

A STUDY OF CORIOLIS-TYPE  
RESONANCE IN HYDROGEN SULFIDE

Thesis for the Degree of Ph. D.  
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LEWIS E. SNYDER

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THESIS

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RESONANCE IN HYDROGEN SULFIDE

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## ABSTRACT

### A STUDY OF CORIOLIS-TYPE RESONANCE IN HYDROGEN SULFIDE

by Lewis E. Snyder

The second-order quantum-mechanical molecular Hamiltonian expression for the nonlinear XYX asymmetric molecule is modified to include Coriolis-type perturbations between pairs of mutually interacting infrared absorption bands. As a result, expressions are found for the coupled Wang energy matrices which include the centrifugal stretching terms and the perturbation coefficients. The modified Hamiltonian is used to analyze simultaneously the (110) and (011) absorption bands of  $H_2S$  near  $3800\text{ cm}^{-1}$ . Ground state combination differences from these two bands together with those from the (210) and (111) bands (near  $6300\text{ cm}^{-1}$ ) were combined with seven microwave lines to obtain values for the ground state parameters A, B, C, four taus, and  $H_K$  for  $H_2^{32}S$ . Using these ground state values, the (110) and (011) bands of  $H_2^{32}S$  were reanalyzed to obtain final values for the upper state parameters ( $\nu_o$ , A, B, C, four taus, and  $H_K$ ) of each band and the parameters ( $G_{xy}$  and  $G_z$ ) coupling the two bands.

A STUDY OF CORIOLIS-TYPE  
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By

Lewis E. Snyder

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TO MY WIFE  
DORIS JEAN

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## INTRODUCTION

The purpose of this study is to derive a general quantum-mechanical expression for the perturbed energy levels of the nonlinear XYX asymmetric top molecule, while demonstrating the mathematics involved. The derived energy expression will then be used to predict the spectral absorption lines of two interacting hydrogen sulfide bands. The predicted absorption lines will be compared with those of spectra observed under resolution high enough that the effects of the perturbation may be clearly observed.

The basic theoretical groundwork leading to the quantum-mechanical Hamiltonian is found in the literature - many times in a form that the researcher in the laboratory finds to be totally unrelated to experimental research. In addition, the literature contains many "effective" or empirical Hamiltonian expressions which are postulated with little or no theoretical justification. Hamiltonian expressions of this type are often quite successful in explaining spectra as long as no unexpected perturbations appear or the spectrometer resolution is low enough to cover any anomalies between the observed and predicted values of the spectral lines.

The infrared spectra of H<sub>2</sub>S have been observed and

analyzed sporadically for the past thirty years yet very little quantitative information is known about the perturbations which affect the upper states of nearly all the observable vibration-rotation bands. With improved high resolution spectroscopy, a theoretical approach to the problem with experimental verification is now possible.

## CHAPTER I

### GENERAL CONSIDERATIONS FOR AN ASYMMETRIC TOP MOLECULE

#### The Rigid Asymmetric Rotor Model

If a molecule has no threefold or higher axis of symmetry it is an asymmetric rotor since in general the three principal moments of inertia are different. Common examples of asymmetric rotors include water ( $H_2O$ ), hydrogen sulfide ( $H_2S$ ), hydrogen selenide ( $H_2Se$ ), and acetic acid ( $CH_3COOH$ ). Even though the classical motion of an asymmetric rotor or top is well known (1a), its behavior is not simple and the quantum - mechanical asymmetric rotor Hamiltonian is generally much more difficult to manipulate than that for either the symmetric or the linear rotor. Unlike the usual case for the linear and symmetric rotors, the energy levels of the asymmetric top can not be represented by an explicit formula for all values of its angular momentum; therefore the quantum - mechanical matrix formulation will be relied on heavily.

Fortunately, much information about the general asymmetric rotor may be obtained by examining the behavior of a hypothetical rigid asymmetric rotor as it moves from the oblate to the prolate top limit. The use of a rigid top model is justified for the general discussion which follows

on symmetry and selection rules since wave function symmetry must be independent of the actual values of the moments of inertia and the vibration - rotation interactions, to a first approximation, bring about only a small correction to the effective moments of inertia (2a).

The rigid rotor Hamiltonian operator is given by

$$H_R = A \frac{P_a^2}{\hbar^2} + B \frac{P_b^2}{\hbar^2} + C \frac{P_c^2}{\hbar^2} \quad (I-1)$$

where  $A = h/8\pi^2 c I_a$  etc., in  $\text{cm.}^{-1}$

The range of values for B between A and C customarily is used to describe the various stages of asymmetry. Using this model, a prolate symmetric top is formed in the limit  $B = C < A$  where a is the unique top axis and an oblate symmetric top is formed in the opposite limit  $A = B > C$  where c is the unique top axis. Some authors prefer to always keep c as the unique top axis in which case the oblate definition is unchanged but the prolate definition becomes  $A = B < C$ . Fig. 1 shows qualitatively how the energy levels vary as B varies from C to A for a rigid rotor with  $C = 1.0 \text{ cm}^{-1}$  in the prolate limit and  $A = 2.0 \text{ cm}^{-1}$  in the oblate limit. In practice the energy levels for the intermediate cases must be found by matrix diagonalization but for illustration it is sufficient to join the prolate and oblate limits by continuous lines. Much more detailed drawings of the energy level scheme may be found in the literature (3a).

Several parameters have been constructed to indicate

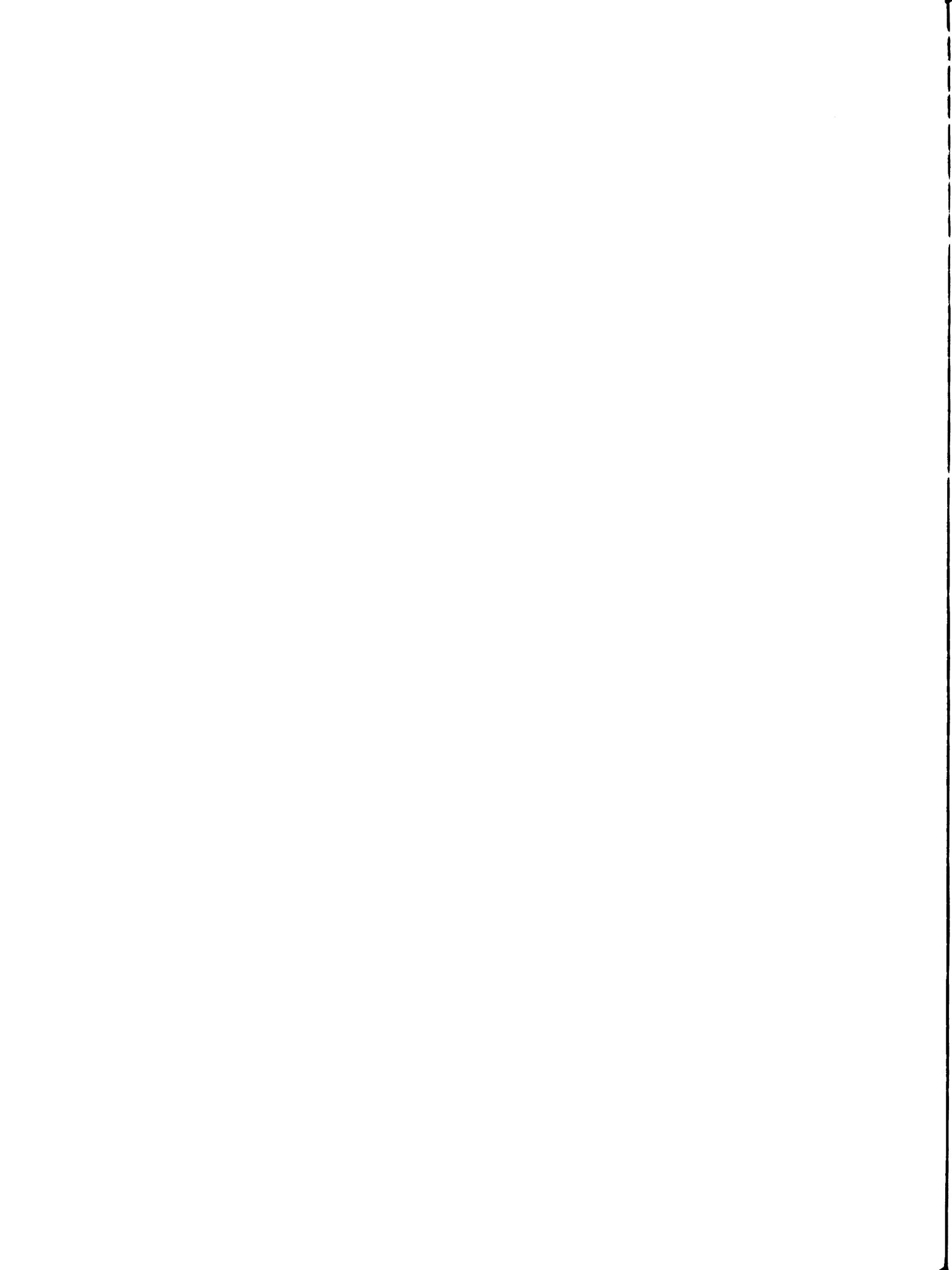
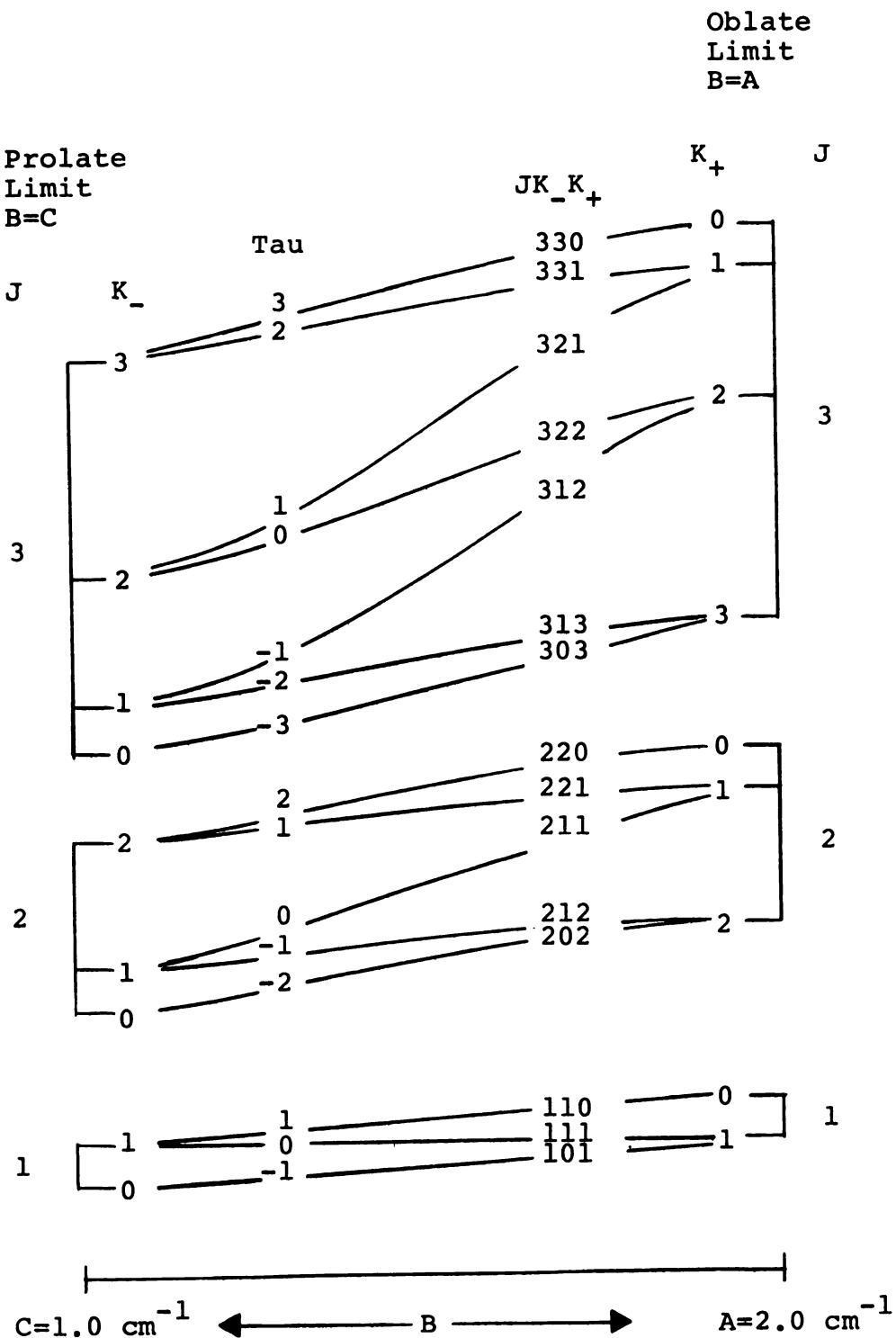


Fig. 1. Rigid Asymmetric Top Energy Levels



the degree of asymmetry (value of B with respect to A and C) but the most popular one is probably Ray's asymmetry parameter kappa where

$$\kappa = \frac{2B - A - C}{A - C} \quad (I-2)$$

In the prolate limit  $\kappa = -1$  and in the oblate limit  $\kappa = +1$ . If the kappa value is known for a given molecule, the energy levels can be found from published interpolation tables without the use of a computer. However, with the increasing availability of high speed digital computers, rigid rotor interpolation tables have lost much of their importance because an entire energy matrix can now be diagonalized in a few minutes using an order of approximation much higher than the rigid rotor. The interested reader is referred to the literature for a discussion of E ( $\kappa$ ) tables (4).

Also, many good approximate solutions have been developed for cases of small asymmetry near either the oblate or the prolate limit in Fig. 1. Townes and Schawlow have summarized many of the approximate solutions and have a general discussion on their range of usefulness (5a).

In the case of no applied external field, the total angular momentum J and its projection on a space - fixed axis, M, are both constants of the motion for an asymmetric top; therefore J and M are called good quantum numbers. However, whereas the projection K of the total angular momentum J on the symmetry axis of a symmetric top is a constant

of the motion, this is no longer true for the asymmetric top and there is no good quantum number which uniquely specifies a rotational energy level. The quantum number K is still used but it is no longer a constant of the motion as is illustrated in the matrix elements given in Chapter IV.

Since K is not a good quantum number, various parameters have been constructed to uniquely specify a rotational energy level. One method is to give the J value along with the corresponding K values for the limiting prolate ( $K_-$ ) and the limiting oblate ( $K_+$ ) symmetric top energy levels. Thus in Fig. 1, the highest energy level is designated by 330 using the JK-K<sub>+</sub> notation. This notation will be used extensively in the experimental aspects of this work. An older method of description using the parameter tau is useful for computer programming purposes. Tau is an ordering index which starts with the highest rotational energy level for a given J and goes to the lowest in order from +J to -J. Thus in Fig. 1 the values of tau for the J = 3 levels are 3, 2, 1, 0, -1, -2, -3 and each level may also be labeled by J<sub>τ</sub>. The relationship

$$\tau = K_- - K_+ \quad (I-3)$$

may be used to determine the value  $K_-$  when working in an oblate representation and vice-versa. For example, in an oblate representation, the quantum number K is  $K_+$  in the oblate limit. By inspecting the energy levels of known J and K, tau may be readily determined for a given level and  $K_-$  for that

level follows immediately. Tau is also of interest because the highest rotational level  $\tau = J$  can be thought of as involving a rotation about the axis of least moment of inertia for a set of levels with given  $J$ . Likewise, the lowest level  $\tau = -J$  may be considered as due to a rotation about the axis of largest moment of inertia (la).

