}} \right] \right] \\
b_3^{(zz)} &= -\frac{3\hbar}{I_{zz}^2} \left[ (\zeta_{13}^{(z)})^2 \frac{3\omega_3^2 + \omega_1^2}{3\omega_3(\omega_3^2 - \omega_1^2)} + (\zeta_{23}^{(z)})^2 \frac{3\omega_3^2 + \omega_2^2}{3\omega_3(\omega_3^2 - \omega_2^2)} \right. \\
&\quad \left. - 2 I_{zz}^{e\frac{1}{2}} \left[ \frac{k_{331} \zeta_{23}^{(z)}}{(\hbar\omega_1)^{3/2}} - \frac{k_{332} \zeta_{13}^{(z)}}{(\hbar\omega_2)^{3/2}} \right] \right]
\end{aligned}$$

(III.86)

## 6. Specialization to HDO Type Molecules

In a vibrational state, an off-diagonal product of inertia appears in HDO, because of the non-vanishing of the corresponding  $b_s^{(gg')}$ ; in a  $I^r$  representation\*, such as we use here, the  $b_s^{(zx)}$  are non-vanishing. As a result, the first term in (62) is no longer a sum of squares, but can be easily made so by a transformation of axes. Let us write

$$\frac{1}{2} \sum_g \sum_{g'} \sigma_{gg'}^v P_g P_{g'} = \frac{1}{2} \tilde{\mathbf{P}} \boldsymbol{\sigma} \mathbf{P} , \quad (\text{III.87})$$

and set

$$\mathbf{P}' = \mathbf{R} \mathbf{P} , \quad (\text{III.88})$$

where  $\mathbf{R}$  is an orthogonal matrix, so that

$$\tilde{\mathbf{P}} \boldsymbol{\sigma} \mathbf{P} = \tilde{\mathbf{P}} \boldsymbol{\sigma}' \mathbf{P}' , \quad (\text{III.89})$$

where  $\boldsymbol{\sigma}'$  is diagonal, and

$$\boldsymbol{\sigma}' = \mathbf{R} \boldsymbol{\sigma} \tilde{\mathbf{R}} . \quad (\text{III.90})$$

It is readily verified that we may take

$$\mathbf{R} = \begin{bmatrix} \cos \theta & 0 & \sin \theta \\ 0 & 1 & 0 \\ -\sin \theta & 0 & \cos \theta \end{bmatrix} \quad (\text{III.91})$$

with

$$\begin{aligned} \sin \theta &= 2^{-\frac{1}{2}} (1-x^{\frac{1}{2}})^{\frac{1}{2}} \\ \cos \theta &= 2^{-\frac{1}{2}} (1+x^{\frac{1}{2}})^{\frac{1}{2}} \end{aligned} \quad (\text{III.92})$$

$$x = \frac{(\sigma_{ZZ}^v - \sigma_{XX}^v)^2}{4(\sigma_{ZX}^v)^2 + (\sigma_{ZZ}^v + \sigma_{XX}^v)^2} \quad (\text{III.93})$$

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\* See Appendix C.

so that, in the new coordinate system,

$$\begin{aligned}\sigma_{xx}^{v'} &= \sigma_{xx}^v \cos^2 \theta + \sigma_{zz}^v \sin^2 \theta + 2\sigma_{zx}^v \sin \theta \cos \theta \\ \sigma_{yy}^{v'} &= \sigma_{yy}^v \\ \sigma_{zz}^{v'} &= \sigma_{xx}^v \sin^2 \theta + \sigma_{zz}^v \cos^2 \theta - 2\sigma_{zx}^v \sin \theta \cos \theta ,\end{aligned}\tag{III.94}$$

which are the principal reciprocal moments of inertia.

The second term in (62) may also be expressed in the new coordinate system by substitution of (88):

$$\mathbf{P} = \tilde{\mathbf{R}} \mathbf{P}'$$

or,

$$\begin{aligned}P_x &= \alpha P'_x - \beta P'_z \\ P_y &= P'_y \\ P_z &= \beta P'_x + \alpha P'_z ,\end{aligned}\tag{III.95}$$

where

$$\alpha = \cos \theta \quad \beta = \sin \theta .\tag{III.96}$$

The new  $\tau$ 's are the coefficients of the new  $P'_x P'_y P'_z P'_z$ , and are given by:

$$\begin{aligned}\tau'_{xxxx} &= \alpha^4 \tau_{xxxx} + \beta^4 \tau_{zzzz} + 2\alpha^2 \beta^2 (\tau_{zzxx} + 2\tau_{zxzx}) \\ &\quad + 4\alpha^3 \beta \tau_{zxzx} + 4\alpha \beta^3 \tau_{zxzz}\end{aligned}$$

$$\tau'_{yyyy} = \tau_{yyyy}$$

$$\begin{aligned}\tau'_{zzzz} &= \beta^4 \tau_{xxxx} + \alpha^4 \tau_{zzzz} + 2\alpha^2 \beta^2 (\tau_{zzxx} + 2\tau_{zxzx}) \\ &\quad - 4\alpha \beta^3 \tau_{zxzx} - 4\alpha^3 \beta \tau_{zxzz}\end{aligned}$$

$$\tau'_{xxyy} = \alpha^2 \tau_{xxyy} + \beta^2 \tau_{yyzz} + 2\alpha \beta \tau_{zxxy}$$

$$\tau'_{yyzz} = \beta^2 \tau_{xxyy} + \alpha^2 \tau_{yyzz} - 2\alpha \beta \tau_{zxxy}$$

$$\begin{aligned}
\tau'_{zzxx} &= a^2\beta^2(\tau_{xxxx} + \tau_{zzzz}) + (a^4 + \beta^4)\tau_{zzxx} - 4a^2\beta^2\tau_{zxzx} \\
&\quad - 2a\beta(a^2 - \beta^2)(\tau_{zxxx} - \tau_{zxzz}) \\
\tau'_{zxzx} &= a^2\beta^2(\tau_{xxxx} + \tau_{zzzz}) + (a^2 - \beta^2)^2\tau_{zxzx} - 2a^2\beta^2\tau_{zzxx} \\
&\quad - 2a\beta(a^2 - \beta^2)(\tau_{zxxx} - \tau_{zxzz}) \\
\tau'_{zxxx} &= -a^3\beta\tau_{xxxx} + a\beta^3\tau_{zzzz} + a\beta(a^2 - \beta^2)(\tau_{zzxx} + 2\tau_{zxzx}) \\
&\quad + a^2(a^2 - 3\beta^2)\tau_{zxxx} + \beta^2(3a^2 - \beta^2)\tau_{zxzz} \\
\tau'_{zxyy} &= -a\beta(\tau_{xxyy} - \tau_{yyzz}) + (a^2 - \beta^2)\tau_{zxyy} \\
\tau'_{zxzz} &= -a\beta^3\tau_{xxxx} + a^3\beta\tau_{zzzz} - a\beta(a^2 - \beta^2)(\tau_{zzxx} + 2\tau_{zxzx}) \\
&\quad + \beta^2(3a^2 - \beta^2)\tau_{zxxx} + a^2(a^2 - 3\beta^2)\tau_{zxzz}
\end{aligned}
\tag{III.97}$$

The primed  $\sigma$ 's and  $\tau$ 's may now be substituted directly into the equations of Section 4.

## IV

MICROWAVE SPECTRUM OF H<sub>2</sub>O

The K-band "radar water line" at 22,235 Mc/sec<sup>8,34</sup>, due to the  $5_{23} \rightarrow 6_{16}$  transition\* of H<sub>2</sub>O, has been examined by a number of workers, and is the only microwave line known to belong to this molecule.

Examination of the King, Hainer and Cross tables\*\* shows that no other H<sub>2</sub>O lines are likely to be found below about 180,000 Mc/sec ( $2_{20} \rightarrow 3_{13}$  transition); the difficulties of working in the latter region, however, make it desirable that a better prediction be available before searching is carried out. The one known H<sub>2</sub>O line does not give us enough information to improve our knowledge -- the KHC II tables based on  $\kappa = -0.436426$ , predict it at the rigid rotor frequency of 23,380 Mc/sec, some 1,000 Mc/sec too high, and the term values of Randall, Dennison, Ginsburg and Weber\*\*\* show it at 20,400 Mc/sec, so it is apparent that better parameters are needed. The present work gives much the same agreement (or disagreement) with experiment; with the effective H<sub>2</sub>O rotational constants of Table C.8 (Appendix C) and the distortion constants of Table C.7, our calculations (by the methods of Appendix D) give the results shown in Table IV.1.

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\* Our notation for the energy levels follows the  $J_{K-1, K_1}$  scheme of KHC I.

\*\* Reference 16; hereafter referred to as KHC II.

\*\*\* Reference 27; also see Appendix F.



TABLE IV.1  
H<sub>2</sub>O - Microwave Absorption Lines

Transition	Frequency (Mc/sec)			Theoretical (This Work)
	Observed	KHC II	RDGW	
$2_{20} \rightarrow 3_{13}$	----	184,000	182,000	187,471
$5_{23} \rightarrow 6_{16}$	22,235.22±0.05	23,380	20,400	24,588

We will show in Chapter VI that we can expect the theoretical parameters to give a good measure of the distortion, so it is interesting to compare our calculated energy levels\* with those of RDGW, as in Table IV.2; here the distortion correction is the energy shown minus the calculated rigid rotor energy.

TABLE IV.2  
H<sub>2</sub>O - Energy Levels

Level	RDGW		This Work	
	Energy (Mc/sec x 10 <sup>6</sup> )	Distortion Correction	Energy (Mc/sec x 10 <sup>6</sup> )	Distortion Correction
$2_{20}$	4.080100	-0.004800	4.066769	-0.008787
$3_{13}$	4.262100	-0.001500	4.254240	0.001449
$5_{23}$	13.386000	-0.026382	13.352540	-0.040304
$6_{16}$	13.407000	-0.015000	13.377127	0.025789

There is little else we can say about H<sub>2</sub>O at present, but it is hoped that eventually an accurate determination of the HDO parameters will lead to better values for H<sub>2</sub>O.

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\* Throughout this work we measure energy in units Mc/sec, or multiples thereof.

## V

MICROWAVE SPECTRUM OF D<sub>2</sub>O

No lines of D<sub>2</sub>O were known prior to the start of this work, although the KHC II tables\* indicate a number of transitions are to be expected in the microwave region.

In the course of this work the  $2_{20} \rightarrow 3_{13}$  and  $5_{32} \rightarrow 4_{41}$  lines were found (Appendix E), though only the first was identified by the writer<sup>26</sup>. The two lines were subsequently reported independently by Beard and Bianco<sup>1</sup>. The frequencies, together with those calculated theoretically from the constants of Tables C.7 and C.8, are shown in Table V.1.

TABLE V.1  
D<sub>2</sub>O - Microwave Absorption Lines

Transition	Frequency (Mc/sec)		Theoretical (This Work)
	Observed (This Work)	FRD*	
$2_{20} \rightarrow 3_{13}$	10,919.39±0.05	7,500	10,670
$5_{32} \rightarrow 4_{41}$	10,947.13±0.05	16,000	17,472

The agreement on the  $2 \rightarrow 3$  line is comparatively good, while for the  $5 \rightarrow 4$  line we do get the correct relative positions of the levels (as shown experimentally by the Stark effect). However, the actual discrepancy between calculated and

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\* The KHC II tables give rigid rotor term values taken from the Fuson, Randall and Dennison paper (FRD, reference 6 -- also see Appendix F); in Tables V.1 and V.2 we use FRD's "corrected" levels.

observed frequencies for the  $5 \rightarrow 4$  line shows the parameters cannot be relied upon for accurate work; accordingly, we have not calculated up any more  $D_2O$  transitions.

It is expected that additional useful work can be done on  $D_2O$ . Jen et al.<sup>12</sup> have observed two weak lines in the water spectrum at  $30,182.57 \pm 0.1$  and  $30,778.62 \pm 0.1$  Mc/sec, and these are as yet unidentified. In the next Chapter we investigate probable HDO transitions, and find none in this region, though these calculations are not conclusive. Thus there is a good chance that these two lines may be due to  $D_2O^*$

In the FRD work, distortion corrections were obtained semi-classically; in Table V.2 we compare the distortion corrections calculated here with those given by FRD.

TABLE V.2  
 $D_2O$  - Energy Levels

Level	<u>FRD</u>		<u>This Work</u>	
	Energy (Mc/sec x $10^6$ )	Distortion Correction	Energy (Mc/sec x $10^6$ )	Distortion Correction
$2_{20}$	2.2193	0	2.2184	-0.003049
$3_{13}$	2.2268	-0.009000	2.2291	-0.000694
$4_{41}$	8.0641	-0.001200	8.0665	-0.049868
$5_{32}$	8.0481	-0.026400	8.0490	-0.016747

As in the case of  $H_2O$  the data is still too meager to enable us to say much about this molecule.

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\* See also Chapter VII.

## VI

MICROWAVE SPECTRUM OF HDO1. Introduction

There has been little infrared work carried out on HDO because of the difficulties of untangling its lines from those of H<sub>2</sub>O and D<sub>2</sub>O. From such infrared analysis as has been made, KHC II deduced  $\kappa = -0.685$ , from which they constructed their rigid rotor tables of expected HDO microwave transitions.

Previous to this publication, the only microwave line of HDO known was the  $5_{33} \rightarrow 5_{32}$  transition<sup>33,34</sup>. On the basis of these tables, however, Strandberg<sup>32</sup> located the  $2_{21} \rightarrow 2_{20}$ ,  $3_{22} \rightarrow 3_{21}$  and  $4_{14} \rightarrow 3_{21}$  lines, and estimated  $\kappa = -0.696$ .

Three other lines were then found by workers in this Laboratory; the  $4_{32} \rightarrow 4_{31}$  line<sup>31</sup>, the  $7_{44} \rightarrow 7_{43}$  line<sup>13</sup>, and an unidentified line at 26,880 Mc/sec. During the present investigations the latter was found to have been originally discovered by McAfee<sup>22</sup> who assigned it to a D<sub>2</sub>O transition; it is the conclusion of this work that it is the  $6_{24} \rightarrow 7_{17}$  transition of HDO.

Concurrently with the present work, Weisbaum and Beers<sup>35</sup> discovered a number of lines in the S-band region, and identified the transitions  $6_{43} \rightarrow 6_{42}$ ,  $9_{55} \rightarrow 9_{54}$ ,  $12_{67} \rightarrow 12_{66}$ , and  $4_{22} \rightarrow 5_{05}$ ; the author was advised of these investigations by private communication, though the final identity of these lines was not reasonably certain until a late stage in the present work.

In 1951 Lewis<sup>21</sup> calculated some theoretical distortion constants for HDO, and attempted to determine  $\kappa$  and  $\frac{a-c}{2}$  from the then known spectrum; he deduced -0.67712 and  $2.468 \times 10^5$  Mc/sec, respectively, for these two values. Lewis also calculated a theoretical inertia defect  $\Delta_0$ , but this was based on an incorrect formula and was considerably in error.

The present author remeasured the  $7_{44} \rightarrow 7_{43}$  frequency, resolved the Stark structure and remeasured the frequency of the 26,880 Mc/sec line, and discovered the  $8_{45} \rightarrow 8_{44}$  transition by prediction from rough calculations. He calculated the theoretical parameters, including rotation constants, from infrared data (Appendices B and C), and carried out detailed calculations of the theoretical frequencies. This led to prediction of certain Q-branch frequencies, and the subsequent observation of the  $10_{56} \rightarrow 10_{55}$  and  $11_{57} \rightarrow 11_{56}$  lines, and provided additional evidence for the identification of the 26,880 Mc/sec line.

The  $8_{45} \rightarrow 8_{44}$  line has been independently observed by Jen et al.<sup>12</sup> who also concluded from the Stark effect that the 26,880 Mc/sec line is to be assigned to the HDO  $6_{24} \rightarrow 7_{17}$  transition.

The present state of experimental knowledge of the HDO microwave spectrum is summarized in Table VI.1.

TABLE VI.1  
HDO - Observed Microwave Absorption Lines

Transition	Frequency (Mc/sec)	Reference
Q-Branch Transitions		
$2_{21} \rightarrow 2_{20}$	10,278.99	32
$3_{22} \rightarrow 3_{21}$	50,236.90	32
$4_{32} \rightarrow 4_{31}$	5,702.78	31
$5_{33} \rightarrow 5_{32}$	22,309 $\pm$ 5 *22,307.67 $\pm$ 0.05	34 33
$6_{43} \rightarrow 6_{42}$	2,394.6	35
$7_{44} \rightarrow 7_{43}$	8,576.89 *8,577.7 $\pm$ 0.1	13 This work
$8_{45} \rightarrow 8_{44}$	*24,884.77 $\pm$ 0.05 24,884.85 $\pm$ 0.1	This work 12
$9_{55} \rightarrow 9_{54}$	3,044.7	35
$10_{56} \rightarrow 10_{55}$	8,836.95 $\pm$ 0.1	This work
$11_{57} \rightarrow 11_{56}$	22,581.1 $\pm$ 0.2	This work
$12_{67} \rightarrow 12_{66}$	2,961	35
P- and R-Branch Transitions		
$4_{14} \rightarrow 3_{21}$	20,460.40	32
$4_{22} \rightarrow 5_{05}$	2,888	35
$6_{24} \rightarrow 7_{17}$	26,880.44 *26,880.38 $\pm$ 0.05 26,880.47 $\pm$ 0.1	22 This work 12
*Measurement indicated was used for computations.		

In the sequel, we will usually use  $J_K$  to denote the Q-branch transition  $J_{K-1, K_1} \rightarrow J_{K-1, K_1-1}$ , with K standing for  $K_{-1}$ , the index denoting the K value of the limiting prolate symmetric top.

## 2. Theoretical Frequencies

In principal, transition frequencies may be calculated by diagonalization of the rotational matrix (III.73) to find the appropriate energy levels, then taking differences. We call this "exact" calculation, although in practice it involves finding characteristic values by numerical methods; in our computations we have used sufficient significant figures to get within the experimental error.

Methods of carrying out this numerical diagonalization are described in Appendix D, where it is indicated that the main problem is the determination of the "reduced energies"; unless otherwise stated, the following discussion will be in terms of "reduced" parameters.