### The Wave Function

In order to understand the selection rules it is helpful to examine the molecular wavefunction in some detail. Disregarding the translational motion of the center of mass of the molecule, the total wavefunction may be approximated as (5 b)

$$\psi_{\text{total}} \approx \psi_e \psi_{VR} \psi_n \approx \psi_e \psi_V \psi_R \psi_n \quad (\text{I-4})$$

where the electronic wave function,  $\psi_e$ , is factorable by the Born-Oppenheimer approximation. The molecular Hamiltonian remaining (after the electronic energy is removed) is mainly the sum of vibrational and rotational energies; hence the vibration - rotation wave function,  $\psi_{VR}$ , may be factored into the product of a vibrational and a rotational contribution. The nuclear spin wave function,  $\psi_n$ , contributes little to the energy and is neglected until the relative intensities of absorption lines are discussed.

The rotational wave functions  $\psi_{JKM}$  of either a prolate or an oblate symmetric rotor form a complete and orthogonal set of functions by which the asymmetric rotor wavefunctions

may be expanded (5c)

$$\psi_{JK-K+M} = \sum_{J'KM'} a_{J'KM'} \psi_{J'KM'} \quad (I-5)$$

where the  $a_{J'KM'}$  terms are the probability amplitudes representing the contributions of each symmetric rotor state. Since  $J$  is still a good quantum number for the asymmetric rotor, no more than one  $J$  value may be represented in a given state. Furthermore, the  $M$  label may be dropped because the energy is independent of molecular orientation in the field-free case. Thus the sum in (I-5) may be reduced to one over  $K$  alone.

The symmetric rotor basis functions in (I-5) are not convenient to use for symmetry reasons which will be discussed in the next section. Instead, it is more convenient to form the Wang linear combinations of symmetric rotor functions (4 )

$$S(J,K,\gamma) = 2^{-\frac{1}{2}} (\psi_{J,K} + (-1)^\gamma \psi_{J,-K}) \quad (I-6)$$

where  $\gamma$  may be either odd or even (for convenience, 1 or 0) and the absolute value of  $K$  is used. For  $K = 0$ , only even  $\gamma$  exists, and the wave function becomes

$$S(J,0,0) = \psi_{J0} \quad (I-7)$$

Using the Wang wave function combinations, the asymmetric top wave functions may be written in a manner analogous to

(I-5) (3a)

$$\psi_{JK-K_+} = \sum_K (a_\gamma)_{JK} S(J, K, \gamma) \quad (I-8)$$

which will be useful for symmetry considerations.

The symmetric rotor wave functions in (I-5), (I-6) and (I-7) are given by (6)

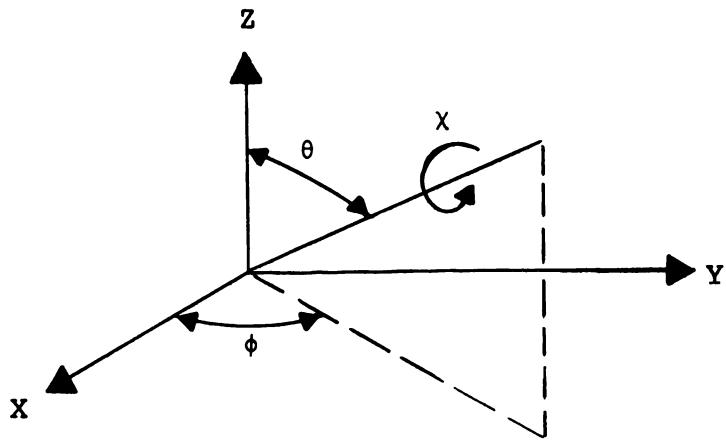
$$\psi_{JKM}(\theta, \phi, \chi) = \Theta_{JKM}(\theta) e^{iM\phi} e^{iK\chi} \quad (I-9)$$

where  $\Theta_{JKM}(\theta)$  is a hypergeometric function. The Eulerian angles are shown in Fig. 2 to avoid confusion with the other sets in the literature. Rotations about the top axis are described by  $\chi$  while  $\theta$  and  $\phi$  measure rotation with respect to the space-fixed axis system XYZ.

#### Rotational Symmetry and Selection Rules

For any asymmetric rotor the selection rules are complicated by the large number of distinct rotational levels and the arbitrary direction of the permanent dipole moment. The parity of the rotational eigenfunctions can be used to classify the energy levels since it is conserved as the rotor moves from the oblate to the prolate limit as shown in Fig. 1. Since a small change in the moments of inertia corresponds to a perturbation which cannot change the symmetry of the eigenfunction, the general selection rules may be derived from the symmetry relations which must be true for the

Fig. 2. Eulerian Angles

Table I. The  $D_2$  Point Group Character Table

$K_- K_+$	Species	E	$C_2^c$	$C_2^b$	$C_2^a$	
e e	A	1	1	1	1	
o e	$B_c$	1	1	-1	-1	$T_c$
o o	$B_b$	1	-1	1	-1	$T_b$
e o	$B_a$	1	-1	-1	1	$T_a$

symmetric rotor eigenfunctions in both the oblate and prolate limits.

The rotational Hamiltonian operator (I-1) remains unchanged when  $P_a$ ,  $P_b$  and  $P_c$  are replaced by their negatives; this is equivalent to performing a two-fold rotation about each of the principal axes (a, b, and c) of the molecule. These three rotations,  $C_2^a$ ,  $C_2^b$  and  $C_2^c$ , along with the identity operator E constitute the point group  $D_2$  (also called V) which requires three mutually perpendicular axes (3a). Each of the nondegenerate asymmetric top eigenfunctions in (I-8) constructed from the Wang linear combinations of symmetric rotor eigenfunctions forms the basis of an irreducible representation for  $D_2$  while the linear combination in (I-5) does not (4). Thus using the Mulliken notation, each of the rotational levels can be assigned rotational symmetry species A,  $B_a$ ,  $B_b$ , or  $B_c$ ; A is used for the totally symmetric representation and the subscripts indicate the particular rotational axis which gives a character of +1 (7).

In the limiting prolate symmetric rotor case,  $C_2^a$  about the symmetry axis a increases  $\chi$  in (I-9) by  $\pm\pi$ . Thus  $S(J, K, \gamma)$  is unchanged if  $K_-$  is even and changes sign if  $K_-$  is odd, giving the parity of the  $\psi_{JK-K+}$  under the operation  $C_2^a$ . In the limiting oblate rotor case,  $C_2^c$  about c gives a character of +1 for  $K_+$  even and -1 for  $K_+$  odd. The four irreducible representations found in this manner may be written as (++), (+-), (-+) and (--) using Dennison's

notation (2a). They may also be labeled by the King, Hainer and Cross notation in terms of the evenness or oddness of  $K_+$  and  $K_-$ . Table I gives the character table for the  $D_2$  point group and correlates the various notations that are used to label the four irreducible representations (3a). The symmetry about the intermediate axis b may be determined from the symmetry about a and c since successive rotations of  $\pi$  about each of the three axes must return the molecule to its original configuration. Hence the wave function is symmetric for a rotation of  $\pi$  about b if  $K_-$  and  $K_+$  are both odd or both even; otherwise it is antisymmetric.

The usual selection rules  $\Delta J = 0, \pm 1$  for dipole radiation of a rotating body also apply to asymmetric rotors. Further selection rules are found from the symmetry properties of the  $\psi_{JK-K_+}$  listed in Table I and the form of the matrix element governing intensities. For a transition between two rotational states 1 and 2 the form of this matrix element is

$$\langle 1 | M_i | 2 \rangle = \int \psi^*(1)_{JK-K_+} M_i \psi(2)_{JK-K_+} d\tau \quad (I-10)$$

where  $M_i$  is the component of the permanent dipole moment of the molecule projected onto the space-fixed axis system. The component of the dipole moment along any principal axis of the molecule is unchanged by a rotation about that axis but changes sign under rotation about either of the other two axes. Such a component thus transforms in the same manner as a translation along that axis when the operations  $C_2^a$ ,  $C_2^b$ ,

$C_2^C$  or  $E$  are applied. The symmetry properties of the possible translations  $T_a$ ,  $T_b$ , and  $T_c$  are listed in Table I. As indicated in Table I,  $T_a$ ,  $T_b$  or  $T_c$  is unchanged by a rotation about the translational axis but changes sign under the other two rotation operations.

It is well known from group theory that an integral of the form (I-10) must be equal to zero unless a representation to which  $M_i$  belongs is contained in the direct product of the representations of the eigenfunctions  $\psi_{(1)JK-K_+}^*$  and  $\psi_{(2)JK-K_+}$  (2b). That is, the representation generated by the integrand must contain the totally symmetric representation if (I-10) is to be nonzero. In simpler terms, the integral (I-10) over coordinate space must give a purely numerical result. If the component of the dipole moment lies along the  $a$  axis, it will reverse direction if rotated by  $\pi$  about  $b$  or  $c$ . But the integral must be invariant under any of the group symmetry operations such as  $C_2^C$ . Thus if  $M_i$  changes sign under  $C_2^C$  then the product of the eigenfunctions in (I-10) must also change sign in order to keep the integral invariant under such a coordinate transformation. Otherwise, the integral must vanish. The direct products of  $D_2$  which contain a representation of  $T_a$ ,  $T_b$ , or  $T_c$  are listed in Table II along with the selection rules which follow from them. In all cases  $\Delta J = 0, \pm 1$ . Table II may be easily verified by inspecting Table I. Experimentally, absorption bands are often labeled as type A, B or C bands depending upon whether the dipole moment lies along  $a$ ,  $b$  or

Table II. Summary of Selection Rules

Direct Products	Allowed Translations	Dipole Moment Species	Allowed Transitions	Band Type
$A \times B_a; B_a \times A$ $B_c \times B_b; B_b \times B_c$	$T_a$	$B_a$	$ee \leftrightarrow eo$ $oe \leftrightarrow oo$	A
$A \times B_b; B_b \times A$ $B_a \times B_c; B_c \times B_a$	$T_b$	$B_b$	$ee \leftrightarrow oo$ $oe \leftrightarrow eo$	B
$A \times B_c; B_c \times A$ $B_b \times B_a; B_a \times B_b$	$T_c$	$B_c$	$ee \leftrightarrow oe$ $oo \leftrightarrow eo$	C

c, as shown in Table II.

### Relative Intensities

Knowing the relative intensities of spectral absorption lines in a given vibration band is an invaluable aid in making proper assignments of rotational transitions.

The intensity of a transition from state  $n''$  to a state  $n'$  is given by (8)

$$I_{n'', n'} = \frac{8\pi^2 v N g_{n''} [1 - \exp(-hv/kT)] \exp(-E_{n''}/kT)}{3hc \sum_n G_n \exp(-E_n/kT)} | \langle n'' | M | n' \rangle |^2 \quad (I-11)$$

where  $v$  is the frequency of the absorption line,  $N$  is the molecular density and  $n$  represents the quantum numbers of the states involved.  $E_{n''}$  is the rotational energy of the lower state and  $g_{n''}$  its statistical weight factor. The fractional number of molecules in the ground vibrational state is  $[1 - \exp(-hv/kT)]$ . The summation term represents the rotational partition function and the last term is the square of the magnitude of the dipole vector matrix element.

The dipole matrix element in (I-II) separates into the product of vibrational and rotational matrix elements. For band analysis, it is only necessary to know that the vibrational part is not zero and observation of the band being analyzed confirms this. The remaining rotational part  $| \langle R'' | M | R' \rangle |^2$  is defined as the line strength and contains the degeneracy factor  $(2J+1)$  due to the  $(2J+1)$ -fold

degeneracy in the absence of an external field. For a given vibration-rotation band, many of the terms in (I-11) are approximately constant. This allows the relative intensities to be found by reducing (I-11) to a product of the statistical weight, Boltzmann factor and line strength. The resulting relative intensity expression may be written

$$I_{n'', n'} = g_{n''} \exp(-E_{n''}/kT) | \langle R'' | M | R' \rangle |^2 \quad (I-12)$$

Tables of line strengths as a function of kappa may be found in the literature (9,10).

The nuclear statistical weight factor  $g_{n''}$  for hydrogen sulfide is easily determined. Since the two hydrogen nuclei are equivalent, i.e. identical isotopes of the same element with the same molecular environment,  $H_2S$  must have a twofold axis of symmetry. The twofold axis is the b axis and a rotation of  $\pi$  about b interchanges the position of the two hydrogen nuclei. Since  $H^1$  is a Fermion, it must always occur in antisymmetric wave functions; hence any true wave function  $\psi_{JK-K_+}\psi_n$  for  $H_2S$  changes sign when the two hydrogen nuclei are interchanged by the operation  $C_2^b$ .

The spin function of each hydrogen nucleus may be written as  $S_i(+)$  or  $S_i(-)$  where + or - indicates the projection on the space-fixed axis to be either  $+\frac{1}{2}$  or  $-\frac{1}{2}$ . The four combinations of the two spin functions of each nucleus are  $S_1(+S_2(+)$ ,  $S_1(-S_2(-)$ ,  $S_1(+S_2(-)$  and  $S_1(-S_2(+)$ . The first two combinations are clearly symmetric with respect

to an interchange of spin coordinates, but the last two are neither antisymmetric nor symmetric. To remedy this, symmetric and antisymmetric combinations may be formed from the last two sets of spin functions. The four proper spin functions are then of the form

$$\begin{aligned}
 S_1 (+) S_2 (+) & \quad (\text{Symmetric}) \\
 S_1 (-) S_2 (-) & \quad (\text{Symmetric}) \\
 S_1 (+) S_2 (-) + S_1 (-) S_2 (+) & \quad (\text{Symmetric}) \\
 S_1 (+) S_2 (-) - S_1 (-) S_2 (+) & \quad (\text{Antisymmetric}) \quad (I-13)
 \end{aligned}$$

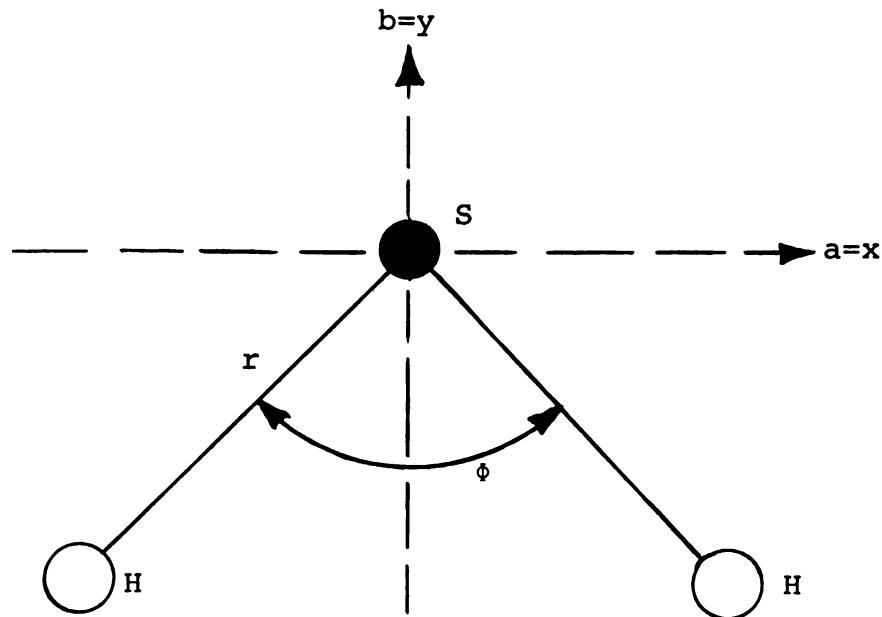
The number of symmetric (ortho) spin functions is three and the number of antisymmetric (para) is one in (I-13). To satisfy Fermi-Dirac statistics, the symmetric spin functions must be combined with the antisymmetric rotational functions  $\psi_{JK-K+}$  and the antisymmetric spin functions with the symmetric rotational functions. Table I shows that the ee and oo states of  $\psi_{JK-K+}$  are symmetric while the oe and eo states are antisymmetric under the operation  $C_2^b$ . Since there are three times as many symmetric spin states as antisymmetric spin states, the statistical weight of the antisymmetric rotational levels is three times greater than the statistical weight of the symmetric rotational levels. Thus, for a transition originating from the ground vibrational state, if  $(K_-+K_+)$  is an odd number in the ground rotational state its relative  $g_n$  factor is three.