In the original belief that  $(K|K\pm 1)$  and  $(K|K\pm 3)$  matrix elements in (III.73) could be safely neglected, we carried out some exact calculations for Q-branch transitions, using the HDO constants of Tables C.7 and C.8, which give the parameters of Table VI.2:

TABLE VI.2  
HDO - Theoretical Parameters (I)

$$\frac{a-c}{2} = 2.52993085 \times 10^5 \text{ Mc/sec}$$

$$\kappa = -0.68105413$$

$$D_{JK} = 1.63925813 \times 10^{-4}$$

$$D_K = 11.06549366 \times 10^{-4}$$

$$\delta_J = 0.12833684 \times 10^{-4}$$

$$R_5 = -0.35698618 \times 10^{-4}$$

$$R_6 = -0.02167643 \times 10^{-4}$$

With  $\nu_{JK}^{\circ}$  and  $\nu_{JK}$  the observed and calculated frequencies, the results are shown in Table VI.3:

TABLE VI.3  
HDO - Q-Branch Theoretical Frequencies (I)

Transition $J_K$	Frequency (Mc/sec)		
	Observed $\nu_{JK}^{\circ}$	Calculated $\nu_{JK}$	$\nu_{JK}^{\circ} - \nu_{JK}$
$2_2$	10,278.99	10,375.742	-96.752
$3_2$	50,236.90	50,705.828	-468.928
$4_3$	5,702.78	5,817.548	-114.768
$5_3$	22,307.67	22,756.857	-449.187
$6_3$	---	65,714.268	---
$6_4$	2,394.6	2,470.073	-75.473
$7_4$	8,577.7	8,849.329	-271.629
$8_4$	24,884.77	25,673.369	-788.599
$9_5$	3,044.7	3,174.077	-129.377
$10_5$	8,836.95	9,211.967	-375.017
$11_5$	22,581.1	23,536.847	-955.747
$12_6$	2,961	3,122.212	-161.212

It is noticed that the magnitude of the difference (last column) increases in an apparently fairly regular manner within each K-family; a significant relationship is obtained by simply taking the ratios  $r_{JK} = \nu_{JK} / \nu_{JK}^{\circ}$ , which are given in Table VI.4, and are seen to be substantially constant for a given value of K:



TABLE VI.4

$J_K$	$r_{J_K} = v_{J_K} / v_{J_K}^0$	Mean $r_K$
$2_2$	1.00941	1.00937
$3_2$	1.00933	
$4_3$	1.02012	1.02013
$5_3$	1.02014	
$6_4$	1.03152	1.03163
$7_4$	1.03167	
$8_4$	1.03169	
$9_5$	1.04249	1.04242
$10_5$	1.04244	
$11_5$	1.04233	
$12_6$	1.05445	1.05445

We note also that

$$\begin{aligned} \frac{r_3}{r_2} &= 1.01066 \\ \frac{r_4}{r_3} &= 1.01127 \\ \frac{r_5}{r_4} &= 1.01046 \\ \frac{r_6}{r_5} &= 1.01154 \end{aligned}$$

$$\begin{aligned} \frac{r_6}{r_4} &= 1.02212 \\ \frac{r_4}{r_2} &= 1.02205 \\ \frac{r_5}{r_3} &= 1.02185 \end{aligned}$$

from which it appears that  $r_K/r_{K-2}$  is the more constant ratio, so we can conclude

$$\frac{r_K}{r_{K-2}} = 1.0220 ,$$

approximately.

At the time of these calculations, only the identities and frequencies of the lines  $2_2$ ,  $3_2$ ,  $4_3$ ,  $5_3$ ,  $7_4$ ,  $8_4$  had been definitely established. Assuming the ratio  $r_K / r_{K-2} = 1.0220$  was significant, we predicted the  $6_4$ ,  $9_5$  and  $12_6$  lines at 2,394.2, 3,045.1, and 2,961.2 Mc/sec. The agreement with the then tentatively reported frequencies of these lines appeared so good that we extended the predictions to the  $6_3$ ,  $10_5$ , and  $11_5$  lines, thus:

$6_3$	64,417 Mc/sec
$10_5$	8,836 Mc/sec
$11_5$	22,577 Mc/sec.

A search for the latter two lines subsequently showed them at 8,837 and 22,581 Mc/sec, respectively.

We may also extrapolate to predict the  $1_1$  line at 80,743 Mc/sec, but the prediction is probably not quite so accurate here because the dependence on the distortion constants is much simpler.

This simple "extrapolation method" of predicting Q-branch frequencies of HDO therefore seems to be quite reliable. It appears to have the following significance.

Let  $\nu_{JK}^R$  be the calculated rigid rotor frequencies, and let

$$\nu_{JK} = \nu_{JK}^R (1 + \Delta_{JK}) \quad (\text{VI.1})$$

define the distortion correction  $\Delta_{JK}$ . A similar relation

$$\nu_{JK}^O = \nu_{JK}^{Ro} (1 + \Delta_{JK}^O) \quad (\text{VI.2})$$

will be true for the observed frequency. Then

$$r_{JK} = \frac{v_{JK}^R (1 + \Delta_{JK})}{v_{JK}^{Ro} (1 + \Delta_{JK}^o)} .$$

We also write

$$v_{JK}^R = \frac{a-c}{2} \Delta E_{JK}(\kappa) , \quad (\text{VI.3})$$

$$v_{JK}^{Ro} = \left(\frac{a-c}{2}\right)^o \Delta E_{JK}^o(\kappa^o) , \quad (\text{VI.4})$$

where  $\Delta E(\kappa)$  is the reduced energy difference for the transition, and the superscript  $^o$  indicates values corresponding to the observed frequencies. By direct expansion of the appropriate secular determinants, or by use of equation (26) of reference 12, one can show that, to first order,

$$\Delta E_{JK}(\kappa) \approx c_{JK} \frac{H^K}{(G-F)^{K-1}} , \quad (\text{VI.5})$$

where  $c_{JK}$  is a function of  $J$  and  $K$  only, and  $F$ ,  $G$ ,  $H$  are functions of  $\kappa$  (see Appendix D). It follows that, to first order,

$$r_{JK} \approx \frac{\frac{a-c}{2}}{\left(\frac{a-c}{2}\right)^o} \left(\frac{H}{H^o}\right)^K \left(\frac{G^o-F^o}{G-F}\right)^{K-1} (1 + \Delta_{JK} - \Delta_{JK}^o) . \quad (\text{VI.6})$$

Since we find  $r_{JK}$  is effectively constant for a given  $K$ , while the ratios  $r_K/r_{K-1}$ ,  $r_K/r_{K-2}$ , etc. are also fairly constant, it appears that  $\Delta_{JK} - \Delta_{JK}^o$  is small, and the major contribution to  $v_{JK}^o - v_{JK}$  comes from variations in  $\frac{a-c}{2}$  and  $\kappa$ . This is reasonable since the transition frequencies are most sensitive to small percentage variations in the effective moments, and these in turn are sensitive to the anharmonic potential constants (which are not known accurately).

The assumption  $\Delta_{JK} \approx \Delta_{JK}^o$  enables one to solve (6) for

new  $\frac{a-c}{2}$  and  $\kappa$  (giving a value of about  $-0.6842$  for the latter), but the accuracy is not very great; later we will use the same assumption, but a different method of obtaining new values of  $\frac{a-c}{2}$  and  $\kappa$ .

Thus we conclude tentatively that the theoretical distortion corrections,  $\Delta_{JK}$ , are good approximations to the true corrections.

The above calculations have neglected the effects of  $(K|K\pm 1)$  and  $(K|K\pm 3)$  matrix elements. We find the major contribution from these arises from the off-diagonal moment of inertia  $I_{zx}^0$ ; this term can be readily removed by the transformation to principal axes discussed in Section III.6, and leads to slightly modified theoretical parameters, as given in Table VI.5 (taken from Tables C.12 and C.13):

TABLE VI.5  
HDO - Theoretical Parameters (II)

---

$\frac{a-c}{2} = 2.53006536 \times 10^5 \text{ Mc/sec}$	
$\kappa = -0.68120013$	
$D_{JK} = 1.45503015 \times 10^{-4}$	$R_6 = -0.02261617 \times 10^{-4}$
$D_K = 11.34711157 \times 10^{-4}$	$R_7 = 0.12316025 \times 10^{-4}$
$\delta_J = 0.13174042 \times 10^{-4}$	$R_8 = -0.32408016 \times 10^{-4}$
$R_5 = -0.31134320 \times 10^{-4}$	$R_9 = 1.97296522 \times 10^{-4}$

Table VI.6 gives the reduced energies (characteristic values of the reduced energy matrix) for a number of levels, using the parameters of Table VI.5. In this Table, the rigid

TABLE VI.6  
HDO - Theoretical Reduced Energies

Level	Rigid $\lambda^R(\kappa)$	Incomplete $\lambda$	Complete $\lambda^t$
2 <sub>21</sub>	2.31879987	2.29720670	2.29721126
2 <sub>20</sub>	2.35998264	2.33819174	2.33819602
3 <sub>22</sub>	-2.72480052	-2.74966865	-2.74974580
3 <sub>21</sub>	-2.52325230	-2.54939602	-2.54947155
4 <sub>14</sub>	-16.66290883	-16.65986243	-16.65985287
4 <sub>22</sub>	-8.90426858	-8.93777649	-8.93788816
4 <sub>32</sub>	-0.14909248	-0.26777082	-0.26824000
4 <sub>31</sub>	-0.12580581	-0.24479903	-0.24526867
5 <sub>05</sub>	-26.46981554	-26.46029883	-26.46063663
5 <sub>33</sub>	-8.44529066	-8.57791858	-8.57887089
5 <sub>32</sub>	-8.35391733	-8.48808776	-8.48903331
6 <sub>24</sub>	-25.99223526	-26.05662523	-26.05665157
6 <sub>43</sub>	-5.59451168	-5.98611102	-5.98972977
6 <sub>42</sub>	-5.58447995	-5.97636244	-5.97998081
7 <sub>07</sub>	-50.70728491	-50.66135059	-50.66231671
7 <sub>17</sub>	-50.56026965	-50.51386309	-50.51384154
7 <sub>35</sub>	-29.98625576	-30.15563960	-30.15568508
7 <sub>44</sub>	-17.16764843	-17.59538810	-17.60094304
7 <sub>43</sub>	-17.13151619	-17.56048659	-17.56602192
8 <sub>45</sub>	-30.35534098	-30.82612414	-30.83180844
8 <sub>44</sub>	-30.24988415	-30.72494449	-30.73058122
9 <sub>55</sub>	-28.87747526	-29.93289508	-29.95229164
9 <sub>54</sub>	-28.86418874	-29.92038955	-29.93977352
10 <sub>56</sub>	-45.33982883	-46.48112729	-46.50207359
10 <sub>55</sub>	-45.30091534	-46.44488905	-46.46577812
11 <sub>57</sub>	-63.39290782	-64.63302820	-64.65048256
11 <sub>56</sub>	-63.29250614	-64.54056370	-64.55789050
12 <sub>67</sub>	-63.31450718	-65.66631341	-65.72748624
12 <sub>66</sub>	-63.30079843	-65.65406337	-65.71517686

value,  $\lambda^R(\kappa)$ , is the value in the rigid rotor limit, the "incomplete" value  $\lambda$  is that obtained by neglecting 1- and 3-off matrix elements, while  $\lambda^t$ , the "complete" value, takes all matrix elements into account.

It will be noticed that the correction  $\frac{a-c}{2}(\lambda^t - \lambda)$  to the energy levels, arising from the  $(K|K\pm 1)$  and  $(K|K\pm 3)$  elements, is largest for high K values; for the  $12_6$  levels it is equivalent to some -15,000 Mc/sec (i.e. about  $-0.5 \text{ cm}^{-1}$ !). The major contribution to this correction comes from the  $(K|K\pm 1)$  elements.

Some of the corresponding Q-branch transition frequencies,  $\nu_{JK}$  (incomplete), and  $\nu_{JK}^t$  (complete), are shown in Table VI.7, together with their differences, the correction frequencies  $\nu_{JK}^c = \nu_{JK}^t - \nu_{JK}$  contributed by the 1- and 3-off matrix elements. Relations similar to those of Table VI.4 no longer hold so nicely, either for  $\nu_{JK} / \nu_{JK}^o$  or  $\nu_{JK}^t / \nu_{JK}^o$ ; we believe this may be due to considerable error appearing in the 1- and 3-off matrix elements, particularly in the original off-diagonal moment  $I_{zx}^o$ , which is most sensitive to changes in the anharmonic potential constants.

The theoretical frequencies for the three P- and R-branch transitions of Table VI.1 are shown in Table VI.8; we cannot yet draw any conclusions of significance from the comparisons shown here!

TABLE VI.7  
HDO - Theoretical Q-Branch Frequencies (II)

$J_K$	Observed $\nu_{JK}^o$	Frequency (Mc/sec)		$\nu_{JK}^c$
		$\nu_{JK}$	Calculated $\nu_{JK}^t$	
$2_2$	10,278.99	10,369.484	10,369.413	-0.071
$3_2$	50,236.90	50,670.284	50,670.692	0.408
$4_3$	5,702.78	5,812.013	5,811.893	-0.116
$5_3$	22,307.67	22,727.785	22,729.495	1.710
$6_4$	2,394.6	2,466.454	2,466.551	0.097
$7_4$	8,577.7	8,830.310	8,835.272	4.962
$8_4$	24,884.77	25,599.113	25,611.148	12.035
$9_5$	3,044.7	3,163.981	3,167.166	3.185
$10_5$	8,836.95	9,168.512	9,182.991	14.479
$11_5$	22,581.1	23,394.123	23,426.396	32.273
$12_6$	2,961	3,099.340	3,114.354	15.014

TABLE VI.8  
HDO - P- and R-Branch Theoretical Frequencies

Transition	Frequency (Mc/sec)	
	Observed	Calculated
$4_{14} \rightarrow 3_{21}$	20,460.40	-13,397.134
$4_{22} \rightarrow 5_{05}$	2,888	10,761.553
$6_{24} \rightarrow 7_{17}$	26,880.38	27,811.867

### 3. Approximate Calculations

A much simpler method of calculating Q-branch transitions between K-doublet levels can be obtained by expanding the matrices to first order in the distortion parameters. The method was first described by Hillger and Strandberg<sup>10,11</sup>, who applied it to the analysis of the HDS spectrum. A more general derivation of the appropriate formulae, with some corrections, has been given by Kivelson and Wilson<sup>17</sup>. We refer to the method as the HSKW formula, for short.

We write the HSKW formula in the following manner: let

$$\begin{aligned} \Delta_{JK}^{(1)} = & 2KJ(J+1) \frac{\delta_J}{H} + (K-1)J(J+1) \frac{D_{JK}}{G-F} - \frac{4}{3} K(K^2+2) \frac{R_5}{H} \\ & + \frac{2}{3} K(K-1)(2K-1) \frac{D_K}{G-F} + \frac{8}{3} K(K^2-1) \frac{G-F}{H^2} R_6 . \end{aligned} \quad (\text{VI.7})$$

Then, to first order, the transition frequency is given by

$$v_{JK}^{(1)} = v_{JK}^R (1 + \Delta_{JK}^{(1)}) , \quad (\text{VI.8})$$

in a notation similar to equation (1). This is, in effect, the HSKW formula in terms of reduced distortion constants.

The HSKW formula is not claimed to be anything more than a first order approximation; we will show its limitations for the case of HDO, where the distortion effects are large, and where the approximation cannot be expected to agree perfectly with the exact calculation.

The HSKW formula neglects 1- and 3-off matrix elements, so it is fair to compare  $v_{JK}^{(1)}$ , as calculated by (7) and (8), with  $v_{JK}$  of Table VI.7, using the same parameters, of course. These quantities are shown in Table VI.9, together with the



"exact" calculated distortion correction to the frequency,

$v_{JK}^d = v_{JK} - v_{JK}^R$ , and the difference  $v_{JK} - v_{JK}^{(1)}$  with the

percentage difference  $p = \frac{v_{JK} - v_{JK}^{(1)}}{v_{JK}^d} \times 100$ :

TABLE VI.9

HDO - Theoretical Q-Branch Frequencies (III)

$J_K$	$v_{JK}$ (Mc/sec)	$v_{JK}^d$ (Mc/sec)	$v_{JK}^{(1)}$ (Mc/sec)	$v_{JK} - v_{JK}^{(1)}$ (Mc/sec)	p
2 <sub>2</sub>	10,369.484	-50.026	10,369.603	-0.119	0.24
3 <sub>2</sub>	50,670.284	-322.733	50,671.812	-1.529	0.47
4 <sub>3</sub>	5,812.013	-79.667	5,812.112	-0.099	0.12
5 <sub>3</sub>	22,727.785	-390.265	22,727.744	0.041	-0.011
6 <sub>4</sub>	2,466.454	-71.639	2,466.391	0.063	-0.088
7 <sub>4</sub>	8,830.310	-311.383	8,829.172	1.138	-0.37
8 <sub>4</sub>	25,599.113	-1,082.154	25,588.117	10.996	-1.02
9 <sub>5</sub>	3,163.981	-197.722	3,161.580	2.401	-1.21
10 <sub>5</sub>	9,168.512	-676.855	9,158.796	9.716	-1.44
11 <sub>5</sub>	23,394.123	-2,008.158	23,345.677	48.446	-2.41
12 <sub>6</sub>	3,099.340	-369.063	3,091.899	7.441	-2.02

We see that, for the theoretical parameters, at least, the agreement between the exact and HSKW methods is quite good for low J and K, but cannot be pushed too far.

#### 4. Methods of Analysis of the Spectrum

When attempting to determine the "true" molecular parameters by analysis of the spectrum, we must bear in mind that the distortion is large, and the complexity of the

theory together with the approximations introduced (for example, in Section III.3) makes it not unreasonable that some difficulty be experienced in obtaining agreement with observation, at least to experimental accuracy.

To show orders of magnitude, the energies of the  $11_5$  doublet levels are of the order of  $4 \times 10^7$  Mc/sec, while we measure their difference, of the order of  $2 \times 10^4$  Mc/sec, with an accuracy of better than 1 Mc/sec; the distortion correction here is about  $2 \times 10^3$  Mc/sec, or ten percent of the measured frequency; to account exactly for this "correction" involving differences to 8-figure accuracy is indeed some task when we have (at least) ten parameters involved.

It is apparent from Appendix D (see equations D.5, D.6) that we must first analyze the Q-branch spectrum; only two parameters,  $\frac{a+c}{2}$  and  $D_J$  are then needed to account for the remainder of the spectrum.

An attempt to do this was first made by Lewis<sup>21</sup>, using the HSKW formula and the methods of Hillger and Strandberg<sup>10,11</sup>, but no satisfactory solution was obtained due to the inadequacy of the data then available.

With more absorption lines known, we extended this work, and obtained a reasonable sort of fit, though one of the distortion parameters ( $R_G$ ) so obtained was of the wrong sign (as in the Hillger and Strandberg work). However, with a value of  $\kappa$  near -0.687 we predicted the  $8_4$  line within 10 Mc/sec of its subsequently observed frequency. At this stage, exact calculations were carried out to examine the validity

of the HSKW approximation, and serious differences were obtained, amounting to as much as 20 percent of the distortion correction. Attempts to correct for the differences between  $v_{JK}$  and  $v_{JK}^{(1)}$ , when the "observed" parameters were used, turned out to be quite unsuccessful.

A fresh start was made, recalculating first the theoretical parameters. It is apparent from these (see Table VI.9) that the HSKW formula should agree with exact calculations to a few percent, provided  $\Delta_{JK}$  does not change by much in magnitude. It is our experience that the theoretical distortion parameters cannot be varied by more than a few percent without giving rise to serious discrepancies between the HSKW approximation and exact calculations, even though  $\Delta_{JK}$  remain substantially constant.

We have tried several methods of obtaining a fit, always using the exact calculations to check our results. In these, we have assumed  $v_{JK}^c$ , as given in Table VI.7, to be constant, and made allowance for it, thus attempting to fit the seven parameters  $x_1 = \frac{a-c}{2}$ ,  $\kappa$ ,  $D_{JK}$ ,  $D_K$ ,  $\delta_J$ ,  $R_5$ ,  $R_6$ .

(a) Variation of all parameters:

Assuming a fit can be obtained by making only small changes in the parameters  $x_1$ , we can write, in the notation of Section 2,

$$v_{JK}^o - v_{JK}^c = v_{JK} + \Delta v_{JK} \quad , \quad (\text{VI.9})$$

and

$$\Delta v_{JK} = \sum_1 \frac{\partial v_{JK}}{\partial x_1} \Delta x_1 \quad . \quad (\text{VI.10})$$

Here

$$\frac{\partial v}{\partial \left(\frac{a-c}{2}\right)} = \Delta E(\kappa) \quad , \quad (\text{VI.11})$$

and

$$\frac{\partial v}{\partial \kappa} = \frac{a-c}{2} \left[ \frac{\partial \Delta E(\kappa)}{\partial \kappa} (1 + \Delta_{JK}) + \Delta E(\kappa) \frac{\partial \Delta_{JK}^{(1)}}{\partial \kappa} \right] \quad , \quad (\text{VI.12})$$

approximately, where  $v \equiv v_{JK}$ ,  $\Delta E(\kappa) \equiv \Delta E_{JK}(\kappa)$ , and  $\Delta_{JK}$  is the distortion correction obtained by exact calculation, i.e. from  $v_{JK}$ ,  $v_{JK}^R$ , and equation (1); it is considered that  $\partial \Delta_{JK}^{(1)} / \partial \kappa$  is a good approximation to  $\partial \Delta_{JK} / \partial \kappa$ . We used the HSKW formula to calculate the variations with respect to the distortion parameters.

The resulting set of simultaneous equations may be solved by standard methods\* A preliminary least squares reduction leads to some striving for significant figures, apparently because of close correlation between lines of the same K-family, but a solution can be obtained; it would be preferable to first average members of the same K-dependence, but as yet there are not sufficient K-families known.

Starting from the numbers of Table VI.7, we get a solution which changes the sign of  $R_5$ , resulting in a positive distortion correction  $\Delta_{JK}^{(1)}$ , showing the solution to be inadmissible.

This method was originally applied to the results of

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\* We find it very convenient to use the Crout method; see, for example, the Appendix to reference 9.

Table VI.3, when all 1- and 3-off matrix elements were neglected. Reasonably small changes in the parameters were obtained, but it led to large changes in the values of  $\Delta_{JK}$  (contrary to the expectations of Section 2); the new differences  $v_{JK}^0 - v_{JK}$  were larger than expected, of the order of the later determined  $v_{JK}^c$  (Table VI.7). Repetition of the process led to greater discrepancies, and it became apparent that close agreement could not be obtained with seven parameters.

(b) Variation of  $\frac{a-c}{2}$ ,  $\kappa$ , only:

Keeping the theoretical distortion parameters constant (though modifying the reduced parameters with change of  $\frac{a-c}{2}$ ) we can simplify the method (a) by varying only  $\frac{a-c}{2}$  and  $\kappa$ , using a least squares reduction of the equations. This gives frequency differences of the order of one percent of the distortion corrections, and is the method finally used.

If we were to follow the Hillger and Strandberg method, we would now use the HSKW formula to vary the distortion parameters so as to improve the fit. As in method (a), however, we find that any such attempts -- when checked by exact calculations -- are doomed to failure.

The same difficulties were experienced when 1- and 3-off matrix elements were completely neglected.

(c) Variation of  $\frac{a-c}{2}$ ,  $\kappa$ , keeping  $\Delta_{JK}^{(1)}$  constant:

This method involves small changes in the "fundamental" distortion parameters, since  $\Delta_{JK}^{(1)}$  is a function of  $\frac{a-c}{2}$  and  $\kappa$ .

It does not seem to be much more satisfactory than (b), though it does give somewhat better agreement between  $\nu_{JK}$  and  $\nu_{JK}^{(1)}$ . However, although the theoretical percentage differences  $p$  of Table VI.9 are small, there does not appear to be any reason why the true ones should be exactly the same magnitude, though it would be nice if they were.

As a result of these investigations we conclude that it is not possible to get a "perfect" fit with seven parameters. The next approximation, inclusion of  $(K|K\pm 1)$  and  $(K|K\pm 3)$  matrix elements, gives little better results; we believe this is due to considerable error in the  $\nu_{JK}^c$  and/or the neglect of other approximations, e.g. in the vibrational diagonalization of Section III.3. Unfortunately, there seems to be no convenient way of varying the  $\nu_{JK}^c$  so as to be able to consider them adjustable in the fitting process; in principal, this can be done by making small changes in the three additional parameters  $R_7$ ,  $R_8$  and  $R_9$ , and calculating the effect on the  $\nu$ 's; since we have been unable to find a simple way of doing this, it is apparent that a considerable amount of labor would be involved.

At this stage, then, we have to be satisfied with agreement to a few percent of the distortion corrections. Method (a) does not give this since the changes in the magnitude of the parameters which are required to force a fit become too large for the method to be valid. Methods (b) and (c) do give reasonable agreement, though there is little to

decide between the two. We arbitrarily choose method (b), because it involves variation only of the effective moments, whose theoretical accuracy is more liable to suspicion because of their dependence on the anharmonic potential constants.

### 5. Results of Analysis of the Spectrum

Starting from Table VI.7, but omitting the data on the  $10_5$  and  $11_5$  lines (which were not then known), a least squares solution

$$\Delta\left(\frac{a-c}{2}\right) = 2,538.219 \text{ Mc/sec} ,$$

$$\Delta\kappa = -0.00290891 ,$$

was obtained from the nine equations of the form

$$\Delta v_{JK} = \frac{\partial v_{JK}}{\partial \left(\frac{a-c}{2}\right)} \Delta\left(\frac{a-c}{2}\right) + \frac{\partial v_{JK}}{\partial \kappa} \Delta\kappa . \quad (\text{VI.13})$$

To check the fit, substitution of these values of  $\Delta\left(\frac{a-c}{2}\right)$  and  $\Delta\kappa$  back into (13), giving  $\Delta v_{JK}^!$ , led to the results shown in Table VI.10:

TABLE VI.10  
HDO - Least Squares Fit

$J_K$	$\Delta v_{JK}$ (Mc/sec)	$\Delta v_{JK} - \Delta v_{JK}^!$ (Mc/sec)
$2_2$	-92.855	2.432
$3_2$	-433.373	-0.419
$4_3$	-110.273	1.159
$5_3$	-422.401	0.576
$6_4$	-72.098	0.147
$7_4$	-255.188	-2.384
$8_4$	-725.591	-0.787
$9_5$	-125.155	2.689
$12_6$	-156.029	2.675

It is seen that the differences are only an order of magnitude or so larger than the experimental inaccuracy; however, this good agreement does not carry through when a detailed check is made.

After adjusting the reduced distortion constants for the new  $\frac{a-c}{2}$ , our "observed" parameters become as shown in Table VI.11:

TABLE VI.11  
HDO - "Observed" Parameters

$$\frac{a-c}{2} = 2.55544755 \times 10^5 \text{ Mc/sec}$$

$$\kappa = -0.68410904$$

$$D_{JK} = 1.44057795 \times 10^{-4}$$

$$D_K = 11.23440546 \times 10^{-4}$$

$$\delta_J = 0.13043190 \times 10^{-4}$$

$$R_5 = -0.30825076 \times 10^{-4}$$

$$R_6 = -0.02239153 \times 10^{-4}$$

The results of calculating Q-branch frequencies with these constants together with the  $\nu_{JK}^c$  of Table VI.7, are shown in Table VI.12; here  $p$  and  $\nu_{JK}^d$  have the same meaning as in Table VI.9, while  $\nu_{JK}^D = \nu_{JK}^t - \nu_{JK}^R$  is the total distortion correction, and  $P = \frac{\nu_{JK}^o - \nu_{JK}^t}{\nu_{JK}^D} \times 100$  is the percentage discrepancy, referred to the total distortion, between observed and calculated frequencies:



TABLE VI.12

HDO - Comparison of Calculated and Observed Q-Branch Frequencies

$J_K$	$v_{JK}^t = v_{JK}^c + v_{JK}^c$ (Mc/sec)	$v_{JK}^o - v_{JK}^t$ (Mc/sec)	$v_{JK}^d$ (Mc/sec)	P	$v_{JK}^D$ (Mc/sec)	P
2 <sub>2</sub>	10,275.660	3.330	-50.099	-2.2	-50.170	-6.6
3 <sub>2</sub>	50,232.692	4.208	-322.636	-1.4	-322.228	-1.3
4 <sub>3</sub>	5,701.757	1.023	-79.600	-3.3	-79.716	-1.3
5 <sub>3</sub>	22,307.350	0.320	-388.924	-2.8	-387.214	-0.083
6 <sub>4</sub>	2,395.019	-0.419	-71.277	-4.2	-71.180	0.59
7 <sub>4</sub>	8,582.081	-4.381	-308.872	-3.8	-303.910	1.4
8 <sub>4</sub>	24,865.250	19.520	-1,096.841	-1.5	-1,084.806	-1.8
9 <sub>5</sub>	3,041.952	2.748	-196.823	-4.2	-193.638	-1.4
10 <sub>5</sub>	8,829.125	7.825	-666.128	-4.8	-651.649	-1.2
11 <sub>5</sub>	22,538.263	42.837	-1,972.977	-5.4	-1,940.704	-2.2
12 <sub>6</sub>	2,961.394	-0.394	-360.668	-5.9	-345.654	0.11

The worst (percentage) discrepancy occurs for the 2<sub>2</sub> line, which also has the least distortion. We believe this is a result of the least squares analysis, which weights this line the least.

Although P for the 11<sub>5</sub> line (which was not included in the analysis) is of the same order of magnitude as for the other lines, the actual frequency difference, 42 Mc/sec, between calculated and observed frequencies is much larger than we would expect from consideration of the extrapolation method of Section 2; by keeping  $\Delta_{JK}^{(1)}$  constant -- method (b) of the preceding Section -- the difference is reduced to only about 3 Mc/sec, but the fit on the 8<sub>4</sub> line becomes worse (about 25 Mc/sec), and the overall picture is about the same.

It is interesting to refer to Table VI.9 and note how small changes in  $\Delta_{JK}^{(1)}$ , due to the variation of  $\frac{a-c}{2}$  and  $\kappa$ , markedly affect  $p$ , even though  $v_{JK}^d$  is almost the same in the two cases.

We believe the general agreement shown in Table VI.12 is as good as one can get using the present methods. Slight improvement might be obtained by now feeding in the  $10_5$  and  $11_5$  data, but this will not lead to any significant change in our final results.

With the Q-branch spectrum "solved", it is a simple matter to analyze the P- and R-branch lines. Since we have concluded the theoretical distortion constants are good approximations to the true ones, we ought to get fairly consistent values of  $\frac{a+c}{2}$  from the  $|\Delta J| = 1$  transitions on the assumption that  $D_J$  is also good. Using the value (from Table C.12)  $D_J = 9.14172899$  Mc/sec ( $D_J$  is not a "reduced" parameter -- see equation D.5), we obtain from the three lines of Table VI.8 (after making allowances for 1- and 3-off matrix elements by taking the frequency correction, obtained from Table VI.6, as constant):

$$\frac{a+c}{2} = \begin{cases} 4.48345524 \times 10^5 \text{ Mc/sec} & (4_{14} \rightarrow 3_{21}) \\ 4.48285425 \times 10^5 \text{ Mc/sec} & (4_{22} \rightarrow 5_{05}) \\ 4.48181198 \times 10^5 \text{ Mc/sec} & (6_{24} \rightarrow 7_{17}) \end{cases}$$

with an average value of  $4.48270716 \times 10^5$  Mc/sec which is apparently good to about 4 significant figures (we take this

to be a measure of just how reliable our major parameters are).  
With this average value, the calculated frequencies become:

Transition	Frequency (Mc/sec)		$\nu^0 - \nu$
	Observed $\nu^0$	Calculated $\nu$	
$4_{14} \rightarrow 3_{21}$	20,460.40	21,058.871	598.471
$4_{22} \rightarrow 5_{05}$	2,888	2,740.896	147.104
$6_{24} \rightarrow 7_{17}$	26,880.38	28,133.594	1,253.214

Although the agreement cannot be described as excellent, it is a great improvement on Table VI.8, and argues for some consistency in our work, as well as providing support for the identification of the 26,880 Mc/sec line (see Appendix E). It shows again that the distortion constants are fairly good, and that reasonable correlation with experiment can be obtained by changes in the effective moments alone.

The P- and R-branch lines can be brought into closer agreement if we allow  $D_J$  to vary. First we solve for  $\frac{a+c}{2}$  and  $D_J$  from the  $4 \rightarrow 3$  and  $4 \rightarrow 5$  lines; using these values to calculate the  $7 \rightarrow 6$  line gives 26,095.865 Mc/sec, again supporting its identification. A least squares solution on the three lines  $4 \rightarrow 3$ ,  $4 \rightarrow 5$  and  $6 \rightarrow 7$  now gives:

$$\frac{a+c}{2} = 4.48416164 \times 10^5 \text{ Mc/sec}$$

$$D_J = 11.56583333 \text{ Mc/sec ,}$$

leading to the  $|\Delta J| = 1$  frequencies of Table VI.13:

TABLE VI.13  
HDO - Comparison of Observed and  
Calculated P- and R-Branch Frequencies

Transition	Frequency (Mc/sec)		
	Observed 0 $\nu^0$	Calculated $\nu$	$\nu^0 - \nu$
$4_{14} \rightarrow 3_{21}$	20,460.40	20,515.856	-55.456
$4_{22} \rightarrow 5_{05}$	2,888	2,983.326	-95.326
$6_{24} \rightarrow 7_{17}$	26,880.38	26,843.995	36.385

Since these results are obtained in a very straightforward manner, the agreement must be regarded as quite good, even though we have had to change  $D_J$  by some 25 percent.

Table VI.14 summarizes the results of the foregoing analysis of the HDO microwave spectrum, the distortion constants quoted being the "fundamental" values:

TABLE VI.14  
HDO - "Observed" Rotation-Distortion Constants

$\frac{a+c}{2} = 4.48416164 \times 10^5$ Mc/sec	$\delta_J = 3.33311881$ Mc/sec
$\frac{a-c}{2} = 2.55544755 \times 10^5$ Mc/sec	$R_5 = -7.87718656$ Mc/sec
$\kappa = -0.68410904$	$R_6 = -0.57220390$ Mc/sec
$D_J = 11.56583333$ Mc/sec	$R_7^{(x)} = 3.11603472$ Mc/sec
$D_{JK} = 36.81321390$ Mc/sec	$R_8^{(y)} = -8.19943988$ Mc/sec
$D_K = 287.08933921$ Mc/sec	$R_9^{(y)} = 49.91730954$ Mc/sec

From  $\frac{a+c}{2}$ ,  $\frac{a-c}{2}$  and  $\kappa$ , the effective moments and reciprocal moments of inertia are easily obtained, and are shown in Table VI.15:

TABLE VI.15  
HDO - Effective Moments and  
Reciprocal Moments of Inertia

	Theoretical	Observed
a	$6.97876766 \times 10^5$ Mc/sec	$7.03960919 \times 10^5$ Mc/sec
b	$2.72522145 \times 10^5$ Mc/sec	$2.73595687 \times 10^5$ Mc/sec
c	$1.91863695 \times 10^5$ Mc/sec	$1.91863695 \times 10^5$ Mc/sec
$I_a$	$1.20206397 \times 10^{-40}$ g cm <sup>2</sup>	$1.19167485 \times 10^{-40}$ g cm <sup>2</sup>
$I_b$	$3.07825449 \times 10^{-40}$ g cm <sup>2</sup>	$3.06617597 \times 10^{-40}$ g cm <sup>2</sup>
$I_c$	$4.37233588 \times 10^{-40}$ g cm <sup>2</sup>	$4.34949132 \times 10^{-40}$ g cm <sup>2</sup>
$\Delta$	$0.09201742 \times 10^{-40}$ g cm <sup>2</sup>	$0.09164050 \times 10^{-40}$ g cm <sup>2</sup>

There is less than one percent difference between theoretical and observed values, and this change in three parameters, together with a comparatively large variation in  $D_J$ , has been all we have introduced to get a reasonably good fit to the spectrum.

Some rotational energy levels, calculated from the constants of Table VI.14, are shown in Table VI.16. As indicated, the effects of  $(K|K\pm 1)$  and  $(K|K\pm 3)$  matrix elements have not been taken into account exactly here, though in some cases the corresponding energy corrections, taken from Table VI.6, have been included.

TABLE VI.16  
HDO - Rotational Energies

Level	Energy (Mc/sec x 10 <sup>6</sup> )		
	Rigid W <sup>R</sup>	Non-Rigid W <sup>N</sup>	Distortion W <sup>N</sup> - W <sup>R</sup>
2 <sub>21</sub>	3.282311	3.276432*	-0.005879
2 <sub>20</sub>	3.292637	3.286708*	-0.005929
3 <sub>22</sub>	4.681712	4.673735*	-0.007977
3 <sub>21</sub>	4.732267	4.723968*	-0.008299
4 <sub>14</sub>	4.707305	4.703452*	-0.003853
4 <sub>22</sub>	6.684485	6.671355*	-0.013130
4 <sub>32</sub>	8.925689	8.890918*	-0.034771
4 <sub>31</sub>	8.931471	8.896619*	-0.034852
5 <sub>05</sub>	6.682430	6.674338*	-0.008092
5 <sub>24</sub>	8.848938	8.834291	-0.014648
5 <sub>23</sub>	9.163016	9.141062	-0.021954
5 <sub>33</sub>	11.285626	11.241421*	-0.044205
5 <sub>32</sub>	11.308320	11.263728*	-0.044592
6 <sub>06</sub>	9.225386	9.210664	-0.014722
6 <sub>24</sub>	12.169757	12.133066*	-0.036691
6 <sub>33</sub>	14.186789	14.127912	-0.058877
6 <sub>43</sub>	17.392922	17.272528*	-0.120394
6 <sub>42</sub>	17.395389	17.274923*	-0.120466
7 <sub>07</sub>	12.145962	12.120853*	-0.025109
7 <sub>17</sub>	12.184437	12.159910*	-0.024527
7 <sub>16</sub>	14.288870	14.245622	-0.043248
7 <sub>35</sub>	17.429084	17.349701*	-0.079383
7 <sub>44</sub>	20.707197	20.561306*	-0.145891
7 <sub>43</sub>	20.716083	20.569888*	-0.146195

TABLE VI.16  
(Continued)

Level	$W^R$	$W^N$	$W^N - W^R$
$8_{45}$	24.504725	24.324235*	-0.180490
$8_{44}$	24.530675	24.349100*	-0.181575
$8_{53}$	28.685244	28.376901	-0.308343
$9_{46}$	28.786442	28.560607	-0.225835
$9_{55}$	32.950146	32.584549*	-0.365597
$9_{54}$	32.953382	32.587591*	-0.365791
$10_{56}$	37.702535	37.268638*	-0.433897
$10_{55}$	37.712015	37.277468*	-0.434547
$11_{57}$	42.944157	42.424541*	-0.519616
$11_{56}$	42.968636	42.447079*	-0.521557
$12_{67}$	53.721091	52.829222*	-0.891869
$12_{66}$	53.724398	52.832183*	-0.892215

\* Indicates that correction  $\lambda^t - \lambda$  from Table VI.6 has been taken into account.

Using Table VI.16, some of the  $|\Delta J| = 1$  transitions expected from KHC II have been calculated, and are shown in Table VI.17:

TABLE VI.17  
HDO - Predicted P- and R-Branch Frequencies

Transition	Frequency (Mc/sec)
$7_{07} \rightarrow 6_{24}$	12,198
$5_{24} \rightarrow 4_{31}$	62,447
$5_{23} \rightarrow 6_{06}$	69,602
$6_{42} \rightarrow 7_{35}$	74,778
$6_{33} \rightarrow 7_{16}$	117,710
$8_{53} \rightarrow 9_{46}$	183,710

For some of these lines the effects of  $(K|K\pm 1)$  and  $(K|K\pm 3)$  matrix elements have been neglected. From Table VI.6, we see that these effects will be comparatively small for the levels of low K appearing here.