Experimentally, it is confirmed that the odd component of an absorption line usually has a greater intensity than its even component.

### Coriolis-Type Perturbations

Coriolis-type perturbations occur in hydrogen sulfide between vibrational levels of different symmetry species as a consequence of molecular rotation. This effect is experimentally observed as an irregular deviation of the spectral absorption lines from those predicted by a Hamiltonian which assumes that the excited vibrational states are uncoupled (11). Justification for the existence of Coriolis-type perturbations usually comes from group theoretical consideration; however, for a pure Coriolis perturbation a simple classical picture may be used for visualizing the general effect. Both approaches will be discussed.

In order to correlate this discussion with that of others, the coordinates of the hydrogen sulfide molecule are chosen such that  $x = a$ ,  $y = b$  and  $z = c$  as shown in Fig. 3. The  $a$  and  $b$  axes lie in the plane formed by the molecule while  $c$  is perpendicular to this plane. The  $C_{2v}$  character table for the point group of the molecule is constructed in Table III to be consistent with the axis labeling chosen. The symmetry species of the rotations about and the translations along each axis are also given in Table III. By convention,  $A$  denotes species that are symmetric with respect to rotation about the symmetry axis  $b$  and  $B$  denotes

Fig. 3. Geometry of the  $\text{H}_2\text{S}$  MoleculeTable III. The  $\text{C}_{2v}$  Character Table

Species	E	$\text{C}_2$ (b)	$\sigma$ (bc)	$\sigma$ (ab)	
$\text{A}_1$	1	1	1	1	$\text{T}_b$
$\text{A}_2$	1	1	-1	-1	$\text{R}_b$
$\text{B}_1$	1	-1	1	-1	$\text{T}_c \text{ R}_a$
$\text{B}_2$	1	-1	-1	1	$\text{T}_a \text{ R}_c$

those that are antisymmetric. Thus three rotations  $R_a$ ,  $R_b$  and  $R_c$  have symmetry species  $B_1$ ,  $A_2$  and  $B_2$  respectively. The three approximate normal modes of  $H_2S$  are indicated in Fig. 4 along with the appropriate normal frequencies (12). Each normal mode is represented by the attached set of displacement vectors and may be assigned a symmetry species by examination of the manner in which the vectors transform under the operations of the  $C_{2v}$  point group. By one convention, lower case letters are used for vibrations while capital letters are reserved for representations generated by vibrational, vibronic and electronic wave functions (3b). Thus  $Q_1$ , the symmetrical bond stretching mode, and  $Q_2$ , the deformation mode, both have symmetry species  $a_1$  while  $Q_3$ , the asymmetric bond stretching mode, has species  $b_2$ .

The discussion by Herzberg is quite helpful for visualizing a pure Coriolis perturbation from a classical approach but due to a different choice of axis labeling, his symmetry species for normal mode  $Q_3$  is  $b_1$  instead of  $b_2$  (1b). The effect of the rotation  $R_c$  on the molecule as it vibrates in the normal mode  $Q_3$  is shown in Fig. 5. The Coriolis force  $2m \underline{v} \times \underline{\omega}$  acting on each nucleus mainly tends to excite normal mode  $Q_2$  with frequency  $\nu_3$ . To a slight extent the mode  $Q_1$  is also excited since the displacement vectors for  $Q_1$  and  $Q_2$  (which have the same symmetry species) are not strictly orthogonal to one another. Since the hydrogen sulfide normal frequency  $\nu_1$  is very close to  $\nu_3$ , the effect of the

Fig. 4. Normal Modes of H<sub>2</sub>S

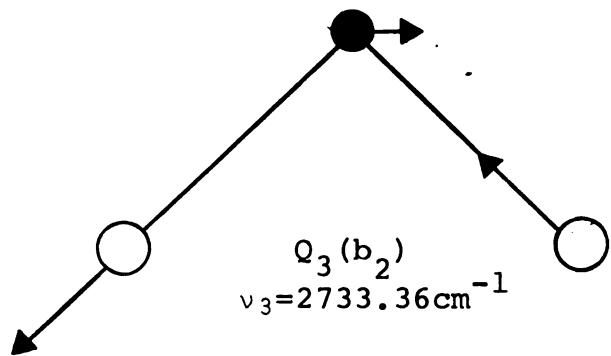
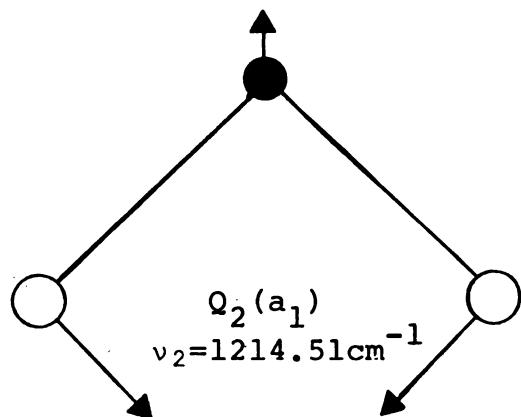
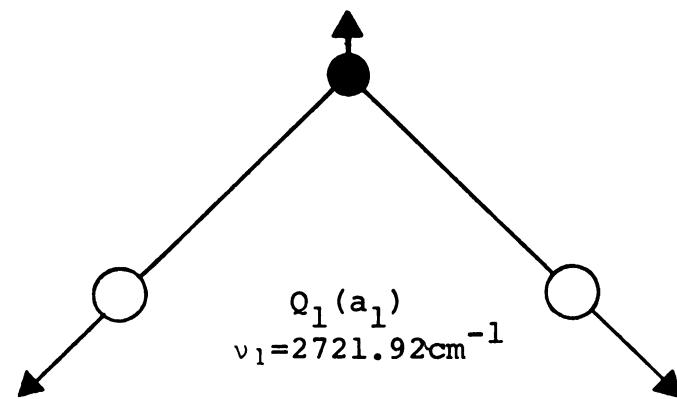
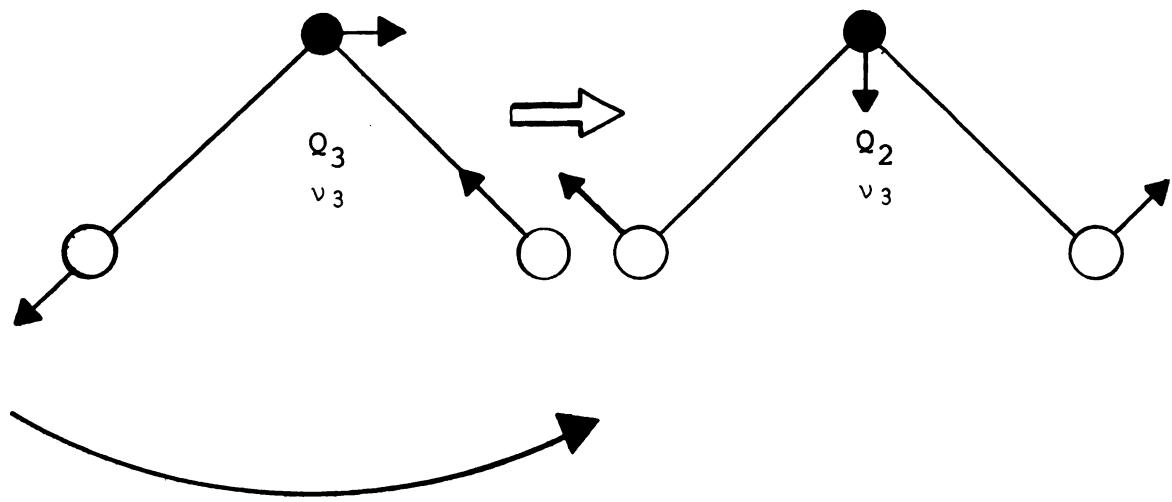


Fig. 5. Classical Coriolis Perturbation

Table IV. Direct Product Multiplication Table for  $C_{2v}$ 

	$A_1$	$A_2$	$B_1$	$B_2$
$A_1$	$A_1$	$A_2$	$B_1$	$B_2$
$A_2$	$A_2$	$A_1$	$B_2$	$B_1$
$B_1$	$B_1$	$B_2$	$A_1$	$A_2$
$B_2$	$B_2$	$B_1$	$A_2$	$A_1$

Coriolis interaction between  $Q_1$  and  $Q_3$  is actually greater than that between  $Q_2$  and  $Q_3$ . Thus the Coriolis resonance occurs between  $Q_1$  and  $Q_3$ .

Jahn's rule is often mentioned in the literature as a test for predicting which pairs of absorption bands are likely to be subject to Coriolis perturbation (13). One statement of Jahn's rule is that a Coriolis perturbation between two vibrational states is possible if the direct product of the two vibrational species involved contains the symmetry species of a rotation  $R_a$ ,  $R_b$  or  $R_c$ . The possible direct products for the  $C_{2v}$  symmetry species are given in Table IV; they may be confirmed from Table III (3c). It is readily seen from Table IV that the vibrational species  $a_1$  and  $b_2$  have only one direct product containing the species of a rotation. That is, the direct product of  $a_1$  and  $b_2$  contains  $B_2$  which is the species of  $R_c$ . Thus, by Jahn's rule the Coriolis perturbation shown in Fig. 5 is possible.

Jahn's rule is a specific application of the general group theoretical result used to evaluate (I-10) since perturbations between a pair of excited vibrational states  $v_i$  and  $v_j$  can occur when vibrational representation matrix elements of the type

$$\int \psi_{v_i}^* H_{op} \psi_{v_j} d\tau \quad (I-14)$$

are nonzero. Jahn's rule describes the special case when  $H_{op}$  in (I-14) is an angular momentum operator  $P_i$  because  $P_i$  has the species of a rotation  $R_i$  (lc). From a mathematical viewpoint, the nonvanishing of the coupling matrix element (I-14) is a necessary but not sufficient condition for a perturbation to occur. In addition, several other conditions must be satisfied. The two vibrational states involved must be close to each other in energy and differ from one another in vibrational quantum number  $v_k$  and  $v_n$  such that  $v_k$  in  $V_i$  changes to  $v_k \pm 1$  in  $V_j$  and  $v_n$  in  $V_i$  changes to  $v_n \pm 1$  in  $V_j$  in the harmonic approximation (14). This condition will be discussed in some detail in Chapter II. Also, there is a strictly dynamic condition in that the motion of the molecule must be such that the coupling matrix element (I-14) is not too small for a noticeable effect to occur.

Along with a pure Coriolis perturbation, a term of operator form  $P_x P_y$  has been found to contribute to the perturbation in hydrogen sulfide. This operator may be loosely classified as a Coriolis-type term because it causes a rotation-vibration interaction which has the same location in the vibrational array as the pure Coriolis interaction term. The effect of this term is discussed in Chapter II.

## CHAPTER II

### THE HAMILTONIAN OPERATOR

#### The Untransformed General Hamiltonian

The general molecular quantum - mechanical Hamiltonian is well known and may be found in the literature (15).

$$2H = \mu^{\frac{1}{4}} \sum_{\alpha\beta} (P_\alpha - p_\alpha) \mu_{\alpha\beta} \mu^{-\frac{1}{2}} (P_\beta - p_\beta) \mu^{\frac{1}{4}}$$

$$+ \mu^{\frac{1}{4}} \sum_s p_s^* \mu^{-\frac{1}{2}} p_s^* \mu^{\frac{1}{4}} + V(Q_s)$$
(II-1)

It is called the Darling - Dennison Hamiltonian although an earlier version originally was derived by Wilson and Howard (16). This is an exact expression involving only the Born - Oppenheimer approximation in its derivation. The components of total angular momentum are  $P_\alpha = \frac{\partial T}{\partial \omega_\alpha}$  and the components of internal angular momentum (angular momentum due to only vibration) are  $p_\alpha = \sum_{ss'} \zeta_{ss'}^\alpha Q_s p_{s'}^*$ . The  $Q_s$  represent mass adjusted normal coordinates and  $p_s^* = -im(\frac{\partial}{\partial Q_s})$  the conjugate momentum. The  $\zeta_{ss'}^\alpha$  are Coriolis coupling coefficients and will be discussed in detail for the nonlinear XYX molecule. The  $\mu$  and  $\mu_{\alpha\beta}$  depend on the normal coordinates and are given by (15)

$$\mu_{\alpha\beta} = (I'_{\gamma\gamma} I'_{\alpha\beta} + I'_{\alpha\gamma} I'_{\gamma\beta}) \mu$$

$$\mu_{\alpha\alpha} = (I'_{\beta\beta} I'_{\gamma\gamma} - I'_{\beta\gamma}^2) \mu$$

$$\mu^{-1} = \begin{bmatrix} I'_{xx} & -I'_{xy} & -I'_{xz} \\ -I'_{xy} & I'_{yy} & -I'_{yz} \\ -I'_{xz} & -I'_{yz} & I'_{zz} \end{bmatrix} \quad (\text{II-2})$$

where the moments of inertia in the principal axis system are given by

$$I'_{\alpha\alpha} = I_{\alpha\alpha}^e + \sum_s a_s^{\alpha\alpha} Q_s + \sum_{ss'} A'_{ss'}^{\alpha\alpha} Q_s Q_{s'},$$

$$I'_{\alpha\beta} = - \sum_s a_s^{\alpha\beta} Q_s - \sum_{ss'} A'_{ss'}^{\alpha\beta} Q_s Q_{s'},$$
(II-3)

Since the a's and A's will be treated later, they will not be discussed here. Finally,  $V = V(Q_s)$  represents the potential energy. In general, the Schroedinger equation of the Darling - Dennison Hamiltonian operator can not be solved exactly, so an approximate solution must be found.

In order to do this, the Hamiltonian was ordered in the following equivalent form by Goldsmith, Amat, and Nielsen (15):

$$\begin{aligned}
 2H = & \sum_{\alpha\beta} \mu_{\alpha\beta} P_\alpha P_\beta - \sum_{\alpha\beta} (p_\alpha \mu_{\alpha\beta} + \mu_{\alpha\beta} p_\alpha) P_\beta \\
 & + \sum_{\alpha\beta} p_\alpha \mu_{\alpha\beta} P_\beta + \mu^{\frac{1}{4}} \sum_{\alpha\beta} (p_\alpha \mu_{\alpha\beta}^{-\frac{1}{2}} (p_\beta \mu^{\frac{1}{4}})) \\
 & + \mu^{\frac{1}{4}} \sum_s (p_s * \mu^{-\frac{1}{2}} (p_s * \mu^{\frac{1}{4}})) + \sum_s p_s^* {}^2 + 2V
 \end{aligned} \tag{II-4}$$

The first term in (II-4) represents pure rotational energy, the next four represent Coriolis coupling energy, followed by the vibrational energy and the potential energy. Goldsmith, Amat and Nielsen have expanded  $\mu$  and  $\mu_{\alpha\beta}$  in power series as functions of the normal coordinates. Also, they have expanded the potential function  $V(Q_i)$  about an equilibrium configuration in a Taylor's series. Next the expansions for  $\mu_{\alpha\beta}$ ,  $\mu$ , and  $V$  are substituted into (II-4) and terms of like order are collected according to  $H = H_0 + \gamma H_1 + \gamma^2 H_2 + \dots$ . The following general results are found (to second order):

$$H_0 = \frac{1}{2} \sum_{\alpha} \frac{P_\alpha^2}{I_\alpha} + \frac{\kappa}{2} \sum_s \lambda_s^{\frac{1}{2}} \left( \frac{P_s^2}{\kappa^2} + q_s^2 \right) \tag{II-5}$$

$$H_1 = \frac{1}{2} \sum_{s\alpha\beta} \frac{\Omega_s^{(1)\alpha\beta}}{I_\alpha I_\beta} \left( \frac{\kappa^2}{\lambda_s} \right)^{\frac{1}{4}} q_s P_\alpha P_\beta$$

$$- \sum_{\alpha} \frac{P_\alpha P_\alpha}{I_\alpha} + hc \sum_{s,s',s''} k_{ss's''} q_s q_{s'} q_{s''} \tag{II-6}$$

$$H_2 = \frac{1}{2} \sum_{ss'} \sum_{\alpha\beta} \frac{\Omega_{ss'}^{(2)\alpha\beta}}{I_\alpha I_\beta} \left( \frac{\kappa^4}{\lambda_s \lambda_{s'}} \right)^{\frac{1}{4}} q_s q_{s'} P_\alpha P_\beta$$

$$\begin{aligned}
 & - \frac{1}{2} \sum_s \sum_{\alpha\beta} \frac{\Omega_s^{(1)\alpha\beta}}{I_\alpha I_\beta} \left(\frac{\hbar^2}{\lambda_s}\right)^{\frac{1}{4}} (p_\alpha q_s + q_s p_\alpha) p_\beta \\
 & + \frac{1}{2} \sum_\alpha \frac{p_\alpha^2}{I_\alpha} + hc \sum_{ss's''s'''} k_{ss's''s'''} q_s q_s' q_{s''} q_{s'''}
 \end{aligned} \tag{II-7}$$

Goldsmith, Amat, and Nielsen have carried this expansion through  $H_4$ , but for this work only terms through  $H_2$  will be considered.

The notation introduced in (II-5), (II-6) and (II-7) includes the dimensionless normal coordinate  $q_s = (\frac{\lambda_s}{\hbar^2})^{\frac{1}{4}} Q_s$ ,  $p_s = -i\hbar \frac{\partial}{\partial q_s}$ , and  $\lambda_s = (2\pi c \omega_s)^2$  where  $\omega_s$  is the frequency (in  $\text{cm}^{-1}$ ) of the  $s$  th normal mode. The  $k$ 's are molecular force constants. The  $\Omega$ 's used in (II-6) and (II-7) are defined in a principal axis system as

$$\Omega_s^{(1)\alpha\beta} = -a_s^{\alpha\beta}$$

$$\Omega_{ss'}^{(2)\alpha\beta} = -A_{ss'}^{\alpha\beta} + \sum_{s''} \zeta_{ss''}^\alpha \zeta_{s's''}^\beta + \sum_{\delta=x,y,z} \frac{a_s^{\alpha\delta} a_s^{\beta\delta}}{I_\delta} \tag{II-8}$$

To simplify the notation, the conventional "e" superscript on the equilibrium moments of inertia has been dropped. Also, since there are no essential degeneracies for the nonlinear XYX molecule, the degeneracy index  $\sigma$  has been eliminated.

Table V. The Nonvanishing Coefficients  $a_s^{\alpha\beta}$

$a_1^{xx} = 2I_x^{\frac{1}{2}} \sin\gamma$	$a_2^{xx} = 2I_x^{\frac{1}{2}} \cos\gamma$
$a_1^{yy} = 2I_y^{\frac{1}{2}} \cos\gamma$	$a_2^{yy} = -2I_y^{\frac{1}{2}} \sin\gamma$
$a_1^{zz} = a_1^{xx} + a_1^{yy} = -2I_z^{\frac{1}{2}} \zeta_{23}$	$a_2^{zz} = a_2^{xx} + a_2^{yy} = 2I_z^{\frac{1}{2}} \zeta_{13}$
$a_3^{xy} = -2(I_x I_y / I_z)^{\frac{1}{2}}$	
Where:	
$\sin\gamma = \frac{-1}{2} \left( 1 - \frac{(k_{11} - k_{22})}{[(k_{11} - k_{22})^2 + 4k_{12}^2]^{\frac{1}{2}}} \right)^{\frac{1}{2}}$	
$\zeta_{13}^z = -\zeta_{31}^z = (I_x/I_z)^{\frac{1}{2}} \cos\gamma - (I_y/I_z)^{\frac{1}{2}} \sin\gamma$	
$\zeta_{23}^z = -\zeta_{32}^z = -(I_x/I_z)^{\frac{1}{2}} \sin\gamma - (I_y/I_z)^{\frac{1}{2}} \cos\gamma$	
$(\zeta_{13}^z)^2 + (\zeta_{23}^z)^2 = 1$	

The Untransformed Hamiltonian Operator for the Nonlinear XYX Molecule

In this section, the results of Chung and Parker (17) from Table V will be used to apply the expansions for  $H_1$  and  $H_2$  to the nonlinear XYX molecule.

Since there are only three components of the total angular momentum and three normal modes of vibration,  $H_0$  can be written immediately as

$$H_0 = \frac{1}{2} \sum_{\alpha=x,y,z} \frac{P_\alpha^2}{I_\alpha} + \frac{\hbar}{2} \sum_{s=1}^3 \lambda_s^{\frac{1}{2}} \left( \frac{P_s^2}{\hbar} + q_s^2 \right) \quad (\text{II-9})$$

$H_0$  gives the familiar rigid rotator and harmonic oscillator energies. The development of  $H_1$  may be done by separately considering the three sums of (II-6) and by noting that  $\Omega_s^{(1)\alpha\beta} = -a_s^{\alpha\beta}$  from (II-8). Table V includes the nonvanishing coefficients  $a_s^{\alpha\beta}$  as listed by Chung and Parker for the nonlinear XYX molecule. The first sum in (II-6) may be written

$$\frac{1}{2} \sum_{\alpha,\beta} \sum_s \frac{(-a_s^{\alpha\beta})}{I_\alpha I_\beta} \left( \frac{\hbar^2}{\lambda_s} \right)^{\frac{1}{4}} q_s P_\alpha P_\beta$$

$$= - \frac{\hbar^2}{2} \sum_{s=1}^3 \frac{q_s}{\lambda_s^{\frac{1}{4}}} \left[ \frac{a_s^{xx} P_x^2}{I_x^2} + \frac{a_s^{yy} P_y^2}{I_y^2} + \frac{a_s^{zz} P_z^2}{I_z^2} + \frac{a_s^{xy}}{I_x I_y} [P_x, P_y] \right]$$

$$\begin{aligned}
&= -\frac{1}{\kappa^2} \left( \frac{q_1 \sin \gamma}{\lambda_1^{1/4}} + \frac{q_2 \cos \gamma}{\lambda_2^{1/4}} \right) \frac{P_x^2}{I_{x^2}^3} - \frac{1}{\kappa^2} \left( \frac{q_1 \cos \gamma}{\lambda_1^{1/2}} - \frac{q_2 \sin \gamma}{\lambda_2^{1/4}} \right) \frac{P_y^2}{I_{y^2}^3} \\
&+ \frac{1}{\kappa^2} \left( \frac{q_1}{\lambda_1^{1/4}} \zeta_{23} - \frac{q_2}{\lambda_2^{1/4}} \zeta_{13} \right) \frac{P_z^2}{I_{x^2}^3} + \frac{1}{\kappa^2} \left( \frac{q_3}{\lambda_3^{1/4}} \right) \frac{[P_x, P_y]^{\frac{1}{2}}}{(I_x I_y I_z)^{\frac{1}{2}}} \quad (\text{II-10})
\end{aligned}$$

The z superscript has been dropped from the Coriolis term and  $[P_x, P_y]^+ = P_x P_y + P_y P_x$  in (II-10).

The second sum in (II-6) may be simplified using Table V and the definition of  $p_\alpha$ :

$$\begin{aligned}
-\sum_\alpha \frac{p_\alpha P_\alpha}{I_\alpha} &= -\frac{p_z P_z}{I_z} = -\sum_{ss} \zeta_{ss} (Q_s p_s^* s) \frac{P_z}{I_z} \\
&= -\sum_{ss} \zeta_{ss} \left( \frac{\lambda_s}{\lambda_s} \right)^{\frac{1}{4}} q_s p_s \left( \frac{P_z}{I_z} \right) \\
&= -\zeta_{31} \left[ \left( \frac{\lambda_1}{\lambda_3} \right)^{\frac{1}{4}} q_3 p_1 - \left( \frac{\lambda_3}{\lambda_1} \right)^{\frac{1}{4}} q_1 p_3 \right] \frac{P_z}{I_z} - \zeta_{23} \left[ \left( \frac{\lambda_3}{\lambda_2} \right)^{\frac{1}{4}} q_2 p_3 - \left( \frac{\lambda_2}{\lambda_3} \right)^{\frac{1}{4}} p_2 q_3 \right] \frac{P_z}{I_z} \quad (\text{II-11})
\end{aligned}$$

The last sum in (II-6) is reduced by requiring that  $V(q_1, q_2, q_3) = V(q_1, q_2, -q_3)$  (18).

$$\begin{aligned}
&\text{hc} \sum_{ss's''} k_{ss's''} q_s q_s q_s q_s \\
&= \text{hc} k_{111} q_1^3 + \text{hc} k_{222} q_2^3 + 3 \text{hc} k_{112} q_1^2 q_2 + 3 \text{hc} k_{122} q_1 q_2^2
\end{aligned}$$

$$+ 3hck_{133}q_1q_3^2 + 3hck_{233}q_2q_3^2 \quad (II-12)$$

where the convention  $k_{211} + k_{112} + k_{121} = 3k_{112}$ , etc., is used.

The development of  $H_2$  is more tedious. When the results of Table V and the A's from Appendix I are applied to the  $\Omega_{ss}^{(2)\alpha\beta}$  in (II-8) the first sum in (II-7) becomes

$$\begin{aligned} & \frac{1}{2} \sum_{ss} \sum_{\alpha\beta} \frac{\Omega_{ss}^{(2)\alpha\beta}}{I_\alpha I_\beta} \left( \frac{m^4}{\lambda_s \lambda_s} \right)^{\frac{1}{4}} q_s q_s P_\alpha P_\beta \\ &= \frac{3\pi}{2} \left[ \left( \frac{q_1 \sin \gamma}{\lambda_1^{\frac{1}{4}}} + \frac{q_2 \cos \gamma}{\lambda_2^{\frac{1}{4}}} \right)^2 + \frac{q_3^2 I_x}{\lambda_3^{\frac{1}{2}} I_z} \right] \frac{P_x^2}{I_x^2} \\ &+ \frac{3\pi}{2} \left[ \left( \frac{q_1 \cos \gamma}{\lambda_1^{\frac{1}{4}}} - \frac{q_2 \sin \gamma}{\lambda_2^{\frac{1}{4}}} \right)^2 + \frac{q_3^2 I_y}{\lambda_3^{\frac{1}{2}} I_z} \right] \frac{P_y^2}{I_y^2} \\ &+ \frac{3\pi}{2} \left[ \frac{q_1 \zeta_{23}}{\lambda_1^{\frac{1}{4}}} - \frac{q_2 \zeta_{13}}{\lambda_2^{\frac{1}{4}}} \right]^2 \frac{P_z^2}{I_z^2} \\ &+ \frac{3\pi}{2} \left( \frac{q_3}{\lambda_3^{\frac{1}{4}}} \right) \left[ \frac{q_2 (I_x^{\frac{1}{2}} \sin \gamma - I_y^{\frac{1}{2}} \cos \gamma)}{\lambda_2^{\frac{1}{4}}} \right. \\ &\quad \left. - q_1 \frac{(I_x^{\frac{1}{2}} \cos \gamma + I_y^{\frac{1}{2}} \sin \gamma)}{\lambda_1^{\frac{1}{4}}} \right] \frac{[P_x, P_y]}{I_x I_y I_z^{\frac{1}{2}}} \end{aligned} \quad (II-13)$$

The second sum in  $H_2$  may be evaluated by using  $p_\alpha = p_z$  and Table V since  $\Omega_s^{(1)\alpha\beta} = -a_s^{\alpha\beta}$ .

$$\begin{aligned}
 & -\frac{1}{2} \sum_{s \in \alpha \beta} \frac{\Omega_s^{(1)\alpha\beta}}{I_\alpha I_\beta} \left( \frac{\pi^2}{\lambda_s} \right)^{\frac{1}{4}} (p_\alpha q_s + q_s p_\alpha) p_\beta = \\
 & \frac{\frac{1}{2} p_z}{I_z^{\frac{3}{2}}} \left[ 2 \zeta_{13} \zeta_{23} \lambda_3^{\frac{1}{4}} \left[ \frac{q_2^2}{\lambda_2^{\frac{1}{2}}} - \frac{q_1^2}{\lambda_1^{\frac{1}{2}}} \right] p_3 + \frac{\zeta_{13} \zeta_{23}}{\lambda_3^{\frac{1}{4}}} ([p_1, q_1]^+ - [p_2, q_2]^+) q_3 \right. \\
 & \left. + 2 \left( \frac{\lambda_3}{\lambda_1 \lambda_2} \right)^{\frac{1}{4}} (\zeta_1^2 - \zeta_2^2) q_1 q_2 p_3 + 2 \left[ \frac{\zeta_2^2 (\lambda_2)}{\lambda_3^{\frac{1}{4}}} q_1 p_2 - \zeta_1^2 (\frac{\lambda_1}{\lambda_2})^{\frac{1}{4}} p_1 q_2 \right] q_3 \right]
 \end{aligned} \tag{II-14}$$

The third sum of  $H_2$  is given by

$$\begin{aligned}
 & \frac{1}{2} \sum_{\alpha} \frac{p_\alpha^2}{I_\alpha} = \frac{1}{2} \frac{p_z^2}{I_z} \\
 & = \frac{\zeta_{13}^2}{2I_z} \left[ \left( \frac{\lambda_3}{\lambda_1} \right)^{\frac{1}{2}} q_1^2 p_3^2 + \left( \frac{\lambda_1}{\lambda_3} \right)^{\frac{1}{2}} q_3^2 p_1^2 - q_1 p_1 p_3 q_3 - p_1 q_1 q_3 p_3 \right] \\
 & + \frac{\zeta_{23}^2}{2I_z} \left[ \left( \frac{\lambda_3}{\lambda_2} \right)^{\frac{1}{2}} q_2^2 p_3^2 + \left( \frac{\lambda_2}{\lambda_3} \right)^{\frac{1}{2}} p_2^2 q_3^2 - q_2 p_2 p_3 q_3 - p_2 q_2 q_3 p_3 \right] \\
 & + \frac{\zeta_{13} \zeta_{23}}{I_z} \left[ \left( \frac{\lambda_3^2}{\lambda_1 \lambda_2} \right)^{\frac{1}{4}} q_1 q_2 p_3^2 + \left( \frac{\lambda_1 \lambda_2}{\lambda_3^2} \right)^{\frac{1}{4}} p_1 p_2 q_3^2 \right] \\
 & - \frac{\zeta_{13} \zeta_{23}}{2I_z} \left[ \left( \frac{\lambda_1}{\lambda_2} \right)^{\frac{1}{4}} p_1 q_2 + \left( \frac{\lambda_2}{\lambda_1} \right)^{\frac{1}{4}} q_1 p_2 \right] [q_3, p_3]^+
 \end{aligned} \tag{II-15}$$

For completeness, the last sum in  $H_2$  may be written (18)

$$\begin{aligned}
 & hc \sum_{ss's''s'''} k_{ss's''s'''} q_s q_s' q_s'' q_s''' \\
 & = hc k_{1111} q_1^4 + hc k_{2222} q_2^4 + hc k_{3333} q_3^4 \\
 & + 4hc k_{1112} q_1^3 q_2 + 4hc k_{1222} q_1 q_2^3 + 6hc k_{1122} q_1^2 q_2^2 \\
 & + 6hc k_{1133} q_1^2 q_3^2 + 6hc k_{2233} q_2^2 q_3^2 + 12hc k_{1233} q_1 q_2 q_3^2 \\
 & \quad .
 \end{aligned} \tag{II-16}$$

The convention  $(k_{1112} + k_{1121} + k_{1211} + k_{2111}) = 4k_{1112}$  has been used.