Only the  $7_{07} \rightarrow 6_{24}$  line lies in a readily available region; unfortunately, it is quite weak, the absorption coefficient being about  $3 \times 10^{-8} \text{ cm}^{-1}$ , and we have not succeeded in finding it. If our identification of the 26,880 Mc/sec line is correct, thus fixing the relative positions of the  $6_{24}$  and  $7_{17}$  levels, with the  $7_{07}$  below these, this prediction should be reliable to a few hundred Mc/sec (which is the order of the inaccuracy of  $v^c$ ).

## 6. Discussion of Results

Although the agreement in Table VI.13 is considered good, the large change we had to make in  $D_J$  is inconsistent with our assumption that the theoretical distortion constants are very close to the true ones. But it is apparent that the



parameters entering into the Q-branch frequencies must be known more accurately before we can draw precise conclusions about  $\frac{a+c}{2}$  and  $D_J$ .

We would like to have Q-branch parameters that are good enough to exactly calculate frequencies to agree with observation within something like 1 Mc/sec, if not better. Any such agreement obtained by the use of approximation methods (specifically, the HSKW method) must be checked by exact calculations, otherwise the constants obtained cannot be considered the true molecular parameters, but are merely constants in a semi-empirical formula. The writer believes that the results obtained by Weisbaum<sup>35</sup> should be described in this manner.

The present work has shown that such desirable Q-branch parameters are impossible to attain if only the seven quantities  $\frac{a-c}{2}$ ,  $\kappa$ ,  $D_{JK}$ ,  $D_K$ ,  $\delta_J$ ,  $R_5$ ,  $R_6$  are considered. Remaining discrepancies turn out to be of the order of magnitude of the corrections introduced by taking  $R_7$ ,  $R_8$  and  $R_9$  into account, but inclusion of these corrections still leaves much to be desired. The ever-present assumption of the essential correctness of the theoretical distortion parameters leads one to expect that only small changes in  $R_7$ ,  $R_8$ ,  $R_9$  should be tolerated, and it is unlikely that such small changes would lead to significant differences in the corrections  $v_{JK}^c$ . Thus it is probable that either our theories and/or calculations involving  $R_7$ ,  $R_8$ ,  $R_9$  are incorrect, or that we must look elsewhere to improve our results. The

latter means examination of higher terms in the vibration-rotation theory, e.g. terms in the Hamiltonian of the order of  $\mathbf{P}^6$ , where  $\mathbf{P}$  is an angular momentum operator. Rough calculations, based on orders of magnitude, indicate that such terms probably will be negligible for the present work, but one cannot be conclusive about this without going into considerable detail.

It is the writer's opinion that any improvement in the present results will have to be obtained with the aid of a high-speed digital computer to set up exactly and solve equations of the type of (10). Notwithstanding the conclusions of the previous paragraph, it may still be possible to get a satisfactory solution by including variations of  $R_7$ ,  $R_8$  and  $R_9$ , the corresponding  $\partial v/\partial x_i$  being obtained by computer diagonalization of the complete matrices; this possibility ought to be considered early in any extension of this work, since even small changes in the  $v_{JK}^C$  could conceivably bring about a neat fit -- the transition frequencies are much more sensitive to changes in certain parameters (e.g.  $\kappa$ ) than in others. Also, the discrepancies we have now result from a least squares solution, which does not necessarily lead to the most significant parameters though it seems to be all we can do with the present methods.

The good agreement we get in Table VI.13 for  $|\Delta J| = 1$  transitions gives some confidence in our final results. However, it must be pointed out that the consistency vanishes if the 26,880 Mc/sec line is not the  $6_{24} \rightarrow 7_{17}$  transition, or

if the 2,888 Mc/sec line is actually the  $5_{05} \rightarrow 4_{22}$  transition. Our information<sup>35</sup> is that the latter is the  $4_{22} \rightarrow 5_{05}$  line, though we do not know whether or not there is any evidence (e.g. Stark data) to show the relative positions of the levels.

To conclude this Chapter, we give in Tables VI.18 and VI.19 what we consider to be reasonable HDO parameters; these are obtained by rounding off the constants of Tables VI.14 and VI.15; the accuracies indicated have been estimated by the writer on the basis of his experience with the problem, and are rather difficult to justify in detail.

TABLE VI.18  
HDO - Rotation-Distortion Constants

$\frac{a+c}{2}$	=	4.484	±0.002	$\times 10^5$	Mc/sec
$\frac{a-c}{2}$	=	2.555	±0.005	$\times 10^5$	Mc/sec
$\kappa$	=	-0.6841	±0.0002		
$D_J$	=	9.1	±1.5		Mc/sec
$D_{JK}$	=	36.8	±0.5		Mc/sec
$D_K$	=	287	±5		Mc/sec
$\delta_J$	=	3.333	±0.005		Mc/sec
$R_5$	=	-7.877	±0.010		Mc/sec
$R_6$	=	-0.572	±0.005		Mc/sec
$R_7^{(x)}$	=	3.12	±0.05		Mc/sec
$R_8^{(y)}$	=	-8.20	±0.05		Mc/sec
$R_9^{(y)}$	=	50.0	±0.5		Mc/sec

TABLE VI.19  
HDO - Effective Moments and  
Reciprocal Moments of Inertia

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$$\begin{aligned} a &= 7.0396 \pm 0.0005 \times 10^5 \text{ Mc/sec} \\ b &= 2.7360 \pm 0.0005 \times 10^5 \text{ Mc/sec} \\ c &= 1.9186 \pm 0.0005 \times 10^5 \text{ Mc/sec} \end{aligned}$$

$$\begin{aligned} I_a &= 1.1917 \pm 0.0005 \times 10^{-40} \text{ g cm}^2 \\ I_b &= 3.0662 \pm 0.0005 \times 10^{-40} \text{ g cm}^2 \\ I_c &= 4.3495 \pm 0.0005 \times 10^{-40} \text{ g cm}^2 \end{aligned}$$

## VII

CONCLUSION

By analysis of the microwave rotational spectrum of HDO we have obtained approximate values of the molecular parameters which are in fairly good agreement with the theoretically calculated constants. The theoretical values, derived from infrared data on H<sub>2</sub>O and D<sub>2</sub>O, enabled us to calculate HDO Q-branch frequencies with rather unexpected accuracy; it must be considered very gratifying that we can do this in view of the rather tortuous calculations that have had to be carried out in going from one isotopic molecule to another.

Distortion effects in this type of molecule have been found to be large, so large that to get detailed agreement between theory and observation (in the microwave region) one must go to higher approximations in the theory than had previously been considered necessary. Our results are by no means final, and possible methods of improving them have been indicated.

It is also desirable to increase our experimental knowledge of the water spectrum; quite a number of lines are still available and waiting to be found, but most lie in the high-frequency region of the microwave spectrum, and the experimental work will be fairly difficult because of the general inaccuracy of the predictions.

Jen et al.<sup>12</sup> have reported two unidentified lines at

30,182.57 and 30,778.62 Mc/sec, we do not believe our HDO parameters are far enough out for these to be any of the lines listed in Table VI.17, and it seems probable that the two lines are due to the only other likely alternative,  $D_2O$ ; if further work (e.g. Zeeman investigations) shows that this is the case, it may be possible to improve the  $D_2O$  parameters by simple adjustment of the effective moments, using the assumption that the theoretical distortion corrections are satisfactory, as appears to be the case for HDO.

It will be interesting to examine the spectra of other isotopic modifications of water, e.g.  $H_2O^{18}$  (which may be no more useful than  $H_2O^{16}$  itself) and HTO. The latter should give plenty of information from its Q-branch spectrum, which should be predictable fairly accurately by the methods we have used here to handle HDO.

When a more accurate solution of the HDO problem is obtained, it will be necessary to analyze the parameters thus determined, and work back to improve the  $H_2O$  and  $D_2O$  constants. In this connection, the work of Kivelson and Wilson<sup>18</sup> on relating distortion constants to force constants etc. will be of considerable assistance.

As a final project, calculation of the equilibrium structures and force constants of the molecules should be carried out. In principal, the data on HDO is already sufficient to enable this to be done, but the results obtained here are not sufficiently accurate to warrant the very complex calculations which would be involved.

## APPENDIX A

SOME MATRIX ELEMENTS OF ANGULAR MOMENTUM OPERATORS

We are interested in the matrix elements of certain sums of angular momentum operators which are multiplied by coefficients that are unchanged by permuting some of the indices. Consequently, the results are conveniently expressed in terms of the matrix elements of symmetrized operator products.

Let us define

$$\begin{aligned} g(J, K \pm 1) &= J(J+1) - K(K \pm 1) , \\ F(J, K) &= g(J, K+1)g(J, K-1) . \end{aligned}$$

As our basic matrix elements, we follow the phase choice of KHC I and take the following non-vanishing matrix elements of  $P_g$ :

$$\begin{aligned} (K | P_x | K \pm 1) &= \pm \frac{1}{2} i \hbar [g(J, K \pm 1)]^{\frac{1}{2}} , \\ (K | P_y | K \pm 1) &= \frac{1}{2} \hbar [g(J, K \pm 1)]^{\frac{1}{2}} , \\ (K | P_z | K) &= \hbar K . \end{aligned}$$

For the non-vanishing matrix elements of  $P_g P_{g'}$ , we have:

$$\begin{aligned} (K | P_x^2 | K \pm 2) &= - (K | P_y^2 | K \pm 2) = - \frac{1}{4} \hbar^2 [F(J, K \pm 1)]^{\frac{1}{2}} \\ (K | P_x^2 | K) &= (K | P_y^2 | K) = \frac{1}{2} \hbar^2 [J(J+1) - K^2] \\ (K | P_z^2 | K) &= \hbar^2 K^2 \\ (K | P_x P_y + P_y P_x | K \pm 2) &= \pm \frac{1}{2} i \hbar^2 [F(J, K \pm 1)]^{\frac{1}{2}} \\ (K | P_y P_z + P_z P_y | K \pm 1) &= \mp i (K | P_z P_x + P_x P_z | K \pm 1) = \frac{1}{2} \hbar^2 [g(J, K \pm 1)]^{\frac{1}{2}} (2K \pm 1) . \end{aligned}$$

The non-vanishing matrix elements of  $P_g P_g P_g P_g$  are:

$$(K|P_x^4|K\pm 4) = (K|P_y^4|K\pm 4) = \frac{1}{16}\hbar^4 [F(J, K\pm 1)F(J, K\pm 3)]^{\frac{1}{2}}$$

$$\begin{aligned} (K|P_x^4|K\pm 2) &= - (K|P_y^4|K\pm 2) \\ &= -\frac{1}{8}\hbar^4 [F(J, K\pm 1)]^{\frac{1}{2}} [2J(J+1) - K^2 - (K\pm 2)^2] \end{aligned}$$

$$(K|P_x^4|K) = (K|P_y^4|K) = \frac{1}{8}\hbar^4 [3J^2(J+1)^2 - 2(3K^2+1)J(J+1) + K^2(3K^2+5)]$$

$$(K|P_z^4|K) = \hbar^4 K^4$$

$$(K|P_x^2 P_y^2 + P_y^2 P_x^2 |K\pm 4) = -\frac{1}{8}\hbar^4 [F(J, K\pm 1)F(J, K\pm 3)]^{\frac{1}{2}}$$

$$(K|P_x^2 P_y^2 + P_y^2 P_x^2 |K) = \frac{1}{4}\hbar^4 [J^2(J+1)^2 - 2(K^2-1)J(J+1) + K^2(K^2-5)]$$

$$\begin{aligned} (K|P_y^2 P_z^2 + P_z^2 P_y^2 |K\pm 2) &= - (K|P_z^2 P_x^2 + P_x^2 P_z^2 |K\pm 2) \\ &= \frac{1}{4}\hbar^4 [F(J, K\pm 1)]^{\frac{1}{2}} [K^2 + (K\pm 2)^2] \end{aligned}$$

$$(K|P_y^2 P_z^2 + P_z^2 P_y^2 |K) = (K|P_z^2 P_x^2 + P_x^2 P_z^2 |K) = \hbar^4 [J(J+1) - K^2] K^2$$

$$(K|(P_x P_y + P_y P_x)^2 |K\pm 4) = -\frac{1}{4}\hbar^4 [F(J, K\pm 1)F(J, K\pm 3)]^{\frac{1}{2}}$$

$$(K|(P_x P_y + P_y P_x)^2 |K) = \frac{1}{2}\hbar^4 [J^2(J+1)^2 - 2(K^2+1)J(J+1) + K^2(K^2+5)]$$

$$\begin{aligned} (K|(P_y P_z + P_z P_y)^2 |K\pm 2) &= - (K|(P_z P_x + P_x P_z)^2 |K\pm 2) \\ &= \frac{1}{4}\hbar^4 [F(J, K\pm 1)]^{\frac{1}{2}} (2K\pm 1)(2K\pm 3) \end{aligned}$$

$$\begin{aligned} (K|(P_y P_z + P_z P_y)^2 |K) &= (K|(P_z P_x + P_x P_z)^2 |K) \\ &= \frac{1}{2}\hbar^4 [4K^2 J(J+1) + J(J+1) - 4K^4 - 5K^2] \end{aligned}$$

$$\begin{aligned} (K|P_x^2 (P_x P_y + P_y P_x) + (P_x P_y + P_y P_x) P_x^2 |K\pm 4) \\ &= \mp (K|P_y^2 (P_x P_y + P_y P_x) + (P_x P_y + P_y P_x) P_y^2 |K\pm 4) \\ &= \mp \frac{1}{4}\hbar^4 [F(J, K\pm 1)F(J, K\pm 3)]^{\frac{1}{2}} \end{aligned}$$



$$\begin{aligned}
& (K|P_x^2(P_x P_y + P_y P_x) + (P_x P_y + P_y P_x)P_x^2|K\pm 2) \\
&= (K|P_y^2(P_x P_y + P_y P_x) + (P_x P_y + P_y P_x)P_y^2|K\pm 2) \\
&= \frac{1}{4} \hbar^4 [F(J, K\pm 1)]^{\frac{1}{2}} [(2J(J+1) - K^2 - (K\pm 2)^2)]
\end{aligned}$$

$$\begin{aligned}
& (K|P_z^2(P_x P_y + P_y P_x) + (P_x P_y + P_y P_x)P_z^2|K\pm 2) \\
&= \pm \frac{1}{2} \hbar^4 [F(J, K\pm 1)]^{\frac{1}{2}} [K^2 + (K\pm 2)^2]
\end{aligned}$$

$$\begin{aligned}
& (K|P_x^2(P_y P_z + P_z P_y) + (P_y P_z + P_z P_y)P_x^2|K\pm 3) \\
&= \pm 1 (K|P_y^2(P_z P_x + P_x P_z) + (P_z P_x + P_x P_z)P_y^2|K\pm 3) \\
&= -\frac{1}{4} \hbar^4 [g(J, K\pm 1)F(J, K\pm 2)]^{\frac{1}{2}} (2K\pm 3)
\end{aligned}$$

$$\begin{aligned}
& (K|P_x^2(P_y P_z + P_z P_y) + (P_y P_z + P_z P_y)P_x^2|K\pm 1) \\
&= \mp 1 (K|P_y^2(P_z P_x + P_x P_z) + (P_z P_x + P_x P_z)P_y^2|K\pm 1) \\
&= \frac{1}{4} \hbar^4 [g(J, K\pm 1)]^{\frac{1}{2}} [2KJ(J+1) \pm J(J+1) - 2K^3 \mp 3K^2 + 3K\pm 2]
\end{aligned}$$

$$\begin{aligned}
& (K|P_y^2(P_y P_z + P_z P_y) + (P_y P_z + P_z P_y)P_y^2|K\pm 3) \\
&= \pm 1 (K|P_x^2(P_z P_x + P_x P_z) + (P_z P_x + P_x P_z)P_x^2|K\pm 3) \\
&= \frac{1}{4} \hbar^4 [g(J, K\pm 1)F(J, K\pm 2)]^{\frac{1}{2}} (2K\pm 3)
\end{aligned}$$

$$\begin{aligned}
& (K|P_y^2(P_y P_z + P_z P_y) + (P_y P_z + P_z P_y)P_y^2|K\pm 1) \\
&= \mp 1 (K|P_x^2(P_z P_x + P_x P_z) + (P_z P_x + P_x P_z)P_x^2|K\pm 1) \\
&= \frac{1}{4} \hbar^4 [g(J, K\pm 1)]^{\frac{1}{2}} [6KJ(J+1) \pm 3J(J+1) - 6K^3 \mp 9K^2 - 11K\mp 4]
\end{aligned}$$

$$\begin{aligned}
& (K|P_z^2(P_y P_z + P_z P_y) + (P_y P_z + P_z P_y)P_z^2|K\pm 1) \\
&= \mp 1 (K|P_z^2(P_z P_x + P_x P_z) + (P_z P_x + P_x P_z)P_z^2|K\pm 1) \\
&= \frac{1}{2} \hbar^4 [g(J, K\pm 1)]^{\frac{1}{2}} (2K\pm 1) [K^2 + (K\pm 1)^2]
\end{aligned}$$

$$\begin{aligned}
& (K | (P_x P_y + P_y P_x) (P_y P_z + P_z P_y) + (P_y P_z + P_z P_y) (P_x P_y + P_y P_x) | K \pm 3) \\
&= \mp 1 (K | (P_z P_x + P_x P_z) (P_x P_y + P_y P_x) + (P_x P_y + P_y P_x) (P_z P_x + P_x P_z) | K \pm 3) \\
&= \pm \frac{1}{2} 1 \hbar^4 [g(J, K \pm 1) F(J, K \pm 2)]^{\frac{1}{2}} (2K \pm 3)
\end{aligned}$$

$$\begin{aligned}
& (K | (P_x P_y + P_y P_x) (P_y P_z + P_z P_y) + (P_y P_z + P_z P_y) (P_x P_y + P_y P_x) | K \pm 1) \\
&= \pm 1 (K | (P_z P_x + P_x P_z) (P_x P_y + P_y P_x) + (P_x P_y + P_y P_x) (P_z P_x + P_x P_z) | K \pm 1) \\
&= \pm \frac{1}{2} 1 \hbar^4 [g(J, K \pm 1)]^{\frac{1}{2}} [2KJ(J+1) \pm J(J+1) - 2K^3 \mp 3K^2 - 7K \mp 3]
\end{aligned}$$

$$\begin{aligned}
& (K | (P_y P_z + P_z P_y) (P_z P_x + P_x P_z) + (P_z P_x + P_x P_z) (P_y P_z + P_z P_y) | K \pm 2) \\
&= \pm \frac{1}{2} 1 \hbar^4 [F(J, K \pm 1)]^{\frac{1}{2}} (2K \pm 1) (2K \pm 3)
\end{aligned}$$

APPENDIX B  
NUMERICAL CALCULATIONS  
GEOMETRY, NORMAL COORDINATES, AND POTENTIAL FUNCTIONS

1. Basic Constants Used

We use the following constants in these and subsequent calculations:

Equilibrium Geometry\*

$$r_e = 0.9584 \times 10^{-8} \text{ cm}$$

$$2\alpha = 104^\circ 27'$$

$$\sin \alpha = 0.7905293$$

$$\cos \alpha = 0.6124243$$

Atomic Masses

$$m_H = 1.67341233 \times 10^{-24} \text{ g}$$

$$m_D = 3.34428232 \times 10^{-24} \text{ g}$$

$$m_O = 26.55872000 \times 10^{-24} \text{ g}$$

Fundamental Constants\*\*

$$c = 2.9979 \times 10^{10} \text{ cm/sec}$$

$$h = 6.62363 \times 10^{-27} \text{ erg sec}$$

Normal Frequencies\*\*\*

	$H_2O$	$D_2O$
$\bar{\nu}_1$	3825.32 $\text{cm}^{-1}$	2758.06 $\text{cm}^{-1}$
$\bar{\nu}_2$	1653.91 $\text{cm}^{-1}$	1210.25 $\text{cm}^{-1}$
$\bar{\nu}_3$	3935.59 $\text{cm}^{-1}$	2883.79 $\text{cm}^{-1}$

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\* reference 7, p.489.