Eqns. (II-5) through (II-7) will now be specialized to the nonlinear XYX molecule.

$$\begin{aligned}
 H_O &= \frac{1}{2} \left( \frac{P_x^2}{I_x} + \frac{P_y^2}{I_y} + \frac{P_z^2}{I_z} \right) \\
 &+ \frac{\hbar}{2} [\lambda_1^{\frac{1}{2}} \left( \frac{p_1^2}{\hbar^2} + q_1^2 \right) + \lambda_2^{\frac{1}{2}} \left( \frac{p_2^2}{\hbar^2} + q_2^2 \right) + \lambda_3^{\frac{1}{2}} \left( \frac{p_3^2}{\hbar^2} + q_3^2 \right)] \quad .
 \end{aligned} \tag{II-17}$$

$$\begin{aligned}
 H_1 &= -\hbar^{\frac{1}{2}} \left( \frac{q_1 \sin \gamma}{\lambda_1^{\frac{1}{4}}} + \frac{q_2 \cos \gamma}{\lambda_2^{\frac{1}{4}}} \right) \frac{P_x^2}{I_x^{\frac{3}{2}}} - \hbar^{\frac{1}{2}} \left( \frac{q_1 \cos \gamma}{\lambda_1^{\frac{1}{4}}} - \frac{q_2 \sin \gamma}{\lambda_2^{\frac{1}{4}}} \right) \frac{P_y^2}{I_y^{\frac{3}{2}}} \\
 &+ \hbar^{\frac{1}{2}} \left( \frac{q_1 \zeta_{23}}{\lambda_1^{\frac{1}{4}}} - \frac{q_2 \zeta_{13}}{\lambda_2^{\frac{1}{4}}} \right) \frac{P_z^2}{I_z^{\frac{3}{2}}} + \frac{\hbar^{\frac{1}{2}} q_3}{\lambda_3^{\frac{1}{4}}} \frac{[P_x, P_y]^+}{(I_x I_y I_z)^{\frac{1}{2}}}
 \end{aligned}$$

$$\begin{aligned}
& -\zeta_{31} \left[ \left( \frac{\lambda_1}{\lambda_3} \right)^{\frac{1}{4}} p_1 q_3 - \left( \frac{\lambda_3}{\lambda_1} \right)^{\frac{1}{4}} q_1 p_3 \right] \frac{P_z}{I_z} - \zeta_{23} \left[ \left( \frac{\lambda_3}{\lambda_2} \right)^{\frac{1}{4}} q_2 p_3 - \left( \frac{\lambda_2}{\lambda_3} \right)^{\frac{1}{4}} p_2 q_3 \right] \frac{P_z}{I_z} \\
& + hck_{111} q_1^3 + hck_{222} q_2^3 + 3hck_{112} q_1^2 q_2 \\
& + 3hck_{122} q_1 q_2^2 + 3hck_{133} q_1 q_3^2 + 3hck_{233} q_2 q_3^2
\end{aligned} \tag{II-18}$$

$$\begin{aligned}
H_2 &= \frac{3\kappa}{2} \left[ \left( \frac{q_1 \sin \gamma}{\lambda_1^{\frac{1}{4}}} + \frac{q_2 \cos \gamma}{\lambda_2^{\frac{1}{4}}} \right)^2 + \frac{q_3^2}{\lambda_3^{\frac{1}{2}}} \left( \frac{I_x}{I_z} \right) \right] \frac{P_x^2}{I_x^2} \\
&+ \frac{3\kappa}{2} \left[ \left( \frac{q_1 \cos \gamma}{\lambda_1^{\frac{1}{4}}} - \frac{q_2 \sin \gamma}{\lambda_2^{\frac{1}{4}}} \right)^2 + \frac{q_3^2}{\lambda_3^{\frac{1}{2}}} \left( \frac{I_y}{I_z} \right) \right] \frac{P_y^2}{I_y^2} \\
&+ \frac{3\kappa}{2} \left( \frac{q_1 \zeta_{23}}{\lambda_1^{\frac{1}{4}}} - \frac{q_2 \zeta_{13}}{\lambda_2^{\frac{1}{4}}} \right)^2 \frac{P_z^2}{I_z^2} \\
&+ \frac{3\kappa}{2} \frac{q_3}{\lambda_3^{\frac{1}{4}}} \left[ \frac{q_2}{\lambda_2^{\frac{1}{4}}} (I_x^{\frac{1}{2}} \sin \gamma - I_y^{\frac{1}{2}} \cos \gamma) - \frac{q_1}{\lambda_1^{\frac{1}{4}}} (I_x^{\frac{1}{2}} \cos \gamma + I_y^{\frac{1}{2}} \sin \gamma) \right] \frac{[P_x, P_y]}{I_x I_y I_z^{\frac{1}{2}}} \\
&+ \frac{\frac{1}{n^2} P_z}{I_z^{\frac{3}{2}}} \left[ \begin{aligned}
& 2\zeta_{13} \zeta_{23} \lambda_3^{\frac{1}{4}} \left( \frac{q_2^2}{\lambda_2^{\frac{1}{2}}} - \frac{q_1^2}{\lambda_1^{\frac{1}{2}}} \right) p_3 + \frac{\zeta_{13} \zeta_{23}}{\lambda_3^{\frac{1}{4}}} ([p_1, q_1]^+ - [p_2, q_2]^+) q_3 \\
& + 2 \left( \frac{\lambda_3}{\lambda_1 \lambda_2} \right)^{\frac{1}{4}} \left( \zeta_{13}^2 - \zeta_{23}^2 \right) q_1 q_2 p_3 + \frac{2}{\lambda_3^{\frac{1}{4}}} \left( \zeta_{23}^2 \left( \frac{\lambda_2}{\lambda_1} \right)^{\frac{1}{4}} q_1 p_2 - \zeta_{13}^2 \left( \frac{\lambda_1}{\lambda_2} \right)^{\frac{1}{4}} p_1 q_2 \right) q_3
\end{aligned} \right]
\end{aligned}$$

$$\begin{aligned}
& + \frac{\zeta_{13}^2}{2I_z} \left[ \left( \frac{\lambda_3}{\lambda_1} \right)^{\frac{1}{2}} q_1^2 p_3^2 + \left( \frac{\lambda_1}{\lambda_3} \right)^{\frac{1}{2}} q_3^2 p_1^2 - q_1 p_1 p_3 q_3 - p_1 q_1 q_3 p_3 \right] \\
& + \frac{\zeta_{23}^2}{2I_z} \left[ \left( \frac{\lambda_3}{\lambda_2} \right)^{\frac{1}{2}} q_2^2 p_3^2 + \left( \frac{\lambda_2}{\lambda_3} \right)^{\frac{1}{2}} p_2^2 q_3^2 - q_2 p_2 p_3 q_3 - p_2 q_2 q_3 p_3 \right] \\
& + \frac{\zeta_{1323}^2}{I_z} \left[ \left( \frac{\lambda_3}{\lambda_1 \lambda_2} \right)^{\frac{1}{4}} q_1 q_2 p_3^2 + \left( \frac{\lambda_1 \lambda_2}{\lambda_3^2} \right)^{\frac{1}{4}} p_1 p_2 q_3^2 \right] + hck_{1111} q_1^4 + hck_{2222} q_2^4 \\
& - \frac{\zeta_{1323}^2}{2I_z} \left[ \left( \frac{\lambda_1}{\lambda_2} \right)^{\frac{1}{4}} p_1 q_2 + \left( \frac{\lambda_2}{\lambda_1} \right)^{\frac{1}{4}} q_1 p_2 \right] [q_3, p_3]^+ + hck_{3333} q_3^4 + 4hck_{1112} q_1^3 q_2 \\
& + 4hck_{1222} q_1 q_2^3 + 6hck_{1122} q_1^2 q_2^2 + 6hck_{1133} q_1^2 q_3^2 + 6hck_{2233} q_2^2 q_3^2 \\
& + 12hck_{1233} q_1 q_2 q_3^2 \tag{II-19}
\end{aligned}$$

### Examination of the Untransformed Hamiltonian Operator

When a vibration-rotation resonance is present, the conventional methods for diagonalizing the Hamiltonian in the vibrational representation are usually no longer valid. The two common methods of diagonalizing the Hamiltonian to second order require the use of either a conventional contact transformation, e.g. the Herman-Shaffer operator, or the tedious but straightforward application of nondegenerate perturbation theory (19) to obtain the equivalent results. It is useful to use second order nondegenerate perturbation theory to examine the Hamiltonian operator (II-17) through (II-19) for the case of a Coriolis resonance. The general solution for an eigenvalue in the vibrational representation

is given by

$$\langle v | H' | v \rangle = \langle v | H_0 + H_2 | v \rangle + \sum_{v'}' \frac{|\langle v | H_1 | v' \rangle|^2}{(E_v - E_{v'})} \quad (\text{II-20})$$

since  $H_1$  has no diagonal elements. The usual approximations have been made in (II-20), namely that any rotational contributions in the energy denominator will be small compared to the vibrational energy contributions and that

$$E_v = \pi \sum_i (v_i + \frac{1}{2}) \lambda_i^{\frac{1}{2}} \quad (\text{II-21})$$

In Chapter I, the general conditions for the existence of Coriolis resonance have been outlined; the specific application to hydrogen sulfide will be used here. Since  $\lambda_1^{\frac{1}{2}} \approx \lambda_3^{\frac{1}{2}}$  for hydrogen sulfide, it follows immediately from (II-20) and (II-21) that a resonance condition exists when the set of vibrational quantum numbers satisfies the condition

$$v : v_1, v_2, v_3$$

$$v' : v_1^{\pm 1}, v_2, v_3^{\mp 1}$$

(II-22)

That is, if the conditions (II-22) are satisfied and  $\lambda_1^{\frac{1}{2}} \approx \lambda_3^{\frac{1}{2}}$ , then the energy denominator of (II-20) is given by

$$E_v - E_{v'} = \pm \hbar [\lambda_3^{\frac{1}{2}} - \lambda_1^{\frac{1}{2}}] \rightarrow 0 \quad (\text{II-23})$$

In this case, nondegenerate perturbation theory may no longer be valid and some form of degenerate perturbation theory must be applied to diagonalize the Hamiltonian. In essence, this means that the terms affected by the resonance must be diagonalized exactly.

The off-diagonal vibrational matrix elements of  $H$  [(II-17), (II-18) and (II-19)] must be searched to determine which of them contribute to the resonance. Of the one hundred and fifty-two off-diagonal elements, only those of the form  $(v_1, v_2, v_3 | H | v_1 \pm 1, v_2, v_3 \mp 1)$  can contribute for the hydrogen sulfide molecule. To evaluate these elements in the vibrational representation, harmonic oscillator matrix elements are used (20).

$$(v_1, v_2, v_3 | H_1 + H_2 | v_1 + 1, v_2, v_3 - 1)$$

$$= \hbar \left\{ -i \frac{\zeta}{I_3} \left( \lambda_1^{\frac{1}{2}} + \lambda_3^{\frac{1}{2}} \right) \frac{P_z}{I_z} - \left( \frac{3}{2} \right) \left( I_x^{\frac{1}{2}} \cos \gamma + I_y^{\frac{1}{2}} \sin \gamma \right) \frac{[P_x, P_y]^+}{I_x I_y I_z^{\frac{1}{2}}} \right\} \frac{[(v_1 + 1) v_3]^{\frac{1}{2}}}{2(\lambda_1 \lambda_3)^{\frac{1}{4}}} \quad (\text{II-24})$$

$$(v_1, v_2, v_3 | H_1 + H_2 | v_1 - 1, v_2, v_3 + 1)$$

$$= \hbar \left\{ i \frac{\zeta}{I_3} \left( \lambda_1^{\frac{1}{2}} + \lambda_3^{\frac{1}{2}} \right) \frac{P_z}{I_z} - \left( \frac{3}{2} \right) \left( I_x^{\frac{1}{2}} \cos \gamma + I_y^{\frac{1}{2}} \sin \gamma \right) \frac{[P_x, P_y]^+}{I_x I_y I_z^{\frac{1}{2}}} \right\} \frac{[v_1 (v_3 + 1)]^{\frac{1}{2}}}{2(\lambda_1 \lambda_3)^{\frac{1}{4}}} \quad (\text{II-25})$$

Note that (II-24) and (II-25) will have a denominator of the form (II-23) if the non-degenerate perturbation diagonalization (II-20) is used. In general, for the case  $\lambda_1^{\frac{1}{2}} \approx \lambda_3^{\frac{1}{2}}$  the submatrices containing (II-24) will have to be diagonalized exactly using degenerate perturbation theory.

It is interesting to note that Nielsen (21) modified the conventional Herman-Shaffer operator so that the  $\zeta_{13}$  terms are left in an untransformed submatrix after the transformation is applied. That submatrix must then be diagonalized exactly. However, for asymmetric top molecules such as ozone (22) and hydrogen sulfide, this procedure does not seem to be sufficient as Nielsen tacitly assumed that the magnitude of the  $P_z$  term in (II-24) and (II-25) is much greater than the  $[P_x, P_y]^+$  term and the latter could therefore be neglected. The next section utilizes some numerical estimates to show that this assumption is probably not true for hydrogen sulfide. Thus the  $[P_x, P_y]^+$  term must be taken into account after Nielsen's modified contact transformation has been applied.

#### A Numerical Investigation of the Resonance Terms

To evaluate the terms in (II-24) and (II-25), it is necessary to get a rough estimate for the values of the force constants and use this to calculate  $\sin\gamma$ . The necessary force constants can be estimated by using isotopic substitution as discussed in Appendix II.

From Table V,

$$\zeta_{13} = \left( \frac{I_x}{I_z} \right)^{\frac{1}{2}} \cos \gamma - \left( \frac{I_y}{I_z} \right)^{\frac{1}{2}} \sin \gamma \quad (\text{II-26})$$

and

$$\sin \gamma = \frac{1}{\sqrt{2}} \left[ 1 - \frac{(k_{11} - k_{22})}{[(k_{11} - k_{22})^2 + 4k_{12}^2]^{\frac{1}{2}}} \right]^{\frac{1}{2}} \quad (\text{II-27})$$

The squares of the normal frequencies (in radians per second) are given by the following equations (17) :

$$\lambda_1 = \frac{1}{2}(k_{11} + k_{22}) + \frac{1}{2}[(k_{11} - k_{22})^2 + 4k_{12}^2]^{\frac{1}{2}}$$

$$\lambda_2 = \frac{1}{2}(k_{11} + k_{22}) - \frac{1}{2}[(k_{11} - k_{22})^2 + 4k_{12}^2]^{\frac{1}{2}}$$

$$\lambda_3 = k_{33}$$

(II-28)

where  $\lambda_s^{\frac{1}{2}} = 2\pi c \omega_s$  with  $\omega_s$  in  $\text{cm.}^{-1}$

From (II-28)

$$(\lambda_1 - \lambda_2) = [(k_{11} - k_{22})^2 + 4k_{12}^2]^{\frac{1}{2}} \quad (\text{II-29})$$

To complete the evaluation of  $\sin \gamma$ , isotopic substitution between hydrogen sulfide and deuterium sulfide is used to estimate  $(k_{11} - k_{22})$ . From Appendix II

$$k_{22} = \frac{(2m_H + M_S) [m_H(\lambda_1 + \lambda_2)^H - m_D(\lambda_1 + \lambda_2)^D]}{2 m_H [m_H - m_D]} \quad (\text{II-30})$$

and

$$k_{11} = \frac{[m_H(2m_D + M_S)(\lambda_1 + \lambda_2)^H - m_D(2m_H + M_S)(\lambda_1 + \lambda_2)^D]}{2 m_H [m_D - m_H]} \quad (\text{II-31})$$

As a check on (II-30) and (II-31) we note that

$$(\lambda_1 + \lambda_2)^H = k_{11} + k_{22} \quad (\text{II-32})$$

in agreement with the results found when equations (II-28) are added together.

There is enough information to find an estimate for  $\sin \gamma$  (II-27) from experimental values since combining (II-29), (II-30) and (II-31) gives:

$$\frac{(k_{11} - k_{22})}{[(k_{11} - k_{22})^2 + 4k_{12}^2]^{\frac{1}{2}}} = \frac{[(\lambda_1 + \lambda_2)^H m_H(m_D + m_H + M_S) - (\lambda_1 + \lambda_2)^D m_D(2m_H + M_S)]}{m_H(m_D - m_H)(\lambda_1 - \lambda_2)^H} \quad (\text{II-33})$$

The masses (23), in atomic mass units, are:

$$\begin{aligned} m_{\text{Hydrogen}} &= 1.00782522 \\ m_{\text{Deuterium}} &= 2.0141022 \\ M_{\text{Sulfur}} &= 31.972074 \end{aligned}$$

The values of the normal frequencies of hydrogen sulfide (12) are

$$\omega_1 = 2721.92 \text{ cm}^{-1}$$

$$\omega_2 = 1214.51 \text{ cm}^{-1}$$

and the normal frequencies of deuterium sulfide (24) are

$$\omega_1 = 1952.98 \text{ cm}^{-1}$$

$$\omega_2 = 872.17 \text{ cm}^{-1}$$

From (II-33) it follows that:

$$\sin \gamma \doteq .6984$$

$$\cos \gamma \doteq .7157$$

$$\gamma \doteq 44^{\circ}18' \quad (\text{II-34})$$

Using our published values of the equilibrium moments of inertia (25),

$$I_x = 2.7046 \times 10^{-40} \text{ gm. - cm.}^2$$

$$I_y = 3.0954 \times 10^{-40} \text{ gm. - cm.}^2$$

$$I_z = 5.8000 \times 10^{-40} \text{ gm. - cm.}^2$$

and (II-34) may be used to find  $\zeta_{13}$  from (II-26).

$$\zeta_{13} \doteq (.53368)^{\frac{1}{2}} \sin \gamma - (.46632)^{\frac{1}{2}} \cos \gamma \doteq -.0214 \quad (\text{II-35})$$

Finally, numerical estimates for the coefficients of the rotational operators in (II-24) and (II-25) may be found. In the following, the coefficients of  $P_z$  and  $[P_x, P_y]^+$  have been divided by  $hc$  to give term values in  $\text{cm}^{-1}$  and the

substitutions  $\lambda_s = 4\pi^2 c^2 \omega_s^2$  and  $I_x = h/(8\pi^2 cA)$ , etc., have been made:

$$i\zeta_{13} \left[ \left( \frac{\omega_1}{\omega_3} \right)^{\frac{1}{2}} + \left( \frac{\omega_3}{\omega_1} \right)^{\frac{1}{2}} \right] C \left( \frac{P_z}{\hbar} \right) \sqrt{(v_i+1)v_j} \equiv -i(.2075) \left( \frac{P_z}{\hbar} \right) \sqrt{(v_i+1)v_j} \quad (\text{II-36})$$

$$\frac{6AB}{(\omega_1 \omega_3)^{\frac{1}{2}}} \left[ \left( \frac{C}{A} \right)^{\frac{1}{2}} \cos \gamma + \left( \frac{C}{B} \right)^{\frac{1}{2}} \sin \gamma \right] \frac{[P_x, P_y]^+ \sqrt{(v_i+1)v_j}}{\hbar^2} \equiv \\ (.1028) \frac{[P_x, P_y]^+ \sqrt{(v_i+1)v_j}}{\hbar^2} \quad (\text{II-37})$$

where  $i=1$ ,  $j=3$  in (II-24) and  $i=3$ ,  $j=1$  in (II-25).

So these calculations indicate that the  $[P_x, P_y]^+$  term should not be neglected in an accurate treatment of hydrogen sulfide. This was also found to be the case for ozone (22). Therefore both the pure Coriolis term (term containing  $P_z$ ) and the higher order stretching term (term containing  $[P_x, P_y]^+$ ) in (II-24) and (II-25) will be taken into account in the computations. Also, it should be noted that the value of  $\zeta_{13}$  depends greatly on the values found for  $\gamma, A, B$ , and  $C$  in contrast to the higher order stretching term which is less sensitive to small change in  $\gamma, A, B$ , or  $C$ .

## CHAPTER III

### APPLICATION OF THE MODIFIED CONTACT TRANSFORMATION

#### The Vibrational Representation

Much of the difficult mathematics associated with a Coriolis-type vibrational resonance may be circumvented by use of Nielsen's modified contact transformation (21) which is also called the modified Herman-Shaffer operator (26). This particular use of the operator simplifies the matrix diagonalization in the vibrational representation by removing most of the important off-diagonal terms in  $H_1$  to diagonal positions in  $H'_2$ . There are no diagonal elements in  $H_1$  or  $H'_1$ . The matrix elements coupling interacting vibrational energy matrices are left unchanged by the modified contact transformation and must be treated by an exact diagonalization routine rather than by perturbation theory.

After the contact transformation  $S$  has been applied, the components of the new Hamiltonian,  $H'$ , are related to those of the untransformed Hamiltonian,  $H$ , by the following equations (26):

$$H_O' = H_O$$

$$H_1' = H_1 - i(H_O S - S H_O)$$

$$H_2' = H_2 + \left(\frac{i}{2}\right) [S(H_1 + H_1') - (H_1 + H_1')S] \quad (\text{III-1})$$

As usual, the rotational operators are treated as constants for purposes of the transformation in the vibrational representation but their commutator properties are strictly observed in the rotational representation.

#### Finding the Transformed Hamiltonian $H_1'$

To facilitate computation of the transformed Hamiltonian, (II-18) is written as

$$\begin{aligned} H_1 = & \sum_{n=1}^3 a_{in} q_n + \sum_{n=1}^2 (a_{3n} q_n^3 + a_{5in2} q_n q_1 q_2 + a_{5n33} q_n q_3^2) \\ & + a_{71} \left[ \left( \frac{\lambda_1}{\lambda_3} \right)^{\frac{1}{4}} p_1 q_3 - \left( \frac{\lambda_3}{\lambda_1} \right)^{\frac{1}{4}} q_1 p_3 \right] + a_{72} \left[ \left( \frac{\lambda_2}{\lambda_3} \right)^{\frac{1}{4}} p_2 q_3 - \left( \frac{\lambda_3}{\lambda_2} \right)^{\frac{1}{4}} q_2 p_3 \right] \end{aligned} \quad (\text{III-2})$$

where the a's are listed in Table VI. This notation is similar to that of Herman and Shaffer but these a's are not exactly the same as theirs. It should be noted that the a's do not necessarily commute with one another.

$H_1'$  may be found by evaluating

$$H_1' = H_1 - i[H_O, \sum_{\rho} S_{\rho}] \quad (\text{III-3})$$

where the components of S needed to perform the transformation are

Table VI. The Hamiltonian Coefficients for  $H_1$ 

$a_{11} = -\frac{\hbar^2}{\lambda_1^4} \left( \sin\gamma \frac{p_x^2}{I_x^2} + \cos\gamma \frac{p_y^2}{I_y^2} - \zeta_{23} \frac{p_z^2}{I_z^2} \right)$	$a_{12} = -\frac{\hbar^2}{\lambda_2^4} \left( \cos\gamma \frac{p_x^2}{I_x^2} - \sin\gamma \frac{p_y^2}{I_y^2} + \zeta_{13} \frac{p_z^2}{I_z^2} \right)$
$a_{13} = \left( \frac{\hbar}{I_x I_y I_z \lambda_3^2} \right)^{\frac{1}{2}} [p_x, p_y]^+$	
$a_{71} = \frac{\zeta_{13} p_z}{I_z}$	$a_{72} = \frac{\zeta_{23} p_z}{I_z}$
$a_{31} = hck_{111}$	$a_{32} = hck_{222}$
$a_{5112} = 3hck_{112}$	$a_{5122} = 3hck_{122}$
$a_{5133} = 3hck_{133}$	$a_{5233} = 3hck_{233}$

$$\sum S_o = \sum_{n=1}^3 S_{in} + \sum_{n=1}^2 (S_{3n} + S_{5in_2} + S_{5n_3}) + S_{71}^* + S_{72}$$

(III-4)

The values for the transformation components in (III-4) are listed in Table VII.

Using (III-2) and (III-4),  $H_1'$  may be decomposed as

$$\begin{aligned}
H_1' &= \sum_{n=1}^3 (a_{in} q_n - i[H_O, S_{in}]) + \sum_{n=1}^2 (a_{3n} q_n^3 - i[H_O, S_{3n}]) \\
&\quad + \sum_{n=1}^2 (a_{5in_2} q_n q_1 q_2 + a_{5n_3} q_n q_3^2 - i[H_O, (S_{5in_2} + S_{5n_3})]) \\
&\quad + \{a_{71} [(\frac{\lambda_1}{\lambda_3})^{\frac{1}{4}} p_1 q_3 - (\frac{\lambda_3}{\lambda_1})^{\frac{1}{4}} q_1 p_3] - i[H_O, S_{71}^*]\} \\
&\quad + \{a_{72} [(\frac{\lambda_2}{\lambda_3})^{\frac{1}{4}} p_2 q_3 - (\frac{\lambda_3}{\lambda_2})^{\frac{1}{4}} q_2 p_3] - i[H_O, S_{72}]\} \\
&= H_1',_1 + H_1',,_3 + H_1',,_5 + H_1',,_71 + H_1',,_72
\end{aligned}$$

(III-5)

It is shown in Appendix III that all components of  $H_1'$  vanish except  $H_1',,_71$ ; this was the reason for using the modified contact transformation. The commutator in  $H_1',,_71$  is given by

$$i[H_O, S_{71}^*] = -\frac{a_{71}}{2} [(\frac{\lambda_3}{\lambda_1})^{\frac{1}{4}} - (\frac{\lambda_1}{\lambda_3})^{\frac{1}{4}}] (p_1 q_3 + q_1 p_3) \quad (III-6)$$

Table VII. Contact Transformation Components

$s_{1n} = -\frac{a_{1n}}{\hbar^2 \lambda_n^2}$	$s_{3n} = -\frac{2a_{3n}}{\hbar^2 \lambda_n^2} \left( \frac{p_n^3}{3\hbar^2} + \frac{q_n p_n q_n}{2} \right)$
$s_{5n33} = -\frac{a_{5n33}}{\hbar^2 \lambda_n^2 \frac{1}{2} (4\lambda_3 - \lambda_n)} [(2\lambda_3 - \lambda_n) q_3^2 p_n + \lambda_3^2 \lambda_n^2 [p_3, q_3] q_n + \frac{2\lambda_3 p_3 p_n}{\hbar^2}]$	
$s_{5112} = -\frac{a_{5112}}{\hbar^2 \lambda_1^2 \frac{1}{2} (4\lambda_1 - \lambda_2)} [(2\lambda_1 - \lambda_2) q_1^2 p_2 + \lambda_1^2 \lambda_2^2 [p_1, q_1] q_2 + \frac{2\lambda_1 p_1^2 p_2}{\hbar^2}]$	
$s_{5122} = -\frac{a_{5122}}{\hbar^2 \lambda_1^2 \frac{1}{2} (4\lambda_2 - \lambda_1)} [(2\lambda_2 - \lambda_1) q_2^2 p_1 + \lambda_1^2 \lambda_2^2 [p_2, q_2] q_1 + \frac{2\lambda_2 p_2^2 p_1}{\hbar^2}]$	
$s_{71}^* = -\frac{a_{71} (\lambda_3^{\frac{1}{2}} - \lambda_1^{\frac{1}{2}})}{2(\lambda_1 \lambda_3)^{\frac{1}{4}} (\lambda_1^{\frac{1}{2}} + \lambda_3^{\frac{1}{2}})} [q_1 q_3 - \frac{p_1 p_3}{\hbar^2}]$	
$s_{72} = -\frac{a_{72}}{(\lambda_2 \lambda_3)^{\frac{1}{4}} (\lambda_3 - \lambda_2)} [(\lambda_2 + \lambda_3) q_2 q_3 + 2(\lambda_2 \lambda_3)^{\frac{1}{2}} \frac{p_2 p_3}{\hbar^2}]$	

From (III-5) and (III-6) the final expression for the transformed first order Hamiltonian  $H_1'$  is found to be

$$H_1' = H_1' \Big|_{\gamma_1} = \frac{a_{71}}{2} \frac{(\lambda_1^{\frac{1}{2}} + \lambda_3^{\frac{1}{2}})}{(\lambda_1 \lambda_3)^{\frac{1}{4}}} (p_1 q_3 - q_1 p_3) \quad (\text{III-7})$$

### Finding the Transformed Hamiltonian $H_2'$

$H_2'$  may be evaluated by extending (III-1) as

$$\begin{aligned} H_2' &= H_2 + \frac{i}{2} [\sum_{n=1}^3 S_{in}, (H_1 + H_1')] \\ &+ \frac{i}{2} [\sum_{n=1}^2 (S_{3n} + S_{5in2} + S_{5n33}), (H_1 + H_1')] \\ &+ [(S_{71}^* + S_{72}), (H_1 + H_1')] \end{aligned} \quad (\text{III-8})$$

The quantity  $(H_1 + H_1')$  in (III-8) is given by

$$\begin{aligned} H_1 + H_1' &= \sum_{j=1}^3 a_{1j} q_j + \sum_{j=1}^2 (a_{3j} q_j^2 + a_{51j2} q_1 q_2 + a_{5j33} q_3^2) q_j \\ &+ a_{72} [N_2 p_2 q_3 - M_1 q_2 p_3] + a_{71} [N_1 p_1 q_3 - M_2 q_1 p_3] \end{aligned} \quad (\text{III-9})$$

where the notation

$$N_1 = \frac{1}{2} [3(\frac{\lambda_1}{\lambda_3})^{\frac{1}{4}} + (\frac{\lambda_3}{\lambda_1})^{\frac{1}{4}}]$$

$$M_2 = \frac{1}{2} [ 3 \left( \frac{\lambda_3}{\lambda_1} \right)^{\frac{1}{4}} + \left( \frac{\lambda_1}{\lambda_3} \right)^{\frac{1}{4}} ]$$

$$N_2 = \frac{1}{M_1} = \left( \frac{\lambda_2}{\lambda_3} \right)^{\frac{1}{4}}$$

has been introduced for convenience. The commutator operations in (III-8) are worked out in Appendix IV. When vibrational representation matrix elements are formed (20) the commutators in (III-8) make a diagonal contribution of the form

$$\begin{aligned}
 & \langle v_1 v_2 v_3 | \left( \frac{i}{2} [S, (H_1 + H_1')] \right) | v_1 v_2 v_3 \rangle \\
 &= - \frac{1}{2n} \sum_{n=1}^3 \frac{a_{in}^2}{\lambda_n^2} - \frac{3}{n} \sum_{n=1}^2 \frac{a_{in} a_{3n} (v_n + \frac{1}{2})}{\lambda_n^2} \\
 & - \frac{1}{n} \sum_{nj=1}^2 \frac{D_{nj} a_{in} a_{51j2} (v_j + \frac{1}{2})}{\lambda_n^2} \\
 & - (v_3 + \frac{1}{2}) \left\{ \frac{1}{n} \sum_{n=1}^2 \frac{a_{5n33} a_{in}}{\lambda_n^2} - \frac{a_{71}^2 (\lambda_3^{\frac{1}{2}} - \lambda_1^{\frac{1}{2}})^2 n}{4(\lambda_1 \lambda_3)^{\frac{1}{2}} (\lambda_1^{\frac{1}{2}} + \lambda_3^{\frac{1}{2}})} + \frac{a_{72}^2 n (3\lambda_3 + \lambda_2)}{2\lambda_3^{\frac{1}{2}} (\lambda_3 - \lambda_2)} \right\} \\
 & - \frac{(v_1 + \frac{1}{2}) a_{71}^2 n (\lambda_3^{\frac{1}{2}} - \lambda_1^{\frac{1}{2}})^2}{4(\lambda_1 \lambda_3)^{\frac{1}{2}} (\lambda_1^{\frac{1}{2}} + \lambda_3^{\frac{1}{2}})} - \frac{(v_2 + \frac{1}{2}) a_{72}^2 n (3\lambda_2 + \lambda_3)}{2\lambda_2^{\frac{1}{2}} (\lambda_3 - \lambda_2)} \\
 & + E_v'
 \end{aligned} \tag{III-10}$$

The contribution from  $H_2$  may be found in a similar manner to be

$$\langle v_1 v_2 v_3 | H_2 | v_1 v_2 v_3 \rangle$$

$$= (v_1 + \frac{1}{2}) \left( \frac{3\hbar}{2\lambda_1^2} \right) [\sin^2 \gamma \frac{P_x^2}{I_x^2} + \cos^2 \gamma \frac{P_y^2}{I_y^2} + \zeta_{23}^2 \frac{P_z^2}{I_z^2}]$$

$$+ (v_2 + \frac{1}{2}) \left( \frac{3\hbar}{2\lambda_2^2} \right) [\cos^2 \gamma \frac{P_x^2}{I_x^2} + \sin^2 \gamma \frac{P_y^2}{I_y^2} + \zeta_{13}^2 \frac{P_z^2}{I_z^2}]$$

$$+ (v_3 + \frac{1}{2}) \left( \frac{3\hbar}{2\lambda_3^2} \right) [\frac{P_x^2}{I_x I_z} + \frac{P_y^2}{I_y I_z}] + E_v''$$

(III-11)

The symbol  $D_{nj} = (1 - \delta_{nj})$ .  $E_v'$  and  $E_v''$  are purely vibrational contributions listed in Appendix V.