\*\* reference 2.

\*\*\* reference 5.

## 2. $\text{H}_2\text{O}$ and $\text{D}_2\text{O}$ Calculations

The following quantities are readily calculated from the above data:

TABLE B.1  
Equilibrium Principal Moments of Inertia  
(In units  $10^{-40}$  g cm<sup>2</sup>)

	$\text{H}_2\text{O}$	$\text{D}_2\text{O}$
$I_{xx}^e$	1.02396902	1.84069708
$I_{yy}^e$	1.92115546	3.83939220
$I_{zz}^e$	2.94512448	5.68008928

TABLE B.2  
Normal Angular Frequencies  
(In units  $10^{14}$  sec<sup>-1</sup>)

	$\text{H}_2\text{O}$	$\text{D}_2\text{O}$
$\omega_1$	7.20551102	5.19518154
$\omega_2$	3.11536467	2.27967067
$\omega_3$	7.41321962	5.43201107

The equations (II.103), (II.104) can now be applied to obtain the  $k$ 's; the sign of  $k_4^i$  is not determined, but Darling and Dennison<sup>5</sup> point out that, from physical considerations, it should be positive. Taking for the final values of  $k_3^i$  and  $k_4^i$  the average of the corresponding quantities for  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  separately, we find:

$$\begin{aligned}
 k_1' &= 3.13462138 \times 10^5 \text{ dyne/cm} \\
 k_2' &= 7.18132196 \\
 k_3'(Av) &= 10.65581660 \\
 k_4'(Av) &= 6.31795909
 \end{aligned}$$

	H <sub>2</sub> O	D <sub>2</sub> O
k <sub>1</sub>	3.74638255 x 10 <sup>29</sup> sec <sup>-2</sup>	1.87461529 x 10 <sup>29</sup> sec <sup>-2</sup>
k <sub>2</sub>	2.41610617	1.34406574
k <sub>3</sub>	5.49590854	2.95049939
k <sub>4</sub>	4.00632463	2.11372458

TABLE B.3  
Harmonic Potential Constants

(In units 10<sup>5</sup> dyne/cm)

K <sub>1212</sub> = K <sub>11</sub> '	=	9.04949641
K <sub>1213</sub> = K <sub>12</sub> '	=	0.52397791
K <sub>1223</sub> = K <sub>13</sub> '	=	-1.20497839
K <sub>2323</sub> = K <sub>33</sub> '	=	2.04835571

Using (II.105), the transformation coefficients are:

	H <sub>2</sub> O	D <sub>2</sub> O
sin γ	0.58518046	0.61504088
cos γ	0.81090309	0.78849521

The following matrices are then easily calculated:

$$\mathbf{T}(\text{H}_2\text{O}) = \begin{bmatrix} -1.21187860 & 0.6124243 & 0.39526465 \\ 1.21187860 & 0.6124243 & 0.39526465 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\mathbf{T}(\text{D}_2\text{O}) = \begin{bmatrix} -1.16952808 & 0.6124243 & 0.39526465 \\ 1.16952808 & 0.6124243 & 0.39526465 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\mathbf{P}(\text{H}_2\text{O}) = \begin{bmatrix} 0 & 0 & 0.46847372 \\ 0.33942641 & 0.47035392 & 0 \\ 0.88650762 & -0.63973974 & 0 \end{bmatrix} \times 10^{12} \text{ g}^{-\frac{1}{2}}$$

$$\mathbf{P}(\text{D}_2\text{O}) = \begin{bmatrix} 0 & 0 & 0.35568186 \\ 0.26607988 & 0.34111995 & 0 \\ 0.60976514 & -0.47562811 & 0 \end{bmatrix} \times 10^{12} \text{ g}^{-\frac{1}{2}}$$

$$\mathbf{U}^{(x)}(\text{H}_2\text{O}) = \begin{bmatrix} 0 & 0 & 0.05242838 \\ 0.44325381 & -0.31986987 & -0.41604534 \\ -0.44325381 & 0.31986987 & -0.41604534 \end{bmatrix} \times 10^{12} \text{ g}^{-\frac{1}{2}}$$

$$\mathbf{U}^{(y)}(\text{H}_2\text{O}) = \begin{bmatrix} 0.03798629 & 0.05263880 & 0 \\ -0.30144012 & -0.41771512 & 0.32231098 \\ -0.30144012 & -0.41771512 & -0.32231098 \end{bmatrix} \times 10^{12} \text{ g}^{-\frac{1}{2}}$$

$$\mathbf{U}^{(x)}(\text{D}_2\text{O}) = \begin{bmatrix} 0 & 0 & 0.07155475 \\ 0.30488257 & -0.23781406 & -0.28412711 \\ -0.30488257 & 0.23781406 & -0.28412711 \end{bmatrix} \times 10^{12} \text{ g}^{-\frac{1}{2}}$$

$$\mathbf{U}^{(y)}(\text{D}_2\text{O}) = \begin{bmatrix} 0.05352896 & 0.06862524 & 0 \\ -0.21255092 & -0.27249471 & 0.22011372 \\ -0.21255092 & -0.27249471 & -0.22011372 \end{bmatrix} \times 10^{12} \text{ g}^{-\frac{1}{2}}$$

$$\mathbf{L}^{(x)}(\text{H}_2\text{O}) = \begin{bmatrix} 0 & 0 & 0.27019046 \\ 0.57339508 & -0.41378507 & -0.53819808 \\ -0.57339508 & 0.41378507 & -0.53819808 \end{bmatrix}$$

$$\mathbf{L}^{(y)}(\text{H}_2\text{O}) = \begin{bmatrix} 0.19576293 & 0.27127486 & 0 \\ -0.38994427 & -0.54035812 & 0.41694290 \\ -0.38994427 & -0.54035812 & -0.41694290 \end{bmatrix}$$

$$\mathbf{L}^{(x)}(\text{D}_2\text{O}) = \begin{bmatrix} 0 & 0 & 0.36875850 \\ 0.55755031 & -0.43489958 & -0.51959401 \\ -0.55855031 & 0.43489958 & -0.51959401 \end{bmatrix}$$

$$\mathbf{L}^{(y)}(\text{D}_2\text{O}) = \begin{bmatrix} 0.27586231 & 0.35366122 & 0 \\ -0.38869992 & -0.49832140 & 0.40253030 \\ -0.38869992 & -0.49832140 & -0.40253030 \end{bmatrix}$$

$$\mathbf{S}(\text{H}_2\text{O}) = \begin{bmatrix} 0.55827811 & 0.03518967 & -0.56773328 \\ 0.55827811 & 0.03518967 & 0.56773328 \\ 0.88650762 & -0.63973974 & 0 \end{bmatrix} \times 10^{12} \text{ g}^{-\frac{1}{2}}$$

$$\mathbf{S}^{-1}(\text{H}_2\text{O}) = \begin{bmatrix} 0.82366686 & 0.82366686 & 0.09061360 \\ 1.14138126 & 1.14138126 & -1.43756952 \\ -0.88069525 & 0.88069525 & 0 \end{bmatrix} \times 10^{-12} \text{ g}^{\frac{1}{2}}$$

$$\mathbf{S}(\text{D}_2\text{O}) = \begin{bmatrix} 0.40397239 & 0.02091117 & -0.41597992 \\ 0.40397239 & 0.02091117 & 0.41597992 \\ 0.60976514 & -0.47562811 & 0 \end{bmatrix} \times 10^{12} \text{ g}^{-\frac{1}{2}}$$

From the Darling and Dennison data, we obtain for  $\text{H}_2\text{O}$ :

TABLE B.4  
 $\text{H}_2\text{O}$  - Cubic Potential Constants  
 (In units  $10^{-14}$  erg)

$k_{111} =$	-6.39394768
$k_{112} = k_{121} = k_{211} =$	-0.00661899
$k_{122} = k_{212} = k_{221} =$	1.42970259
$k_{222} =$	0.93327808
$k_{133} = k_{313} = k_{331} =$	-6.01666506
$k_{233} = k_{323} = k_{332} =$	-1.05903895

All other coefficients vanish, since they refer to terms in the potential which are odd in the coordinate  $q_3$ , and this

corresponds to the antisymmetrical vibration  $\omega_3$  -- this coordinate changes sign on reflection of the molecule in the  $\sigma_v$ -plane; this fact is equivalent to the relations (II.79).

From Table B.4 we find

$$\mathbf{k}'(\text{H}_2\text{O}) = \begin{bmatrix} -36.13199770 & -0.07378331 & 0 \\ 10.47934063 & 1.49933996 & 0 \\ -104.94024293 & -12.14563475 & 0 \\ 0 & 0 & 0 \end{bmatrix} \times 10^{48} \text{ dyne cm}^{-2} \text{ g}^{3/2}$$

so that

$$\mathbf{k}(\text{H}_2\text{O}) = \begin{bmatrix} -84.56753212 & 57.47345798 & -35.92925361 \\ 57.47345798 & -84.56753212 & -35.92925361 \\ 24.61366648 & 24.61366648 & -2.51799700 \\ 0 & 0 & -96.56701865 \end{bmatrix} \times 10^{12} \text{ dyne/cm}^2$$

and the coefficients in (II.72) become:

TABLE B.5  
Cubic Potential Constants  
(In units  $10^{12}$  dyne/cm<sup>2</sup>)

$K_{111} = K_{222}$	=	-84.56753212
$K_{112} = K_{122}$	=	57.47345798
$K_{113} = K_{223}$	=	-35.92925361
$K_{133} = K_{233}$	=	24.61366648
$K_{333}$	=	-2.51799700
$K_{123}$	=	-96.56701865

The  $k_{\text{SS}'\text{S}''}$  may now be calculated for  $\text{D}_2\text{O}$ , using the above  $\mathbf{k}$  and the appropriate matrix  $\mathbf{S}$  for  $\text{D}_2\text{O}$ ; we get

$$\mathbf{k}'(\text{D}_2\text{O}) = \begin{bmatrix} -13.50920236 & 0.96683576 & 0 \\ 4.13945419 & 0.53833778 & 0 \\ -40.89726197 & -4.28552185 & 0 \\ 0 & 0 & 0 \end{bmatrix} \times 10^{48} \text{ dyne cm}^{-2} \text{ g}^{3/2}$$

and



TABLE B.6  
 $D_2O$  - Cubic Potential Constants  
 (In units  $10^{-14}$  erg)

$k_{111} =$	$-3.90483690$
$k_{112} = k_{121} = k_{211} =$	$0.14062708$
$k_{122} = k_{212} = k_{221} =$	$0.90891576$
$k_{222} =$	$0.53532925$
$k_{133} = k_{313} = k_{331} =$	$-3.76865386$
$k_{233} = k_{323} = k_{332} =$	$-0.59615616$

### 3. HDO Calculations

For the transformation (II.7) to principal axes, we find

$$\begin{aligned}\tan 2\theta &= 0.90864666 \\ \sin \theta &= 0.36048318 \\ \cos \theta &= 0.93276572 \\ \theta &= 21.12987^\circ\end{aligned}$$

TABLE B.7  
 HDO - Equilibrium Principal Moments of Inertia  
 (In units  $10^{-40}$  g cm<sup>2</sup>)

$I_{xx}^e$	$1.21241595$
$I_{yy}^e$	$3.07104776$
$I_{zz}^e$	$4.28346371$

and the equilibrium positions of the nuclei are given by:

$$\begin{aligned}x_1^e &= 0.07101748 \times 10^{-8} \text{ cm} & y_1^e &= 0.07254673 \times 10^{-8} \text{ cm} \\ x_2^e &= 0.56613647 & y_2^e &= -0.74805539 \\ x_3^e &= -0.84727087 & y_3^e &= -0.20182007\end{aligned}$$

The quantities  $x_{ij}$ ,  $y_{ij}$  are:

$$\begin{aligned} x_{12} &= -0.49511899 \times 10^{-8} \text{ cm} & y_{12} &= 0.82060212 \times 10^{-8} \text{ cm} \\ x_{13} &= 0.91828835 & y_{13} &= 0.27436680 \\ x_{23} &= 1.41340734 & y_{23} &= -0.54623532 \end{aligned}$$

so the kinetic energy matrix is given by

$$\mathbf{p} = \begin{bmatrix} 5.88649894 & -1.63102653 & -0.52682949 \\ -1.63102653 & 5.81699605 & 0.51562418 \\ -0.52682949 & 0.51572418 & 1.28190702 \end{bmatrix} \times 10^{-24} \text{ g}$$

We also have

$$\mathbf{T} = \begin{bmatrix} -1.21410401 & 1.53901209 & 0.56486426 \\ 1.07483884 & 0.17204413 & 0.28264683 \\ -0.44059643 & 0.43130887 & 1.07208056 \end{bmatrix}$$

so that

$$\mathbf{K} = \begin{bmatrix} 22.67630226 & -13.88795405 & -3.65632000 \\ -13.88795405 & 20.58418839 & 6.88480331 \\ -3.65632000 & 6.88480331 & 3.94231275 \end{bmatrix} \times 10^5 \text{ dyne/cm}$$

The characteristic numbers of  $\mathbf{p}$  are found\* to be

$$\begin{aligned} \mu_1 &= 7.569586383 \times 10^{-24} \text{ g} \\ \mu_2 &= 4.220350792 \\ \mu_3 &= 1.195464835 \end{aligned}$$

so that

$$\mathbf{A} = \begin{bmatrix} 0.7097363398 & 0.6995349700 & 0.0832175085 \\ -0.6947754320 & 0.7145983663 & -0.0814633260 \\ -0.1164535406 & 0.0000000018 & 0.9931961406 \end{bmatrix}$$

$$\mathbf{M} = \begin{bmatrix} 0.3634661118 & 0 & 0 \\ 0 & 0.4867721522 & 0 \\ 0 & 0 & 0.9146008420 \end{bmatrix} \times 10^{12} \text{ g}^{-\frac{1}{2}}$$

---

\* The characteristic numbers were determined by the matrix iteration approximation method of reference 9, Section 1.23.

$$\mathbf{B} = \mathbf{M A K A M} = \begin{bmatrix} 4.8651723650 & 0.0831194912 & -1.1878089061 \\ 0.0831194912 & 1.8299805352 & 1.0833604151 \\ -1.1878089061 & 1.0833604151 & 2.2186358018 \end{bmatrix} \times 10^{29} \text{ sec}^{-2}$$

The matrix  $\mathbf{B}$  has the characteristic numbers

$$\omega_1^2 = 2.819180209 \times 10^{29} \text{ sec}^{-2}$$

$$\omega_2^2 = 0.744685129$$

$$\omega_3^2 = 5.3499233637$$

so that the normal frequencies are given by:

TABLE B.8

HDO - Normal Frequencies

$$\omega_1 = 5.309595285 \times 10^{14} \text{ sec}^{-1}$$

$$\omega_2 = 2.728891953$$

$$\omega_3 = 7.3143170315$$

$$\bar{\nu}_1 = 2818.800904 \text{ cm}^{-1}$$

$$\bar{\nu}_2 = 1448.736239$$

$$\bar{\nu}_3 = 3883.083804$$

Diagonalization of  $\mathbf{B}$  is accomplished by the matrix

$$\mathbf{R} = \begin{bmatrix} 0.3322677882 & -0.2111658172 & 0.9192426851 \\ 0.7090694092 & 0.6985980947 & -0.0958189690 \\ 0.6219474977 & -0.6836444250 & -0.3818528649 \end{bmatrix}$$

which leads to

$$\mathbf{P} = \mathbf{A M R} = \begin{bmatrix} 0.3744985817 & 0.1313763923 & 0.1754416960 \\ 0.1164015911 & 0.3472660034 & -0.2370137048 \\ 0.5508995705 & -0.6120695752 & -0.3857754595 \end{bmatrix} \times 10^{12} \text{ g}^{-\frac{1}{2}}$$

We also get

$$\mathbf{F}^{(x)} = \begin{bmatrix} 0.15890641 & 0 & 0 \\ -0.84109359 & 0 & 0.66649778 \\ -0.84109359 & 0 & -0.33350222 \end{bmatrix}$$

$$\mathbf{F}^{(y)} = \begin{bmatrix} 0 & 0.15890641 & 0 \\ 0.81461926 & -1.63854103 & -0.25757941 \\ -0.40761927 & -0.44206676 & 0.12888761 \end{bmatrix}$$

$$\mathbf{m} = \begin{bmatrix} 5.15351531 & 0 & 0 \\ 0 & 1.29360440 & 0 \\ 0 & 0 & 1.82873790 \end{bmatrix} \times 10^{-12} \text{ g}^{\frac{1}{2}}$$

$$\mathbf{U}^{(x)} = \mathbf{F}^{(x)} \mathbf{P} = \begin{bmatrix} 0.05951022 & 0.02087655 & 0.02787881 \\ 0.05218498 & -0.51844285 & -0.40468137 \\ -0.49871459 & 0.09362672 & -0.01890591 \end{bmatrix} \times 10^{12} \text{ g}^{-\frac{1}{2}}$$

$$\mathbf{U}^{(y)} = \mathbf{F}^{(y)} \mathbf{P} = \begin{bmatrix} 0.01849696 & 0.05518279 & -0.03766300 \\ -0.02755541 & -0.30433133 & 0.63064268 \\ -0.13310598 & -0.28595449 & -0.01645921 \end{bmatrix} \times 10^{12} \text{ g}^{-\frac{1}{2}}$$

$$\mathbf{L}^{(x)} = \mathbf{m} \mathbf{U}^{(x)} = \begin{bmatrix} 0.30668685 & 0.10758762 & 0.14367388 \\ 0.06750672 & -0.67065995 & -0.52349761 \\ -0.91201827 & 0.17121874 & -0.03457396 \end{bmatrix}$$

$$\mathbf{L}^{(y)} = \mathbf{m} \mathbf{U}^{(y)} = \begin{bmatrix} 0.09532436 & 0.28438537 & -0.19409683 \\ -0.03564579 & -0.39398435 & 0.81580213 \\ -0.24341595 & -0.52293581 & -0.03009959 \end{bmatrix}$$

$$\mathbf{S} = \mathbf{T} \mathbf{P} = \begin{bmatrix} 0.03564670 & 0.02920574 & -0.79568219 \\ 0.57826185 & 0.02795400 & 0.03875653 \\ 0.47581102 & -0.56429296 & -0.59310747 \end{bmatrix} \times 10^{12} \text{ g}^{-\frac{1}{2}}$$

The cubic potential coefficients are:

$$\mathbf{k}' = \begin{bmatrix} -19.16441347 & -1.99429641 & -2.23137620 \\ 4.48361231 & 0.97679970 & -5.47161888 \\ -8.47066032 & -5.32837221 & 49.66670495 \\ 0 & 0 & -7.76171927 \end{bmatrix} \times 10^{48} \text{ dyne cm}^{-2} \text{ g}^{\frac{3}{2}}$$

and

TABLE B.9  
 HDO - Cubic Potential Constants  
 (In units  $10^{-14}$  erg)

$k_{111} =$	-5.36139356
$k_{112} = k_{121} = k_{211} =$	-0.25941086
$k_{113} = k_{131} = k_{311} =$	-0.17728726
$k_{122} = k_{212} = k_{221} =$	0.81351213
$k_{222} =$	0.74165220
$k_{223} = k_{232} = k_{322} =$	-0.84585445
$k_{133} = k_{313} = k_{331} =$	-0.57341072
$k_{233} = k_{323} = k_{332} =$	-0.50313049
$k_{333} =$	8.59367572
$k_{123} = k_{231} = k_{312}$ $= k_{321} = k_{213} = k_{132} =$	-0.43010075

APPENDIX C  
NUMERICAL CALCULATIONS  
ROTATION-VIBRATION CONSTANTS

In accordance with the convention (III.68), we have

$$I_{aa} \leq I_{bb} \leq I_{cc} ,$$

so it is apparent from the results of Appendix B (Tables B.1 and B.7) that the axes  $x, y, z$  are there identified with  $a, b, c$  respectively, for the three molecules considered; this is the  $III^R$  representation of KHC I.

For convergence of the continued-fraction expansion of the secular determinant associated with the rotational matrix (III.73), as discussed in Appendix D, it is desirable to now relabel the original axes  $z, x, y$  to correspond to  $a, b, c$  respectively; this is the  $I^R$  representation of KHC I.

Let us now write\*

$$\begin{aligned} a &= B_{zz}^V & c &= B_{yy}^V \\ b &= B_{xx}^V & d &= B_{zx}^V . \end{aligned}$$

If we now make use of

---

\* In this work we will not be concerned with  $B_{xy}^V, B_{yz}^V$ , though it should be pointed out that, in a  $III^R$  representation  $B_{xy}^V$  will appear in place of  $B_{zx}^V$  ( $I^R$ ), and this case is applicable to HDO; however,  $B_{xy}^V$  appears in the factored submatrices of KHC I, whereas  $B_{zx}^V$  does not, and for certain purposes it is desirable that this product of inertia be left out and treated as a small perturbation.

$$\kappa = \frac{2b-a-c}{a-c} ,$$

in the manner discussed by KHC I, the first three of the equations (III.74) become, in this representation ( $I^r$ ):

$$R_0 = \frac{a+c}{2} J(J+1) + \frac{a-c}{2} \frac{1}{2} (\kappa-1) J(J+1) - D_J J^2 (J+1)^2$$

$$R_2 = - \frac{a-c}{2} \frac{1}{2} (\kappa-3) - D_{JK} J(J+1)$$

$$R_4 = - \frac{1}{4} \frac{a-c}{2} (\kappa+1) + \delta_J J(J+1) .$$

In the sequel, we will work in the  $I^r$  representation. The results of Appendix B are readily put in this form by the simple relabelling of axes; however, the final results of the present Appendix are subject to modification when change of representation is made, for, while the  $\tau$ 's of (III.64) are easily relabelled, the equations in Section III.4 are unchanged, so the distortion coefficients have different numerical values; the effective moments also change slightly from representation to representation, because of their dependence on the  $D_{gg}$ , of equation (III.77).

In a  $I^r$  representation, using the results of Appendix B with the theory of Chapter III, we obtain:

TABLE C.1:  $\zeta_{ss}^{(g)}$ 

	H <sub>2</sub> O	D <sub>2</sub> O	HDO
$\zeta_{12}^{(y)}$	0	0	0.54508337
$\zeta_{13}^{(y)}$	0.00551823	-0.05679709	-0.01777540
$\zeta_{23}^{(y)}$	-0.99958477	-0.99838573	-0.83819337

TABLE C.2:  $a_s^{(gg')}$ 

In units  $10^{-20} (\text{g cm}^2)^{\frac{1}{2}}$

	H <sub>2</sub> O	D <sub>2</sub> O	HDO
$a_1^{(xx)}$	2.24791666	3.09001292	3.14959494
$a_2^{(xx)}$	-1.62218756	-2.41026736	-1.43415769
$a_3^{(xx)}$	0	0	-0.55446728
$a_1^{(yy)}$	3.43222073	4.75889304	3.46953887
$a_2^{(yy)}$	0.01894007	-0.27072831	-0.07357782
$a_3^{(yy)}$	0	0	-2.25626687
$a_1^{(zz)}$	1.18430406	1.66888012	0.31994393
$a_2^{(zz)}$	1.64112764	2.13953905	1.36057987
$a_3^{(zz)}$	0	0	-1.70179959
$a_1^{(zx)}$	0	0	-0.77187968
$a_2^{(zx)}$	0	0	-1.25204106
$a_3^{(zx)}$	-1.63456738	-2.23087284	-1.14611615



TABLE C.3:  $A_{\text{ss}}^{(\text{gg})}$ 

	H <sub>2</sub> O	D <sub>2</sub> O	HDO
$A_{11}^{(\text{xx})}$	0.65756382	0.62172470	0.93039131
$A_{22}^{(\text{xx})}$	0.34243617	0.37827528	0.49067572
$A_{33}^{(\text{xx})}$	0.65231724	0.67593871	0.29588729
$A_{11}^{(\text{yy})} = A_{22}^{(\text{yy})} = A_{33}^{(\text{yy})} = 1$			
$A_{11}^{(\text{zz})}$	0.34243617	0.37827528	0.06960868
$A_{22}^{(\text{zz})}$	0.65756382	0.62172470	0.50932427
$A_{33}^{(\text{zz})}$	0.34768276	0.32406129	0.70411268
$A_{11}^{(\text{zx})}$	0	0	-0.24882819
$A_{22}^{(\text{zx})}$	0	0	-0.20508826
$A_{33}^{(\text{zx})}$	0	0	0.45391645

TABLE C.4:  $b_s^{(gg')}$   
 In units  $10^{-40} (\text{g cm}^2)^{-1}$

	H <sub>2</sub> O	D <sub>2</sub> O	HDO
$b_1^{(xx)}$	0.01073481	0.00443681	0.00678864
$b_2^{(xx)}$	-0.00668562	-0.00269696	-0.00600179
$b_3^{(xx)}$	0.00214426	0.00087791	0.00088137
$b_1^{(yy)}$	0.00703036	0.00273430	0.00382831
$b_2^{(yy)}$	0.00451081	0.00171093	0.00237112
$b_3^{(yy)}$	0.00508392	0.00180278	0.00299900
$b_1^{(zz)}$	0.02034015	0.00582782	0.00995508
$b_2^{(zz)}$	-0.09592416	-0.03802457	-0.06013689
$b_3^{(zz)}$	0.04595808	0.01902196	0.03624818
$b_1^{(zx)}$	0	0	-0.00645617
$b_2^{(zx)}$	0	0	0.01155260
$b_3^{(zx)}$	0	0	0.00271927
$\frac{1}{2} \sum_s b_s^{(xx)}$	0.00309673	0.00130888	0.00083411
$\frac{1}{2} \sum_s b_s^{(yy)}$	0.00831254	0.00312401	0.00459921
$\frac{1}{2} \sum_s b_s^{(zz)}$	-0.01481296	-0.00658740	-0.00696682
$\frac{1}{2} \sum_s b_s^{(zx)}$	0	0	0.00390785

TABLE C.5:  $\tau_{gg'g''g''''}$   
 In units  $10^{90} (\text{g cm}^2)^{-3} \text{sec}^2$

	H <sub>2</sub> O	D <sub>2</sub> O	HDO*
$\tau_{xxxx}$	-1.35241851	-0.33862371	-0.35627764
$\tau_{yyyy}$	-0.15081584	-0.04098252	-0.07765828
$\tau_{zzzz}$	-13.84950671	-4.28635104	-7.08894402
$\tau_{xxyy}$	-0.22714952	-0.07048001	-0.12884885
$\tau_{yyzz}$	-0.44803283	-0.08361311	-0.18112849
$\tau_{zzxx}$	2.88152784	0.80211647	0.75249734
$\tau_{zxzx}$	-0.62814987	-0.16885299	-0.92397640
$\tau_{zxxx}$	0	0	-0.23745113
$\tau_{zxyy}$	0	0	0.02509463
$\tau_{zxzz}$	0	0	1.83673884

\*Not transformed to principal axes: see Table C.10.

TABLE C.6:  $D_{gg'}$   
 In units  $10^{40} (\text{g cm}^2)^{-1}$

	H <sub>2</sub> O	D <sub>2</sub> O	HDO*
$D_{xx}$	-0.00008438	-0.00002208	-0.00010530
$D_{yy}$	0.00009014	0.00002483	0.00015141
$D_{zz}$	-0.00004795	-0.00001379	-0.00009876
$D_{zx}$	0	0	-0.00001824

\*Not transformed to principal axes: see Table C.11.

TABLE C.7  
Distortion Constants  

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In units Mc/sec

	H <sub>2</sub> O	D <sub>2</sub> O	HDO*
D <sub>J</sub>	28.92348858	7.45681896	9.01676826
D <sub>K</sub>	729.36580935	225.00743493	279.94933771
D <sub>JK</sub>	-112.71978845	-32.66381366	41.47209724
δ <sub>J</sub>	14.00262952	3.46850038	3.24683339
R <sub>5</sub>	31.16163450	8.12053047	-9.03150455
R <sub>6</sub>	-3.05588799	-0.69525362	-0.54839883
R <sub>7</sub> <sup>(x)</sup>	0	0	3.05952301
R <sub>8</sub> <sup>(y)</sup>	0	0	-8.00882857
R <sub>9</sub> <sup>(y)</sup>	0	0	50.81694501

\*Not transformed to principal axes: see Table C.12.

TABLE C.8  
 Rotation Constants  
 In units  $10^5$  Mc/sec  
 ( $\kappa$  dimensionless)

	Equilibrium		
	H <sub>2</sub> O	D <sub>2</sub> O	HDO
a <sup>e</sup>	8.1925576	4.5574718	6.9191808
b <sup>e</sup>	4.3666040	2.1849618	2.7316167
c <sup>e</sup>	2.8484110	1.4769002	1.9584443
$\kappa$ <sup>e</sup>	-0.43182960	-0.54030510	-0.68828325
	Ground	Vibrational	HDO*
	H <sub>2</sub> O	D <sub>2</sub> O	
a <sup>o</sup>	8.3168225	4.6127330	6.9776249
b <sup>o</sup>	4.3406258	2.1739817	2.7246194
c <sup>o</sup>	2.7786778	1.4506931	1.9198619
d <sup>o</sup>	0	0	-0.0327827
$\kappa$ <sup>o</sup>	-0.43593095	-0.54251778	-0.68177336
	Effective		
	H <sub>2</sub> O	D <sub>2</sub> O	HDO*
a	8.3172247	4.6128487	6.97845341
b	4.3413336	2.1741669	2.72550273
c	2.7779216	1.4504848	1.91859173
d	0	0	-0.03262965
$\kappa$	-0.43552032	-0.54231577	-0.68105413

\*Not transformed to principal axes: See Table C.13.

In Table C.9 we give the inertia defect  $\Delta$  for the ground state: (1) calculated approximately from equations (III.72) or (III.84) ( $\Delta_o$ ); (2) calculated exactly from the ground state moments ( $\Delta_o^t$ ), and (3) calculated exactly from the effective moments ( $\Delta_o^{t'}$ ); the agreement is seen to be good to a few percent.

TABLE C.9  
Inertia Defect  
In units  $10^{-40}$  g cm<sup>2</sup>

	H <sub>2</sub> O	D <sub>2</sub> O	HDO
$\Delta_o$	0.07609087	0.10381619	0.08676075
$\Delta_o^t$	0.07771198	0.10527228	0.08835060*
$\Delta_o^{t'}$	0.07889770	0.10647705	0.09238402*

\*Not transformed to principal axes: see Table C.14.

The non-vanishing of the  $b_s^{(zx)}$  for HDO introduces an off-diagonal product of inertia which cannot be neglected; removal of this (Section III.6) modifies the HDO constants, whose new values are given in the following tables. The transformation coefficients (III.91) are:

$$\cos \theta = 0.9999702970$$

$$\sin \theta = 0.0077074347$$

$$\theta = 0^\circ 27'$$

so the axes are rotated through about half a degree.

TABLE C.10  
 HDO - Effective  $\tau'_{gg'g'g'}$   
 In units  $10^{90} (\text{g cm}^2)^{-3} \text{sec}^2$

$\tau'_{xxxx}$	-0.36368202
$\tau'_{yyyy}$	-0.07765828
$\tau'_{zzzz}$	-7.14485265
$\tau'_{xxyy}$	-0.12246549
$\tau'_{yyzz}$	-0.18151185
$\tau'_{zzxx}$	0.78415385
$\tau'_{zxzx}$	-0.89231989
$\tau'_{zxxx}$	-0.24275270
$\tau'_{zxyy}$	0.02464248
$\tau'_{zxzz}$	1.78996036

TABLE C.11  
 HDO - Effective  $D'_{gg'}$   
 In units  $(\text{g cm}^2)^{-1}$

$D'_{xx}$	$-0.00010189 \times 10^{40}$
$D'_{yy}$	$0.00014602 \times 10^{40}$
$D'_{zz}$	$-0.00010610 \times 10^{40}$
$D'_{zx}$	$-1.85723121 \times 10^{35}$

TABLE C.12  
HDO - Effective Distortion Constants

In units Mc/sec	
$D'_J$	9.14172899
$D'_K$	287.08933921
$D'_{JK}$	36.81321390
$\delta'_J$	3.33311881
$R'_5$	-7.87718656
$R'_6$	-0.57220390
$R'_7^{(x)}$	3.11603472
$R'_8^{(y)}$	-8.19943988
$R'_9^{(y)}$	49.91730954

TABLE C.13  
HDO - Rotation Constants

In units $10^5$ Mc/sec ( $\kappa$ dimensionless)			
Ground State		Effective	
$a^{0'}$	6.97787760	$a'$	6.97876766
$b^{0'}$	2.72436671	$b'$	2.72522145
$c^{0'}$	1.91986190	$c'$	1.91863695
$d^{0'}$	0	$d'$	0.00015580
$\kappa^{0'}$	-0.68188916	$\kappa$	-0.68120013



TABLE C.14  
HDO - Effective Inertia Defect

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In units  $10^{-40}$  g cm<sup>2</sup>

$\Delta_o$	0.08676075
$\Delta_o^t$	0.08810858
$\Delta_o^{t'}$	0.09201742

## APPENDIX D

COMPUTATION OF ROTATIONAL ENERGIES

The theory of Chapter III results in the rotational matrix, whose elements are given by (III.73) and which is diagonal in the quantum number  $J$ . In the type of analysis described in Chapter VI, one is interested in only a rather restricted number of the  $2J+1$  energies corresponding to a particular value of  $J$ ; complete diagonalization of each  $J$  matrix is not necessary.

To obtain the desired characteristic values of the rotational energy matrix, we have found it convenient to use an extension of the continued-fraction approximation method described by KHC I for the rigid rotor case. The appropriate representation (i.e. identification of axes) must be chosen to ensure convergence; it is not expected that the addition of a small perturbing matrix to the original rigid rotor matrix will affect the convergence properties, and no difficulties of this type were encountered in the present work.

Since in the present instance we wish to apply the results to HDO (in a  $I^r$  representation), the following discussion is to be considered as specialized for this case. However, the methods are readily extended to other examples where needed; for  $H_2O$  and  $D_2O$  they become much simpler.

When one carries out the transformation described in Section III.6, the elements of the rotational matrix III.73

for HDO in a  $I^r$  representation take the form

$$\begin{aligned}
 (K|H_R|K) &= R_0 + R_2 K^2 - D_K K^4 \\
 (K|H_R|K\pm 1) &= \pm 1 [g(J, K\pm 1)]^{\frac{1}{2}} (2K\pm 1) \\
 &\quad \times \left[ \frac{1}{2}N + R_8 J(J+1) + R_9 [K^2 + (K\pm 1)^2] \right] \\
 (K|H_R|K\pm 2) &= [g(J, K\pm 1)g(J, K\pm 2)]^{\frac{1}{2}} [R_4 - R_5 [K^2 + (K\pm 2)^2]] \\
 (K|H_R|K\pm 3) &= \pm 1 [g(J, K\pm 1)g(J, K\pm 2)g(J, K\pm 3)]^{\frac{1}{2}} (2K\pm 3)R_7 \\
 (K|H_R|K\pm 4) &= [g(J, K\pm 1)g(J, K\pm 2)g(J, K\pm 3)g(J, K\pm 4)]^{\frac{1}{2}} R_6
 \end{aligned} \tag{D.1}$$

where

$$N = -\frac{1}{2} \hbar^2 D_{zx} = 5R_7, \tag{D.2}$$

and  $R_7$ ,  $R_8$  and  $R_9$  stand for  $R_7^{(x)}$ ,  $R_8^{(y)}$  and  $R_9^{(y)}$ .

In the general notation of KHC I we may write

$$\begin{aligned}
 R_0 &= \frac{a+c}{2} J(J+1) + \frac{a-c}{2} FJ(J+1) - D_J J^2(J+1)^2 \\
 R_2 &= \frac{a-c}{2} (G-F) - D_{JK} J(J+1) \\
 R_4 &= \frac{1}{2} \frac{a-c}{2} H + \delta_J J(J+1),
 \end{aligned} \tag{D.3}$$

where, for a  $I^r$  representation,

$$\begin{aligned}
 F &= \frac{1}{2}(\kappa-1) & G &= 1 \\
 H &= -\frac{1}{2}(\kappa+1) & G-F &= -\frac{1}{2}(\kappa+3),
 \end{aligned} \tag{D.4}$$

and  $a, b, c, \kappa$  are defined in Appendix C.

We now re-write the rotational matrix, thus

$$H_R = \frac{a+c}{2} J(J+1) - D_J J^2(J+1)^2 + \frac{a-c}{2} E, \tag{D.5}$$

where  $E$  is the reduced energy matrix, with elements

$$\begin{aligned}
E_{KK} &= (K|E|K) = FJ(J+1) + [(G-F) - D_{JK}J(J+1)]K^2 - D_K K^4 \\
E_{KK\pm 1} &= (K|E|K\pm 1) = (K|H_R|K\pm 1) \\
E_{KK\pm 2} &= (K|E|K\pm 2) = [g(J, K\pm 1)g(J, K\pm 2)]^{\frac{1}{2}} \\
&\quad \times \left[ \frac{1}{2}H + \delta_J J(J+1) - R_5 [K^2 + (K\pm 2)^2] \right] \\
E_{KK\pm 3} &= (K|E|K\pm 3) = (K|H_R|K\pm 3) \\
E_{KK\pm 4} &= (K|E|K\pm 4) = (K|H_R|K\pm 4)
\end{aligned} \tag{D.6}$$

In (6),  $D_{JK}$ ,  $D_K$ ,  $\delta_J$ ,  $R_5$ ,  $R_6$ ,  $N$ ,  $R_7$ ,  $R_8$ ,  $R_9$  now stand for the original ("fundamental") distortion constants divided by  $\frac{a-c}{2}$ , and will have this meaning for the remainder of this Appendix; they are the reduced distortion constants.

It is apparent that the whole complexity of the problem lies in the reduced energy matrix (6), and the methods of handling this will now be discussed.