#### The Diagonal Elements in the Vibrational Representation

Since  $H_O = H_O'$ , the diagonal elements of  $H_O'$  in the vibrational representation give the harmonic oscillator energies

$$\langle v_1 v_2 v_3 | H_O | v_1 v_2 v_3 \rangle = \sum_{\ell=x,y,z} \frac{P_\ell^2}{2I_\ell} + \sum_{n=1}^3 \frac{1}{\hbar\lambda_n^2} (v_n + \frac{1}{2}) \quad (III-12)$$

By combining (III-10), (III-11) and (III-12) the diagonal elements of the Hamiltonian in the vibrational representation may now be found. Division by  $hc$  puts the entire energy

expression in  $\text{cm}^{-1}$ .

$$\langle v_1 v_2 v_3 | \frac{H_O' + H_2'}{hc} | v_1 v_2 v_3 \rangle$$

$$= A(v) \frac{P_x^2}{\hbar^2} + B(v) \frac{P_y^2}{\hbar^2} + C^*(v) \frac{P_z^2}{\hbar^2}$$

$$+ \frac{1}{4\hbar^4} \left[ \tau_1 P_x^4 + \tau_2 P_y^4 + \tau_3 P_z^4 + \tau_9 (P_x P_y + P_y P_x)^2 + \right.$$

$$\left. \tau_5 [P_x^2, P_z^2]^+ + \tau_6 [P_x^2, P_y^2]^+ + \tau_4 [P_y^2, P_z^2]^+ \right]$$

$$+ E(v_1 v_2 v_3)$$

(III-13)

$A(v)$ ,  $B(v)$  and  $C^*(v)$  are the vibrationally corrected reciprocal moments of inertia which are customarily written

$$A(V) = A_e - \sum_{i=1}^3 \alpha_i^A (v_i + \frac{1}{2})$$

$$B(V) = B_e - \sum_{i=1}^3 \alpha_i^B (v_i + \frac{1}{2})$$

$$C^*(V) = C_e - \sum_{i=1}^3 \alpha_i^{C^*} (v_i + \frac{1}{2})$$

(III-14)

In (III-14)  $A_e = \frac{\hbar}{8\pi^2 c I_x}$ , etc. and the  $\alpha$ 's are listed in Table VIII. It is worth pointing out that the Coriolis

Table VIII. The  $\alpha$ 's

$$\begin{aligned}
\alpha_1^A &= -6A_e^2 \left( \frac{\sin^2 \gamma}{\omega_1} + \left( \frac{2}{A_e} \right)^{\frac{1}{2}} \left( \frac{k_{111} \sin \gamma}{\omega_1^{\frac{3}{2}}} + \frac{k_{112} \cos \gamma}{\omega_2^{\frac{3}{2}}} \right) \right) \\
\alpha_2^A &= -6A_e^2 \left( \frac{\cos^2 \gamma}{\omega_2} + \left( \frac{2}{A_e} \right)^{\frac{1}{2}} \left( \frac{k_{222} \cos \gamma}{\omega_2^{\frac{3}{2}}} + \frac{k_{122} \sin \gamma}{\omega_1^{\frac{3}{2}}} \right) \right) \\
\alpha_3^A &= -6A_e C_e \left( \frac{1}{\omega_3} + \frac{(2A_e)^{\frac{1}{2}}}{C_e} \left( \frac{k_{133} \sin \gamma}{\omega_1^{\frac{3}{2}}} + \frac{k_{233} \cos \gamma}{\omega_2^{\frac{3}{2}}} \right) \right) \\
\alpha_1^B &= -6B_e^2 \left( \frac{\cos^2 \gamma}{\omega_1} + \left( \frac{2}{B_e} \right)^{\frac{1}{2}} \left( \frac{k_{111} \cos \gamma}{\omega_1^{\frac{3}{2}}} - \frac{k_{112} \sin \gamma}{\omega_2^{\frac{3}{2}}} \right) \right) \\
\alpha_2^B &= -6B_e^2 \left( \frac{\sin^2 \gamma}{\omega_2} + \left( \frac{2}{B_e} \right)^{\frac{1}{2}} \left( \frac{k_{122} \cos \gamma}{\omega_1^{\frac{3}{2}}} - \frac{k_{222} \sin \gamma}{\omega_2^{\frac{3}{2}}} \right) \right) \\
\alpha_3^B &= -6B_e C_e \left( \frac{1}{\omega_2} + \frac{(2B_e)^{\frac{1}{2}}}{C_e} \left( \frac{k_{133} \cos \gamma}{\omega_1^{\frac{3}{2}}} - \frac{k_{233} \sin \gamma}{\omega_2^{\frac{3}{2}}} \right) \right) \\
\alpha_1^{C*} &= -6C_e^2 \left( \frac{\zeta_{23}^2}{\omega_1} + \left( \frac{2}{C_e} \right)^{\frac{1}{2}} \left( \frac{k_{112} \zeta_{13}}{\omega_2^{\frac{3}{2}}} - \frac{k_{111} \zeta_{23}}{\omega_1^{\frac{3}{2}}} \right) - \frac{\zeta_{13}^2 (\omega_3 - \omega_1)^2}{6\omega_1 \omega_3 (\omega_1 + \omega_3)} \right) \\
\alpha_2^{C*} &= -6C_e^2 \left( \frac{\zeta_{13}^2}{\omega_2} + \left( \frac{2}{C_e} \right)^{\frac{1}{2}} \left( \frac{k_{222} \zeta_{13}}{\omega_2^{\frac{3}{2}}} - \frac{k_{122} \zeta_{23}}{\omega_1^{\frac{3}{2}}} \right) - \frac{\zeta_{23}^2 (3\omega_2^2 + \omega_3^2)}{3\omega_2 (\omega_3^2 - \omega_2^2)} \right) \\
\alpha_3^{C*} &= -6C_e^2 \left( \frac{\zeta_{23}^2 (3\omega_3^2 + \omega_2^2)}{3\omega_3 (\omega_3^2 - \omega_2^2)} + \left( \frac{2}{C_e} \right)^{\frac{1}{2}} \left( \frac{k_{233} \zeta_{13}}{\omega_2^{\frac{3}{2}}} - \frac{k_{133} \zeta_{23}}{\omega_1^{\frac{3}{2}}} \right) - \frac{\zeta_{13}^2 (\omega_3 - \omega_1)^2}{6\omega_1 \omega_3 (\omega_1 + \omega_3)} \right) \\
\alpha_1^C &= -6C_e^2 \left( \frac{\zeta_{23}^2}{\omega_1} + \left( \frac{2}{C_e} \right)^{\frac{1}{2}} \left( \frac{k_{112} \zeta_{13}}{\omega_2^{\frac{3}{2}}} - \frac{k_{111} \zeta_{23}}{\omega_1^{\frac{3}{2}}} \right) + \frac{\zeta_{13}^2 (3\omega_1^2 + \omega_3^2)}{3\omega_1 (\omega_2^2 - \omega_3^2)} \right) \\
\alpha_3^C &= -6C_e^2 \left( \frac{\zeta_{23}^2 (3\omega_3^2 + \omega_2^2)}{3\omega_3 (\omega_3^2 - \omega_2^2)} + \left( \frac{2}{C_e} \right)^{\frac{1}{2}} \left( \frac{k_{233} \zeta_{13} - k_{133} \zeta_{23}}{\omega_2^{\frac{3}{2}}} \right) + \frac{\zeta_{13}^2 (3\omega_3^2 + \omega_1^2)}{3\omega_3 (\omega_3^2 - \omega_1^2)} \right)
\end{aligned}$$

perturbation causes  $\alpha_1^C$  and  $\alpha_3^C$  to be modified to  $\alpha_1^{C*}$  and  $\alpha_3^{C*}$  ( $\alpha_2^C \equiv \alpha_2^{C*}$ ). In the unperturbed case, the expression (III-13) would be the entire Hamiltonian in the vibrational representation if  $\alpha_1^{C*}$  and  $\alpha_3^{C*}$  were replaced by  $\alpha_1^C$  and  $\alpha_3^C$ , since any off-diagonal elements should be ignorable. The main difference between the starred and unstarred  $\alpha^C$ 's listed in Table VIII is that the resonant denominator ( $\omega_3^2 - \omega_1^2$ ) is no longer present in  $\alpha_1^{C*}$  and  $\alpha_3^{C*}$ .

The  $\tau$ 's in (III-13) are centrifugal distortion constants given in  $\text{cm}^{-1}$  and are closely related to the equilibrium  $\tau$ 's ( $\tau_{xxxx}$ ,  $\tau_{yyyy}$ , etc.) of Chung and Parker (17). For experimental work it is convenient to use the relations

$$\tau_1 = \frac{\pi^4}{hc} \quad \tau_{xxxx} = - 16A_e^3 \left( \frac{\sin^2 \gamma}{\omega_1^2} + \frac{\cos^2 \gamma}{\omega_2^2} \right)$$

$$\tau_2 = \frac{\pi^4}{hc} \quad \tau_{yyyy} = - 16B_e^3 \left( \frac{\cos^2 \gamma}{\omega_1^2} + \frac{\sin^2 \gamma}{\omega_2^2} \right)$$

$$\tau_3 = \frac{\pi^4}{hc} \quad \tau_{zzzz} = - 16C_e^3 \left( \frac{\zeta_{23}^2}{\omega_1^2} + \frac{\zeta_{13}^2}{\omega_2^2} \right)$$

$$\tau_4 = \frac{\pi^4}{hc} \quad \tau_{yyzz} = + 16(B_e C_e)^{\frac{3}{2}} \left( \frac{\zeta_{13} \sin \gamma}{\omega_2^2} + \frac{\zeta_{23} \cos \gamma}{\omega_1^2} \right)$$

$$\tau_5 = \frac{\pi^4}{hc} \quad \tau_{xxzz} = - 16(A_e C_e)^{\frac{3}{2}} \left( \frac{\zeta_{13} \cos \gamma}{\omega_2^2} - \frac{\zeta_{23} \sin \gamma}{\omega_1^2} \right)$$

$$\begin{aligned}\tau_6 &= \frac{\pi^4}{hc} \tau_{xxyy} = - 16(A_e B_e)^{\frac{3}{2}} \sin\gamma \cos\gamma \left(\frac{1}{\omega_1^2} - \frac{1}{\omega_2^2}\right) \\ \tau_9 &= \frac{\pi^4}{hc} \tau_{xyxy} = - \frac{16A_e B_e C_e}{\omega_3^2}\end{aligned}\quad (\text{III-15})$$

In (III-15), frequency  $\omega_i$  is in  $\text{cm}^{-1}$  using the conversion  
 $\lambda_i^{\frac{1}{2}} = 2\pi\omega_i c$ .

The vibrational and constant terms remaining are lumped together in  $E(v_1 v_2 v_3)$  which will contribute to the bandcenter only.

The diagonal term (III-13) is usually simplified by using the well-known commutator relation

$$(P_x P_y + P_y P_x)^2 = 2(P_x^2 P_y^2 + P_y^2 P_x^2) - 2\pi^2 P_x^2 - 2\pi^2 P_y^2 + 3\pi^2 P_z^2 \quad (\text{III-16})$$

and the Dowling relations which apply to the equilibrium taus for planar molecules (27).

$$\begin{aligned}\tau_5 &= \left(\frac{C_e}{B_e}\right)^2 \tau_6 + \left(\frac{C_e}{A_e}\right)^2 \tau_1 \\ \tau_4 &= \left(\frac{C_e}{A_e}\right)^2 \tau_6 + \left(\frac{C_e}{B_e}\right)^2 \tau_2 \\ \tau_3 &= \left(\frac{C_e}{A_e}\right)^2 \tau_5 + \left(\frac{C_e}{B_e}\right)^2 \tau_4\end{aligned}\quad (\text{III-17})$$

When the substitutions  $r = \left[ \frac{C_e}{A_e} \right]^2$ ,  $s = \left[ \frac{C_e}{B_e} \right]^2$ , (III-16)  
and (III-17) are made in (III-13) the final result for the  
diagonal elements of the Hamiltonian in the vibrational  
representation may be written

$$\begin{aligned} & \langle v_1 v_2 v_3 | \frac{H_1 + H_2}{hc} | v_1 v_2 v_3 \rangle = (A(v) - \frac{\tau_9}{2}) \frac{P_x^2}{\hbar^2} + (B(v) - \frac{\tau_9}{2}) \frac{P_y^2}{\hbar^2} \\ & + (C^*(v) + \frac{3}{4}\tau_9) \frac{P_z^2}{\hbar^2} \\ & + \frac{1}{4\hbar^4} \left[ \begin{aligned} & \tau_1 P_x^4 + \tau_2 P_y^4 + (r^2 \tau_1 + s^2 \tau_2 + 2rs\tau_6) P_z^4 + (\tau_6 + 2\tau_9) [P_x^2, P_y^2]^\dagger \\ & + [r\tau_1 + s\tau_6] [P_x^2, P_z^2]^\dagger + [r\tau_6 + s\tau_2] [P_y^2, P_z^2]^\dagger \end{aligned} \right] \\ & + E(v_1 v_2 v_3) \end{aligned} \quad (\text{III-18})$$

### The Off-Diagonal Elements in the Vibrational Representation

The off-diagonal matrix elements in the vibrational representation are given (in  $\text{cm}^{-1}$ ) by (II-24) and (II-25).

$$\langle v_1 v_2 v_3 | \frac{H_1 + H_2}{hc} | v_1+1, v_2, v_3-1 \rangle = \{ 2iG_{xy} \frac{P_z}{\hbar} + G_{xz} \frac{[P_x, P_y]}{\hbar^2} \} \frac{\sqrt{(v_1+1)v_3}}{2} \quad (\text{III-19})$$

$$\langle v_1 v_2 v_3 | \frac{H_1 + H_2}{hc} | v_1-1, v_2, v_3+1 \rangle = \{ -2iG_{xy} \frac{P_z}{\hbar} + G_{xz} \frac{[P_x, P_y]}{\hbar^2} \} \frac{\sqrt{v_1(v_3+1)}}{2} \quad (\text{III-20})$$

where

$$G_z = - \frac{\zeta_{13}(\omega_1 + \omega_3)C_e}{(\omega_1\omega_3)^{\frac{1}{2}}} \quad (\text{III-21})$$

and

$$G_{xy} = - \frac{6A_e B_e C_e^{\frac{1}{2}}}{\sqrt{\omega_1 \omega_3}} \left[ \frac{\cos\gamma}{A_e^{\frac{1}{2}}} + \frac{\sin\gamma}{B_e^{\frac{1}{2}}} \right] \quad (\text{III-22})$$

$G_{xy}$  and  $G_z$  are given in  $\text{cm}^{-1}$  in order to facilitate experimental evaluation of their magnitudes.