First one transforms the matrix to a basis of Wang functions, using the transformation  $X$  of KHC I in the usual manner. In the presence of  $(K|K\pm 1)$  and  $(K|K\pm 3)$  elements, the resulting matrix can now be factored into two submatrices only, corresponding to symmetric (+) and antisymmetric (-) Wang functions. When the  $(K|K\pm 1)$  and  $(K|K\pm 3)$  elements are pure imaginary, as in the case of the HDO molecule in a  $I^r$  representation, these submatrices take the forms:

$$(+) = \begin{bmatrix} H_{00} & H_{01} & H_{02} & H_{03} & H_{04} & 0 & 0 & \text{---} & \text{---} \\ H_{10} & H_{11}^+ & H_{12}^+ & H_{13}^+ & H_{14} & H_{15} & 0 & \text{---} & \text{---} \\ H_{20} & H_{21}^+ & H_{22}^+ & H_{23} & H_{24} & H_{25} & H_{26} & \text{---} & \text{---} \\ H_{30} & H_{31}^+ & H_{32} & H_{33} & H_{34} & H_{35} & H_{36} & \text{---} & \text{---} \\ H_{40} & H_{41} & H_{42} & H_{43} & H_{44} & H_{45} & H_{46} & \text{---} & \text{---} \\ 0 & H_{51} & H_{52} & H_{53} & H_{54} & H_{55} & H_{56} & \text{---} & \text{---} \\ 0 & 0 & H_{62} & H_{63} & H_{64} & H_{65} & H_{66} & \text{---} & \text{---} \\ \text{---} & \text{---} & \text{---} & \text{---} & \text{---} & \text{---} & \text{---} & \text{---} & \text{---} \\ \text{---} & \text{---} & \text{---} & \text{---} & \text{---} & \text{---} & \text{---} & \text{---} & \text{---} \end{bmatrix}$$

(D.7)

$$(-) = \begin{bmatrix} H_{11}^- & H_{12}^- & H_{13}^- & H_{14} & H_{15} & 0 & \text{---} & \text{---} \\ H_{21}^- & H_{22}^- & H_{23} & H_{24} & H_{25} & H_{26} & \text{---} & \text{---} \\ H_{31}^- & H_{32} & H_{33} & H_{34} & H_{35} & H_{36} & \text{---} & \text{---} \\ H_{41} & H_{42} & H_{43} & H_{44} & H_{45} & H_{46} & \text{---} & \text{---} \\ H_{51} & H_{52} & H_{53} & H_{54} & H_{55} & H_{56} & \text{---} & \text{---} \\ 0 & H_{62} & H_{63} & H_{64} & H_{65} & H_{66} & \text{---} & \text{---} \\ \text{---} & \text{---} & \text{---} & \text{---} & \text{---} & \text{---} & \text{---} & \text{---} \\ \text{---} & \text{---} & \text{---} & \text{---} & \text{---} & \text{---} & \text{---} & \text{---} \end{bmatrix}$$

where,

$$H_{KK'} = E_{KK'} \quad , \quad (D.8)$$

except that

$$\begin{aligned} H_{0K} &= 2^{\frac{1}{2}} E_{0K} & (K=1,2,3,4) \\ H_{KK'}^{\pm} &= E_{KK'} \pm E_{-KK'} \end{aligned} \quad (D.9)$$

The matrix elements obey the usual relations

$$\begin{aligned} E_{-K -K-1} &= E_{KK+1} \\ E_{-K -K+1} &= E_{KK-1} \end{aligned} \quad (D.10)$$

but the  $(K|K\pm 1)$  and  $(K|K\pm 3)$  elements, being imaginary, are also subject to the Hermitian condition

$$\begin{aligned} E_{K+1K} &= - E_{KK+1} \\ E_{K+3K} &= - E_{KK+3} . \end{aligned} \quad (D.11)$$

For computational purposes, it is now convenient to introduce the symbol  $H_{KK'}^i$ , to denote the rigid rotor limit of the value of the matrix element  $H_{KK'}$ , for  $K' = K, K\pm 1, K\pm 2$ , and to be identical with  $H_{KK'}$ , for  $K' = K\pm 3, K\pm 4$ , with

$$H_{KK'} = H_{KK'}^i A_{KK'} \quad \text{for } K' \neq K. \quad (D.12)$$

In terms of the  $E_{KK'}$ , we have specifically

$$\begin{aligned} E_{KK}^i &= FJ(J+1) + (G-F)K^2 \\ E_{KK+1}^i &= 1 [g(J, K+1)]^{\frac{1}{2}} (2K+1)^{\frac{1}{2}} N \\ E_{KK+2}^i &= [g(J, K+1)g(J, K+2)]^{\frac{1}{2}} \frac{1}{2} H \\ E_{KK+3}^i &= E_{KK+3} = 1 [g(J, K+1)g(J, K+2)g(J, K+3)]^{\frac{1}{2}} (2K+3) R_7 \\ E_{KK+4}^i &= E_{KK+4} = [g(J, K+1)g(J, K+2)g(J, K+3)g(J, K+4)]^{\frac{1}{2}} R_6 . \end{aligned} \quad (D.13)$$

Note that  $N$  is a multiple of  $R_7$ , through (2), though we find it convenient to use the two different symbols.

Further,

$$\begin{aligned} E_{KK} &= E_{KK}^i - D_{JK} J(J+1)K^2 - D_K K^4 \\ E_{KK+1} &= E_{KK+1}^i A_{KK+1} \\ E_{KK+2} &= E_{KK+2}^i A_{KK+2} \\ E_{KK+3} &= E_{KK+3}^i A_{KK+3} \\ E_{KK+4} &= E_{KK+4}^i A_{KK+4} , \end{aligned} \quad (D.14)$$

with

$$\begin{aligned}
 A_{KK+1} &= 1 + 2J(J+1) \frac{R_8}{N} + 2[K^2 + (K+1)^2] \frac{R_9}{N} \\
 A_{KK+2} &= 1 + 2J(J+1) \frac{\delta_J}{H} - 2[K^2 + (K+2)^2] \frac{R_5}{H} \\
 A_{KK+3} &= A_{KK+4} = 1.
 \end{aligned} \tag{D.15}$$

We also write

$$\begin{aligned}
 H_{11}^{\pm} = E_{11}^{\pm} &= E_{11}' \pm E_{-11}' - J(J+1)D_{JK} - D_K \\
 &\quad \pm J^2(J+1)^2\delta_J \mp 2J(J+1)R_5
 \end{aligned} \tag{D.16}$$

$$H_{22}^{\pm} = E_{22}^{\pm} = E_{22}' - 4J(J+1)D_{JK} - 16D_K \pm J(J+1)[J(J+1)-2]R_6$$

and

$$\begin{aligned}
 H_{12}^{\pm} &= E_{12}^{\pm} = E_{12}' A_{12}^{\pm} \\
 H_{13}^{\pm} &= E_{13}^{\pm} = E_{13}' A_{13}^{\pm} \\
 A_{12}^{\pm} &= A_{12} \pm \frac{2}{15} J(J+1) \\
 A_{13}^{\pm} &= A_{13} \pm 2J(J+1) \frac{R_6}{H}.
 \end{aligned} \tag{D.17}$$

To find a particular reduced energy,  $\lambda_{JK}^{\pm}$ , corresponding to a given  $J$  and  $K$ , the appropriate submatrix (+) or (-) is chosen (see KHC I); the leading term in the expansion of the associated secular determinant is then  $H_{KK}$ . The expansion is carried out by reducing the order of the determinant by successively removing rows of off-diagonal elements; an analytical description of the process is readily obtained.

Suppose the matrix has elements of the form  $M_{st}$ . In the determinants under consideration, the roots are non-degenerate because the  $K$ -degeneracy has been separated out by the Wang transformation, and each member of a pair of degenerate

levels will appear in a different submatrix; thus it is legitimate to divide by  $M_{rr} - \lambda$  when  $r \neq K$ .

To remove the  $r$ -th row of the determinant, we multiply each element of the  $r$ -th column by  $\frac{M_{rt}}{M_{rr} - \lambda}$  and subtract from the  $t$ -th column; the elements of the latter column then take the form

$$M_{st} - \frac{M_{sr} M_{rt}}{M_{rr} - \lambda},$$

the  $r, t$ -th element being zero. Doing this for each value of  $t$ , except  $t = r$ , removes all the off-diagonal elements in the  $r$ th row. Since  $M_{rr} - \lambda$  is nonzero, and is the only element remaining in the  $r$ -th row, it may now be factored out, together with the rest of the  $r$ -th column.

The elements of the resulting determinant may be relabelled  $M_{st}^r$  ( $r, s, t$  are not necessarily consecutive numbers), with

$$M_{st}^r = M_{st} - \frac{M_{sr} M_{rt}}{M_{rr} - \lambda}, \quad (\text{D.18})$$

and with diagonal elements

$$M_{ss}^r - \lambda = M_{ss} - \lambda - \frac{M_{sr} M_{rs}}{M_{rr} - \lambda}. \quad (\text{D.19})$$

One can proceed by repeating this process, until there finally remains the term

$$M_{KK} - \lambda - \frac{M_{Ky}^{r \dots x} M_{yK}^{r \dots x}}{M_{yy}^{r \dots x} - \lambda} = M_{KK}^{r \dots xy} - \lambda$$

so that



$$\lambda_{J_K} = M_{KK}^{r\dots xy} . \quad (D.20)$$

Here  $r\dots xy$  indicates the sequence in which the expansion was carried out, in terms of the diagonal elements which appear in the denominators at each stage; for the (+) matrix it will contain the  $J$  numbers  $012\dots J$  with  $K$  omitted, but will not necessarily be in the normal order of integers. For a given  $J_K$  certain sequences will be more convenient for computational purposes than others, but for large  $J$  it is not practical to try and find the best one. Accordingly, we adopt a standard order

$$(0)12\dots K-1:JJ-1\dots K+1 , \quad (D.21)$$

which we call the "primary sequence"; (21), incidentally, is preferable to the more obvious sequence

$$(0)12\dots K-1:K+1\dots J-1J ,$$

for large  $J$ , at least. Here we use (0) to indicate the 0 is to be omitted for the (-) submatrix.

Thus we can write

$$\lambda_{J_K}^{\pm} = H_{KK}^{(0)12\dots K-1:JJ-1\dots K+1} ,$$

or,

$$\lambda_{J_K}^{\pm} = H_{KK}^{K+1} , \quad (D.22)$$

where, for simplicity in practice, only the last member of the assumed standard sequence is written.

When (22) is developed as described below, it may be used to obtain approximate values of  $\lambda$  by the usual iteration

process.

If M and N are two consecutive numbers in the primary sequence -- they may be K-1 and J -- then (18) gives the recurrence relation

$$H_{K'K''}^{(O)1..MN} = H_{K'K''}^{(O)1..M} - \frac{H_{K'N}^{(O)1..M} H_{NK''}^{(O)1..M}}{H_{NN}^{(O)1..M} - \lambda},$$

or, simply,

$$H_{K'K''}^N = H_{K'K''}^M - \frac{H_{K'N}^M H_{NK''}^M}{H_{NN}^M - \lambda}, \quad (D.23)$$

with the particular cases

$$\begin{aligned} H_{K'K'}^N &= H_{K'K'}^M - \frac{|H_{NK'}^M|^2}{H_{NN}^M - \lambda} \\ H_{K'K''}^O &= H_{K'K''} - \frac{H_{K'O} H_{OK''}}{H_{OO} - \lambda} \quad (+) \\ H_{K'K''}^1 &= H_{K'K''} - \frac{H_{K'1} H_{1K''}}{H_{11} - \lambda} \quad (-) \end{aligned} \quad (D.24)$$

Appropriate + or - signs should also be inserted where necessary, as they appear in (7); to simplify the discussion we have left them off, but their presence is implied.

These results are quite general, for any determinant with non-degenerate roots, but the question of convergence is, of course, quite another matter.

From the above recurrence relations we can now write

$$H_{K'K'}^N = H_{K'K'} - \sum_{j=0}^N \frac{|H_{jK'}^1|^2}{H_{jj}^1 - \lambda} = H_{K'K'} - \sum_{j=0}^N \frac{|H_{jK'}^1|^2 (A_{jK'}^1)^2}{H_{jj}^1 - \lambda} \quad (D.25)$$

$$A_{K'K''}^N = A_{K'K''} - \sum_{j=0}^N \frac{B_{K'K''}^j A_{K'j}^1 A_{jK''}^1}{H_{jj}^1 - \lambda} \quad (D.26)$$

where  $N$  is any number in the primary sequence, and  $i, j$  are successive numbers in this sequence. For the (+) submatrix the first terms ( $j=0$ ) in the sums are

$$\frac{|H_{0K'}|^2}{H_{00} - \lambda} \quad \text{and} \quad \frac{B_{K'K''}^0 A_{K'0} A_{0K''}}{H_{00} - \lambda},$$

while for the (-) submatrix these terms vanish, and the first terms are

$$\frac{|H_{1K'}|^2}{H_{11}^- - \lambda} \quad \text{and} \quad \frac{B_{K'K''}^1 A_{K'1} A_{1K''}}{H_{11}^- - \lambda}.$$

The cases  $K = 0$  and  $K = J$  are easily treated, and will not be discussed in detail here.

In (26), the quantities  $A_{K'K''}^1$  and  $B_{K'K''}^1$  are defined by the relations

$$\begin{aligned} H_{K'K''}^1 &= H_{K'K''}^1 A_{K'K''}^1 \\ B_{K'K''}^1 &= \frac{H_{K'1}^1 H_{1K''}^1}{H_{K'K''}^1} = B_{K''K'}^1 \\ A_{K'K''}^1 &= A_{K''K'}^1. \end{aligned} \quad (D.27)$$

The  $B_{K'K''}^1$  may be calculated from Table D.1.

TABLE D.1:  $B_{K,K}^1$ 

In the quantities marked with an \*, the superscript 1 may take on the value 0; when it does, the right hand side is to be multiplied by 2.

$$* B_{KK+1}^{K-3} = -\frac{2}{5} \frac{2K-3}{2K+1} g(J,K-1)g(J,K-2)g(J,K-3)R_6$$

$$* B_{KK+1}^{K-2} = \frac{1}{5} \frac{2K-1}{2K+1} g(J,K-1)g(J,K-2)H$$

$$* B_{KK+1}^{K-1} = -\frac{1}{2} \frac{2K-1}{2K+1} g(J,K-1)H$$

$$B_{KK+1}^{K+2} = -\frac{1}{2} \frac{2K+3}{2K+1} g(J,K+2)H$$

$$B_{KK+1}^{K+3} = \frac{1}{5} \frac{2K+3}{2K+1} g(J,K+2)g(J,K+3)H$$

$$B_{KK+1}^{K+4} = -\frac{2}{5} \frac{2K+5}{2K+1} g(J,K+2)g(J,K+3)g(J,K+4)R_6$$

$$* B_{KK+2}^{K-2} = g(J,K-1)g(J,K-2)R_6$$

$$* B_{KK+2}^{K-1} = 5(2K-1)(2K+1)g(J,K-1) \frac{R_7^2}{H}$$

$$B_{KK+2}^{K+3} = 5(2K+3)(2K+5)g(J,K+3) \frac{R_7^2}{H}$$

$$B_{KK+2}^{K+4} = g(J,K+3)g(J,K+4)R_6$$

$$* B_{KK+3}^{K-1} = -\frac{5}{2} \frac{2K-1}{2K+3} g(J,K-1)R_6$$

$$B_{KK+3}^{K+4} = -\frac{5}{2} \frac{2K+7}{2K+3} g(J,K+4)R_6$$

The relations (25) and (26) may be used to set up directly the expansion for numerical calculations. To explain the procedure, it is convenient to take  $K' < K''$ , so that

$$\begin{aligned} N &= K' - 1 < K'' && \text{when } K' < K'' \\ N &= K'' + 1 > K' && \text{when } K' \geq K'' \end{aligned}$$

Then, from (26), we see that  $A_{K'K'+4}^N = 1$ , and  $A_{K'K''}^N = 0$  if  $K'' > K'+4$ . As a result, for a given  $K'$  there need to be calculated only the quantities

$$\begin{aligned} H_{K'K'}^{K'-1} - \lambda, & \quad A_{K'K'+1}^{K'-1}, & \quad A_{K'K'+2}^{K'-1}, & \quad A_{K'K'+3}^{K'-1}, & \quad K' < K \\ H_{K''K''}^{K''+1} - \lambda, & \quad A_{K''-1K''}^{K''+1}, & \quad A_{K''-2K''}^{K''+1}, & \quad A_{K''-3K''}^{K''+1}, & \quad \begin{array}{l} K'' > K \\ K' \geq K \end{array} \end{aligned} \quad (\text{D.28})$$

and, finally,  $\lambda_{JK} = H_{KK}^{K+1}$ .

From (25), (26) and (28), one can set down systematically the terms that must be calculated for each cycle of the iteration process. As an example, we list some of these, in the correct order, for the  $12_6^+$  level:

$$\begin{aligned} & \lambda \\ & E_{00}^{-\lambda} \\ & H_{11}^0 - \lambda, A_{12}^0, A_{13}^0, A_{14}^0 \\ & H_{22}^1 - \lambda, A_{23}^1, A_{24}^1, A_{25}^1 \\ & \text{-----} \\ & H_{55}^4 - \lambda, A_{56}^4, A_{57}^4, A_{58}^4 \\ & E_{12\ 12}^{-\lambda} \\ & H_{11\ 11}^{12} - \lambda, A_{10\ 11}^{12}, A_{9\ 11}^{12}, A_{8\ 11}^{12} \\ & \text{-----} \end{aligned}$$

$$\begin{aligned}
 H_{99}^{10} - \lambda, A_{89}^{10}, A_{79}^{10}, A_{69}^{10} \\
 H_{88}^9 - \lambda, A_{78}^9, A_{68}^9 \\
 H_{77}^8 - \lambda, A_{67}^8 \\
 H_{66}^7 = \lambda
 \end{aligned}$$

This particular level requires some 500 desk calculator operations per cycle, which can be carried out in about two hours when working to 10-figure accuracy. Of course, one should start with a reasonably good approximation, e.g. the value obtained when  $(K|K\pm 1)$  and  $(K|K\pm 3)$  elements are neglected. From the latter calculation, too, one can obtain a good correction factor to be applied to each cycle of the iteration and thus increase the speed of convergence. In practice, if no numerical errors are made, one can usually obtain a 10-figure solution with three iterations.

This procedure is easily specialized to the case where  $(K|K\pm 1)$  and  $(K|K\pm 3)$  matrix elements are absent, as in  $H_2O$  and  $D_2O$ , and reduces to the rigid rotor formulation of KHC I when  $(K|K\pm 4)$  elements also vanish. In these cases, factoring into odd and even  $K$  submatrices is automatically achieved because of the lack of matrix elements connecting even and odd  $K$ 's.

APPENDIX E  
EXPERIMENTAL RESULTS

The experimental work was carried out using a conventional slow-sweep, 5 kc/sec square-wave Stark modulation spectroscopy, with re-modulation and visual presentation. Frequency measurements were made with the M.I.T. frequency standard, monitored by WWV.

A.E.C. 99.8 percent D<sub>2</sub>O was usually used as a specimen; HDO lines observed seemed no weaker than those in a 50-50 mixture of this D<sub>2</sub>O with distilled water.

Difficulty is sometimes experienced in deciding whether a line is due to HDO or D<sub>2</sub>O. Where possible, we have used Stark and Zeeman effect measurements to provide additional evidence for identification.

D<sub>2</sub>O: 2<sub>20</sub> → 3<sub>13</sub>: 10,919.39 ± 0.05 Mc/sec

This line was found during the progress of a general search for water lines in the X-band region<sup>26</sup>, and was identified on the basis of its Stark effect. It has now also been reported by Beard and Bianco<sup>1</sup>, who agree with our assignment of the transition, and who give the frequency as 10,919.8 ± 0.1 Mc/sec

The line is strong, and its Stark components (M = 0, 1, 2) are readily resolved. We measured:

$$\Delta\nu_{\text{obs.}} = (1.473 - 0.2088M^2)E^2 \text{ Mc/sec} ,$$

where  $\Delta v$  is the frequency shift of the M-th component, and E is the electric field in Kv/cm.

From the KHC II tables of the  $D_2O$  term values (see footnote, p.62) the theoretical Stark effect for the  $D_2O$   $2_{20} \rightarrow 3_{13}$  transition is

$$\Delta v_{th.} = (0.4751 - 0.07264M^2)\mu^2 E^2 \text{ Mc/sec,}$$

where  $\mu$  is the dipole moment in Debye units; using<sup>32</sup>  $\mu = 1.84$ , we obtain

$$\Delta v_{th.} = (1.608 - 0.2459M^2)E^2 \text{ Mc/sec.}$$

The ratios of M-independent and M-dependent coefficients are:

observed	7.05
theoretical	6.54 .

Although the agreement is not very good, the easy resolution and large intensity of the Stark spectrum readily enables identification of the line as a  $J = 2 \leftrightarrow 3$  transition; the assigned transition is the only one in  $D_2O$  or HDO that approximates the observed measurements.

Burke<sup>3</sup> has used the Zeeman effect to confirm our identification of this line.

$D_2O: 5_{32} \rightarrow 4_{41}: 10,947.13 \pm 0.05 \text{ Mc/sec}$

This line was found at the same time as the  $2_{20} \rightarrow 3_{13}$  line<sup>26</sup> but was not identified by the writer up to the time it was reported and identified by Beard and Bianco<sup>1</sup>; the latter authors give the frequency as  $10,947.4 \pm 0.1 \text{ Mc/sec}$ .



Our measurements of the Stark effect give

$$\Delta v_{\text{obs.}} = (0.957 - 0.0402M^2)E^2 \text{ Mc/sec,}$$

while we calculate the theoretical Stark effect for the given transition to be

$$\Delta v_{\text{th.}} = (0.275 - 0.0117M^2)\mu^2 E^2 \text{ Mc/sec.}$$

Observed and theoretical ratios of M-independent and M-dependent terms are

observed	23.8
theoretical	23.5 ,

in very good agreement. With  $\mu = 1.84$  Debye units, the theoretical expression becomes

$$\Delta v_{\text{th.}} = (0.931 - 0.0396M^2)E^2 \text{ Mc/sec,}$$

which is close to that observed.

HDO:  $7_{44} \rightarrow 7_{43}$ :  $8,577.7 \pm 0.1$  Mc/sec

This line was originally found by J.D.Kierstead<sup>13</sup> of this Laboratory; its frequency has been measured as 8,576.89 Mc/sec. We have remeasured the frequency, and find the value  $8,577.7 \pm 0.1$  Mc/sec.

HDO:  $8_{45} \rightarrow 8_{44}$ :  $24,884.77 \pm 0.05$  Mc/sec

We found this line by general searching in a region predicted by rough calculations<sup>26</sup>; the line is quite strong, and it is surprising it has not been observed earlier.

Jen et al.<sup>12</sup> have independently reported the line at  $24,880.85 \pm 0.1$  Mc/sec, and have identified the transition.

We find the Stark splitting to be typical of a Q-branch transition, being given by

$$\Delta v_{\text{obs.}} = 0.0216M^2E^2 \text{ Mc/sec,}$$

in good agreement with the theoretical value of

$$\Delta v_{\text{th.}} = 0.0234M^2E^2 \text{ Mc/sec}$$

for the assigned transition with  $\mu = 1.84$  Debye units.

$$\text{HDO: } 10_{56} \rightarrow 10_{55}: 8,836.95 \pm 0.1 \text{ Mc/sec}$$


---

$$\text{HDO: } 11_{57} \rightarrow 11_{56}: 22,581.1 \pm 0.2 \text{ Mc/sec}$$


---

As indicated in Section VI.2, these lines were predicted at 8,836 and 22,577 Mc/sec, respectively.

Visual observation of the Stark splitting shows the expected behaviour of Q-branch lines in the absence of strong perturbations. No Stark measurements were made, since the lines are weak, and it is considered the identification by position is quite adequate.

$$\text{HDO: } 6_{24} \rightarrow 7_{17}: 26,880.38 \pm 0.05 \text{ Mc/sec}$$


---

Some difficulty arises in accounting satisfactorily for this line. It was first discovered by McAfee<sup>22</sup> who gave the frequency as 26,880.44 Mc/sec, and who believed it to be a  $D_2O$  transition.

The observed Stark effect is most consistent<sup>26</sup> with the

$6_{24} \rightarrow 7_{17}$  transition of HDO; Burke<sup>3</sup> has shown from the Zeeman effect that the line must arise from an HDO transition.

Jen et al.<sup>1,2</sup> have independently examined the line, placing it at  $26,880.47 \pm 0.1$  Mc/sec, and also concluded from the Stark effect that it is the  $6_{24} \rightarrow 7_{17}$  transition of HDO.

It is considered that the present analysis of the HDO spectrum gives a better energy level picture than the KHC II tables, upon which the original Stark effect calculations were based. The final parameters of this thesis, together with  $\mu = 1.84$  Debye units, give for the theoretical Stark effect,

$$\Delta v_{\text{th.}} = (0.2574 - 0.00862M^2)E^2 \text{ Mc/sec,}$$

while we observe

$$\Delta v_{\text{obs.}} = (0.2890 - 0.01037M^2)E^2 \text{ Mc/sec.}$$

The ratios of M-independent and M-dependent terms are

theoretical	29.9
observed	27.87 ,

and the agreement is to be considered fairly good, considering the lack of exact calculations for the line strengths involved in the theoretical expression.

The molecular parameters obtained in this thesis support this assignment (Section VI.5).

## APPENDIX F

COMMENTS ON RELATED WORKDarling and Dennison

Reference 5: B.T.Darling and D.M.Dennison, Phys.Rev.57, 128 (1940); "Water Vapor Molecule".

This paper represents the first successful attempt to account for the observed vibrational spectrum of the water molecule. The writers' results on H<sub>2</sub>O and D<sub>2</sub>O form the basis of some of the computations carried out in the present work.

Some of the theory of vibration-rotation interaction is presented, but only as far as the vibrational problem is concerned; there is no treatment of rotation.

The inertia defect  $\Delta$  for a planar molecule is first introduced in this paper.

Although the work has not been checked right through in detail, it appears to be singularly free from misprints. The notation, however, differs considerably from that used in the present work -- we mention some of the main correlations below.

The coordinates  $x, y, q$  are equivalent to our  $(\mu'/\mu)u, v, w$  respectively; the normal coordinates  $q_1, q_2, q_3$  correspond to our  $Q_1, -Q_2, Q_3$ , and the transformation coefficients  $\delta_{1j}$  are related to our  $P_{1j}$  as follows:

$$\begin{array}{lll} \delta_{11} = P_{31} & - \delta_{12} = P_{32} & \delta_{21} = P_{21} \\ & - \delta_{22} = P_{22} & \frac{\mu}{\mu'} \delta_{33} = P_{13} \end{array}$$

For the quadratic potential constants, we have

<u>Darling and Dennison</u>	<u>This Work</u>
(In units $10^5$ dyne/cm)	
a = 10.672	$k_3'' = 10.6558$
b = 7.1810	$k_2' = 7.18132$
c = 3.1344	$k_1' = 3.13462$
2d = 6.3176	$k_4' = 6.31796$

Slightly different values of the basic constants are, of course, used in the two cases.

Darling and Dennison use  $x_1$  where we have the dimensionless normal coordinates  $q_s$ ; their coefficients  $\alpha_1$  in the cubic part of the potential (in their paper, the term in  $\alpha_6$  should read  $\alpha_6 x_2 x_3^2$ ) are related to our  $k_{ss's''}$  thus:

$$\begin{aligned}
 k_{111} &= hca_1 & k_{133} &= k_{313} = k_{331} = \frac{1}{3}hca_5 \\
 k_{112} &= k_{121} = k_{211} = -\frac{1}{3}hca_3 & k_{233} &= k_{323} = k_{332} = -\frac{1}{3}hca_6 \\
 k_{122} &= k_{212} = k_{221} = \frac{1}{3}hca_4 & k_{222} &= -hca_2,
 \end{aligned}$$

the negative sign in the coefficients odd in the index 2 appearing since their  $q_2$  equals our  $-Q_2$ . For  $H_2O$  the following values of the  $\alpha_1$  are given:

$$\begin{aligned}
 \alpha_1 &= -322 \text{ cm}^{-1} & \alpha_4 &= 216 \text{ cm}^{-1} \\
 \alpha_2 &= -47 & \alpha_5 &= -909 \\
 \alpha_3 &= 1 & \alpha_6 &= 160
 \end{aligned}$$

from these, the  $k_{ss's''}$  in Table B.4 were calculated.

Some of the quartic potential coefficients are also given, but these are not of interest to us here.

Expressions for the effective moments are calculated, together with the inertia defect  $\Delta$ . With the correlation

$$K_1 \equiv -\zeta_{13}^{(y)} \qquad K_2 \equiv \zeta_{23}^{(y)}$$

it may be seen that our equation (III.84) for  $\Delta_0$  is identical with that for Darling and Dennison:

<u>Darling and Dennison</u>	<u>This Work</u>
$\Delta_0 = 0.0761 \times 10^{-40} \text{ g cm}^2$	$\Delta_0 = 0.076091 \times 10^{-40} \text{ g cm}^2.$

This paper should be consulted for any work involving excited vibrational states, when resonance mixing of the effective moments may occur.

The writers give theoretical expressions for the moments of inertia, in the form of our (III.67), with the  $b_s^{(gs)}$  given by (III.86); their equations are equivalent to ours. They use the linear form (III.67) to fit the observed data, and arrive at values which give, for the ground state:

<u>Rotation Constants</u>		
In units $10^5 \text{ Mc/sec}$		
	Observed (D and D)	Calculated (This work)
a	8.32771	8.31682
b	4.34209	4.34063
c	2.78198	2.77868
x	-0.437365	-0.43593

Fuson, Randall and Dennison

Reference 6: N.Fuson, H.M.Randall and D.M.Dennison, Phys.Rev. 56, 982 (1939); "The Far Infra-Red Absorption Spectrum and the Rotational Structure of the Heavy Water Vapor Molecule".

These writers find, from infrared investigations, the following  $D_2O$  rotational constants:

	<u>Rotational Constants</u>	
	In units $10^5$ Mc/sec ( $\kappa$ dimensionless)	
	FRD	This Work
a	4.611	4.613
b	2.173	2.174
c	1.448	1.450
$\kappa$	-0.5412331	-0.54231577

They give rotational energy levels complete through  $J = 12$ , and a few higher ones, together with distortion corrections evaluated by a semi-classical method.

Values of the  $b_s^{(gg)}$  calculated semi-classically agree fairly well with respect to sign and order of magnitude when compared with the more rigorous results of the present work.

The rotational constants given by FRD have been revised slightly by King<sup>9</sup>, from infrared work.

Hillger and Strandberg

Reference 10: R.E.Hillger, Thesis, M.I.T. (1950)

Reference 11: R.E.Hillger and M.W.P.Strandberg, Phys. Rev. 83, 575 (1951); "Centrifugal Distortion in Asymmetric Molecules. II. HDS"

The possibility of using an approximation method to calculate Q-branch frequencies, including distortion effects, was first realized in this work. The HSKW formula was obtained, though it is somewhat in error.

Although the distortion in this molecule is smaller than in HDO, it appears to be still large enough for the HSKW formula (in its correct form) to be subject to the practical limits of accuracy discussed in the present work (Section VI.3); accordingly, it is the present writer's opinion that the whole analysis should be checked against exact calculations, in a manner similar to the present work.

In his Thesis, Hillger derives a formula for  $\Delta$ , similar to our (III.71); this, however, is in error.

Lewis

Reference 21: W.H.Lewis, Thesis, M.I.T. (1951)

Lewis has calculated theoretical distortion constants for HDO; his results are similar to those presented here, though his value for  $R_6$  appears to be in error. A value of  $\Delta$  was obtained from the Hillger formula (see above), but this is incorrect.

An attempt at analysis of the then known HDO spectrum was not very successful owing to inadequacy of the data;



the  $8_4$  line, for example, was predicted some 2,000 Mc/sec away from its subsequently found position.

### Nielsen

(a) Reference 23: H.H.Nielsen, Phys.Rev. 59, 565 (1941); "The Near Infra-Red Spectrum of Water Vapor. Part I. The Perpendicular Bands  $\nu_2$  and  $2\nu_2$ ."

This paper pertains to the present work in that theoretical and "observed" values of several  $H_2O$  distortion coefficients are presented; the theoretical coefficients are calculated from the Shaffer and Nielsen work<sup>29</sup>, and are in substantial agreement with the present writer's calculations from the same formulae; however, as pointed out in the discussion of reference 29, the Shaffer and Nielsen formulation apparently contains an error.

We give below some figures for comparison (these are all in a  $III^R$  representation, and in units  $10^{-4} \text{ cm}^{-1}$ ):

	Nielsen		This Work	
	Observed	Theoretical	Theoretical (Shaffer and Nielsen formulae)	Theoretical (This work)
$D_J$	473	150.3	104.723	82.321
$D_K$	302.8	56.99	56.826	74.168
$D_{JK}$	--	--	-62.084	-154.143
$\delta_J$	45	48.71	48.578	48.578
$R_5$	95	16.7	16.606	23.430
$R_6$	-6.6	-6.75	-6.731	-17.932

(b) Reference 25: H.H.Nielsen, Rev.Mod.Phys. 23, 90 (1951); "The Vibration-Rotation Energies of Molecules."

In our Chapter III we have followed closely the notation of this review article, though a few changes have been made; in particular, our choice of phase factor for the rotational matrix elements differs from Nielsen's.

Although this article goes into considerable detail, and is a good guide to the theoretical background of the present problem, we find the typographical and other errors are so numerous (and not always obvious by inspection!) that no detailed reliance can be placed on the equations.

Randall, Dennison, Ginsburg and Weber

Reference 27: H.M.Randall, D.M.Dennison, N.Ginsburg and L.R.Weber, Phys.Rev. 52, 160 (1937)

This paper contains an analysis of the rotational spectrum of H<sub>2</sub>O, and observed energy levels are listed.

A rigid rotor calculation, using the values

$$a = 8.335811 \times 10^5 \text{ Mc/sec}$$

$$b = 4.346872$$

$$c = 2.781834$$

gives energies whose differences from those "observed" is ascribed to distortion effects; a semi-classical argument is used to attempt to justify this.

Shaffer and Newton

Reference 28: W.H.Shaffer and R.R.Newton, J.Chem.Phys. 10, 405 (1942); "Valence and Central Forces in Bent Symmetrical  $XY_2$  Molecules".

These authors investigate the quadratic and cubic portions of the potential function applicable to the  $H_2O$  type molecule. Their method of determination of the central-force constants from the data of Darling and Dennison is essentially the same as that presented here, and they give numerical values very close to ours, with the correlations:

Shaffer and Newton	This Work
$K_1$	$K'_{11}$
$K_4$	$K'_{12}$
$K_3$	$K'_{13}$
$K_2$	$K'_{33}$
$L_1$	$K_{111} = K_{222}$
$3L_3$	$K_{112} = K_{122}$
$3L_6$	$K_{113} = K_{223}$
$3L_5$	$K_{133} = K_{233}$
$L_2$	$K_{333}$
$6L_4$	$K_{123}$

A concise account of the normal coordinate problem for  $H_2O$  and  $D_2O$  is given; the only misprint detected occurs in their sign for  $l_{33}$ , which should read  $l_{23} = l_{33} = (-\mu/2m)\mu_1^{-\frac{1}{2}}$ .

A discussion of the valence-force formulation of the potential function is also given, with the observation that it leads to a better approximation to the true potential than does the central-force function. However, the results of the present work are not affected by the form of the function

chosen.

No calculations based on the valence-force potential were carried out by the present writer since the Shaffer and Newton paper came to his attention too late for him to investigate such an approach in detail.

The quantities  $K$ ,  $\sigma_1$ ,  $\sigma_2$ , used by Shaffer and Newton, correspond to our  $x^{\frac{1}{2}}$ ,  $\cos \gamma$  and  $\sin \gamma$ , respectively, in the discussion of  $H_2O-D_2O$  transformations. Their  $q_1$ ,  $q_2$ ,  $q_3$  correspond to our  $Q_1$ ,  $Q_2$ ,  $Q_3$ .

#### Shaffer and Nielsen

Reference 29: W.H.Shaffer and H.H.Nielsen, Phys.Rev. 56, 188 (1939); "The Vibration-Rotation Energies of the Nonlinear Triatomic  $XY_2$  Type of Molecule".

The theory of vibration-rotation interaction is carried through in some detail along lines rather similar to that of the present work.

Some misprints have been pointed out by Nielsen -- Phys. Rev. 59, 565 (1941), footnote 11 -- and others remain.

The notation in the normal coordinate discussion is readily correlated with that given in our Section II.5, except that we choose a different matrix  $\mathbf{R}$  (II.90).

The expressions for the rotational matrix elements given in their equation (42) agree with ours, except that the sign of their  $\delta$  as defined in equation (39) is apparently in error: it should read

$$\delta = -\frac{1}{8}h^2 A_o^{\frac{1}{2}} B_o^{\frac{1}{2}} \frac{(\omega_2^2 - \omega_1^2)}{\omega_1^2 \omega_2^2} \sin \gamma \cos \gamma ,$$

in the notation used in the rest of the paper. This appears to be a definite error, rather than a misprint, since calculations made with  $\delta = + ..$  give distortion coefficients in substantial agreement with those quoted by Nielsen in reference 23.

#### Weisbaum

Reference 35: S.Weisbaum, private communication;  
S.Weisbaum, Y.Beers and G.Herrmann, Bull.Am.Phys.Soc.  
28, 9 (1953)

I am greatly indebted to Mr.S.Weisbaum and Dr.Y.Beers for permission to use some of the results of their work prior to publication.

A significant improvement in the available data on the HDO microwave spectrum has been made by the S-band investigations of these workers, who discovered and identified four new lines.

Weisbaum has succeeded in fitting the Q-branch spectrum (except the  $10_5$  and  $11_5$  lines) to a set of parameters by means of the HSKW formula. As discussed in Section VI.6, it is the present writer's opinion that the resulting parameters should be considered semi-empirical, and that they do not necessarily bear any significant relationship to the "true" molecular parameters.

Weisbaum's results are compared below with our values:

	Weisbaum	This Work (Table VI.18)
	In units $\text{cm}^{-1}$ ( $\kappa$ dimensionless)	
$\kappa$	-0.6830	-0.6841
$\frac{a-c}{2}$	8.4895	8.5226
$\delta_J$	$1.39042 \times 10^{-4}$	$1.112 \times 10^{-4}$
$D_{JK}$	$2.29892 \times 10^{-3}$	$1.23 \times 10^{-3}$
$D_K$	$20.90344 \times 10^{-3}$	$9.57 \times 10^{-3}$
$R_5$	$-3.38775 \times 10^{-4}$	$-2.628 \times 10^{-4}$
$R_6$	$-5.35005 \times 10^{-5}$	$-1.91 \times 10^{-5}$

These parameters, used with the HSKW formula, give the frequency of the  $11_5$  line at 22,552 Mc/sec, some 29 Mc/sec below that observed. This agreement is quite good, and it appears that Weisbaum's results show the HSKW formula is adequate for Q-branch transitions, even if the parameters are empirical. Exact calculation with these parameters, however, gives the frequency 22,446 Mc/sec, some 135 Mc/sec low, so it is doubtful that the results would be useful in analysis of the P- and R-branch spectrum.

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