#### Possible Experimental Applications

It is informative to examine the matrix elements for several sets of interacting excited vibrational levels of hydrogen sulfide. For the states (011) and (110), i.e.  $v_1 = 0$  and  $v_2 = v_3 = 1$ , the off-diagonal interaction matrix element is

$$\langle 011 | \frac{H_1 + H_2}{hc} | 110 \rangle = \{ 2iG_z \frac{P_z}{\kappa} - G_{xy} \frac{[P_x, P_y]}{\kappa^2} \} \frac{\sqrt{I}}{2} \quad (\text{III-23})$$

and its hermitian conjugate. The diagonal matrix elements are found by specializing (III-18) to the (110) and (011) states. The general form of the Hamiltonian matrix is shown in Fig. 6 for this two band interaction. Fortunately both the (110) and (011) bands are infrared active so the Coriolis interaction between them can be studied experimentally.

Fig. 6. The Interaction Matrix for the (110) and (011)  
States in the Vibrational Representation

	(110)	(011)
(110)	$E_{ROT.}^{(110)}$ $+ E_{VIB.}^{(110)}$	$- \frac{iG_z}{\hbar} \frac{P_z}{\hbar}$ $- \frac{G_{xy}}{2} \frac{[P_x, P_y]}{\hbar^2}^+$
(011)	$\frac{iG_z}{\hbar} \frac{P_z}{\hbar}$ $- \frac{G_{xy}}{2} \frac{[P_x, P_y]}{\hbar^2}^+$	$E_{ROT.}^{(011)}$ $+ E_{VIB.}^{(011)}$

For a three band interaction, such as found for the (210), (111) and (012) states, the coupling matrix elements are found from (III-19) and (III-20) to be

$$\langle 111 | \frac{H_1 + H_2}{hc} | 012 \rangle = \left\{ -2i \frac{G_z P_z}{\hbar} - \frac{G_{xy} [P_x, P_y]}{\hbar^2} \right\} \frac{+}{2} \sqrt{2} \quad (\text{III-24})$$

and

$$\langle 111 | \frac{H_1 + H_2}{hc} | 210 \rangle = \left\{ 2i \frac{G_z P_z}{\hbar} - \frac{G_{xy} [P_x, P_y]}{\hbar^2} \right\} \frac{+}{2} \sqrt{2} \quad (\text{III-25})$$

along with their hermitian conjugates. The complete form of the Hamiltonian matrix for these three states is shown in Fig. 7. Unfortunately, the (012) band of hydrogen sulfide has not been found to be infrared active. As noted by Wilson (14), even though a vibrational state may not give an infrared band, it may perturb the upper state of another band. Experimentally, it appears that the infrared inactive vibrational state (012) does perturb the infrared active states (210) and (111), so the analysis may be more fruitfully applied to the (110) and (011) bands.

Fig. 7. The Three Band Interaction Matrix for the (210), (111) and (012) States

	(210)	(111)	(012)
(210)	$E_{ROT.} (210)$ $+ E_{VIB.} (210)$	$- \frac{iG_z}{\hbar} \frac{P_z}{\sqrt{2}}$ $- \frac{G_{xy}}{\sqrt{2}} \frac{[P_x, P_y]}{\hbar^2}^+$	
(111)	$iG_z \frac{P_z}{\hbar} \sqrt{2}$ $- \frac{G_{xy}}{\sqrt{2}} \frac{[P_x, P_y]}{\hbar^2}^+$	$E_{ROT.} (111)$ $+ E_{VIB.} (111)$	$- iG_z \frac{P_z}{\hbar} \sqrt{2}$ $- \frac{G_{xy}}{\sqrt{2}} \frac{[P_x, P_y]}{\hbar^2}^+$
(012)		$iG_z \frac{P_z}{\hbar} \sqrt{2}$ $- \frac{G_{xy}}{\sqrt{2}} \frac{[P_x, P_y]}{\hbar^2}^+$	$E_{ROT.} (012)$ $+ E_{VIB.} (012)$

## CHAPTER IV

### THE ROTATIONAL REPRESENTATION

#### Operator Matrix Elements

Each matrix element in the vibrational representation shown in Fig. 6 and Fig. 7 is a complete submatrix of dimension  $(2J + 1)$  in the rotational representation. Thus to complete the mathematical description of the Hamiltonian matrix an appropriate rotational representation must be chosen. King, Hainer and Cross have covered the general details of the various possible choices of rotational representations so only the points pertinent to this problem will be recapitulated here (4).

The operators  $P_a$ ,  $P_b$  and  $P_c$  in (I-1) may be identified with a right-handed system of Cartesian body-fixed axes with origin at the center of mass. The operator commutator rules are

$$[P_i, P_j] = - i \epsilon_{ijk} P_k \quad (\text{IV-1})$$

where the  $ijk$  stand for  $xyz$  and cyclic permutations. Suppressing the  $J$  and  $M$  notation in the matrix elements, a well known solution to the set (IV-1) in a representation diagonalizing  $P^2$  and  $P_z$  is

$$\langle K | P_Y | K+1 \rangle = -i \langle K | P_X | K+1 \rangle = \frac{\hbar}{2} [J(J+1) - K(K+1)]^{\frac{1}{2}}$$

$$\langle K | P_Z | K \rangle = \hbar K$$

(IV-2)

All necessary rotational representation matrix elements have been calculated by Posener from (IV-2) using the same phase factor chosen by King, Hainer and Cross (19). The 3! ways in which  $P_a$ ,  $P_b$  and  $P_c$  may be identified with  $x$ ,  $y$ , and  $z$  are listed by King, Hainer and Cross and shown in Table IX. Thus the choice  $x = a$ ,  $y = b$ ,  $z = c$ , made in Chapter I amounts to choosing a  $\text{III}^r$  representation and allows the direct use of Posener's operator matrix elements. The operator matrix elements used in this work are listed in Appendix VI using the substitution  $f = J(J+1)$ .

When the proper substitutions from Appendix VI are made, the elements of the submatrix for the Hamiltonian operator (III-18) become

$$\begin{aligned} \langle V, K | V, K \rangle &= [f - K^2] \left[ \frac{A(V) + B(V) - \tau_9}{2} + \frac{K^2 R}{4} \right] \\ &+ [f^2 - 2(K^2 - 1)f + K^2(K^2 - 5)] \frac{Y}{16} + \left[ C^*(V) + \frac{3\tau_9}{4} \right] K^2 \\ &+ T \frac{K^4}{4} + [3f^2 - 2(3K^2 + 1)f + K^2(3K^2 + 5)] \frac{X}{32} + E(V) \end{aligned}$$

Table IX. Identification of a b c with x y z

Type	I <sup>r</sup>	I <sup>l</sup>	II <sup>r</sup>	II <sup>l</sup>	III <sup>r</sup>	III <sup>l</sup>
x	b	c	c	a	a	b
y	c	b	a	c	b	a
z	a	a	b	b	c	c

$$\langle V, K | V, K \pm 2 \rangle = F(K \pm 1) F(K \pm 2) \left[ \frac{B(V) - A(V)}{4} + [2f - K^2 - (K \pm 2)^2] \frac{W}{32} \right. \\ \left. + [K^2 + (K \pm 2)^2] \frac{S}{16} \right]$$

$$\langle V, K | V, K \pm 4 \rangle = F(K \pm 1) F(K \pm 2) F(K \pm 3) F(K \pm 4) U$$

(IV-3)

In (IV-3), the symbol V indicates either  $V_1$  ( $v_1 v_2 v_3$ ) or  $V_2$  ( $v_1 v_2 v_3$ ) for a two band interaction. The following substitutions were used in (IV-3) to save space:

$$F(K \pm 1) = [f - K(K \pm 1)]^{\frac{1}{2}}$$

$$F(K \pm 2) = [f - (K \pm 1)(K \pm 2)]^{\frac{1}{2}} \text{ etc.}$$

$$f = J(J+1)$$

$$R = r(\tau_1 + \tau_6) + s(\tau_2 + \tau_6)$$

$$S = \tau_6(r-s) + \tau_2 s - \tau_1 r$$

$$T = (2rs\tau_6 + r^2\tau_1 + s^2\tau_2)$$

$$U = \frac{1}{32} \left[ \frac{X}{2} - \frac{Y}{2} \right]$$

$$W = \tau_2 - \tau_1$$

$$X = \tau_1 + \tau_2$$

$$Y = \tau_6 + 2\tau_9$$

(IV-4)

The vibration-rotation matrix elements coupling the upper vibrational states of the interacting bands are found from (III-19) and (III-20).

$$\langle v_1 v_2 v_3, K | v_1 \pm 1, v_2 v_3 \mp 1, K \rangle = \pm i G_z K [ (v_1 + \frac{1}{2} \pm \frac{1}{2})(v_3 + \frac{1}{2} \mp \frac{1}{2}) ]^{\frac{1}{2}}$$

$$\langle v_1 v_2 v_3 K | v_1 + 1, v_2 v_3 - 1, K \pm 2 \rangle = \pm \frac{i}{4} G_{xy} F(K \pm 1) F(K \pm 2) [ (v_1 + 1) v_3 ]^{\frac{1}{2}}$$

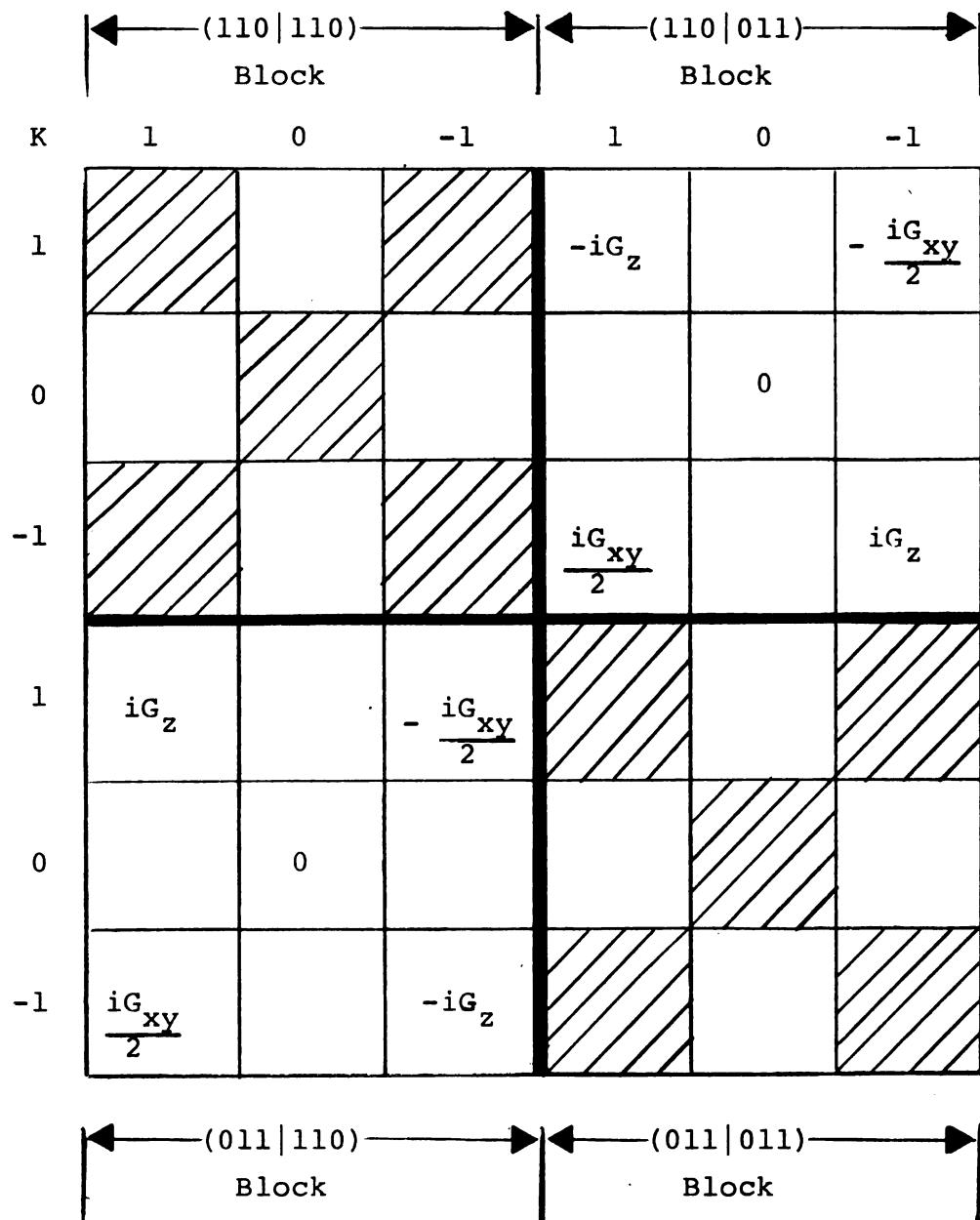
$$\langle v_1 v_2 v_3, K | v_1 - 1, v_2, v_3 + 1, K \pm 2 \rangle = \pm \frac{i}{4} G_{xy} F(K \pm 1) F(K \pm 2) [ v_1 (v_3 + 1) ]^{\frac{1}{2}}$$

(IV-5)

The form of the Hamiltonian matrix for  $J = 1$  generated by (IV-3) and (IV-5) is shown in Fig. 8 for the case when the interacting vibrational states are (110) and (011); i.e.  $v_1 = v_2 = 1$  and  $v_3 = 0$ . It is easily seen from Fig. 8 that the elements (IV-3) and (IV-5) describe a matrix of dimension  $2(2J+1)$  by  $2(2J+1)$ . The size of the Hamiltonian matrix rapidly becomes very large with increasing  $J$  value when left in the form described by (IV-3) and (IV-5); thus an undue amount of computer memory space for an accurate numerical diagonalization process is required if the Hamiltonian is left in this form.

#### The Wang Transformation

The symmetry requirements discussed in Chapter I can be satisfied by applying a modified Wang transformation (28) to the Hamiltonian matrix described by (IV-3) and (IV-5).

Fig. 8. Form of the Untransformed Hamiltonian for  $J = 1$ 

The transformation reduces the Hamiltonian matrix to four uncoupled submatrices which are easier to diagonalize than the cumbersome form shown in Fig. 8. Due to the off-diagonal coupling terms  $G_z$  and  $G_{xy}$  a "double" Wang transformation is necessary to partition the untransformed Hamiltonian into four submatrices. The double Wang transformation  $W$  is of dimensions  $2(2J+1) \times 2(2J+1)$  and is shown in Fig. 9 in a form suitable for operating on the Hamiltonian in Fig. 8. Since  $W$  is unitary,

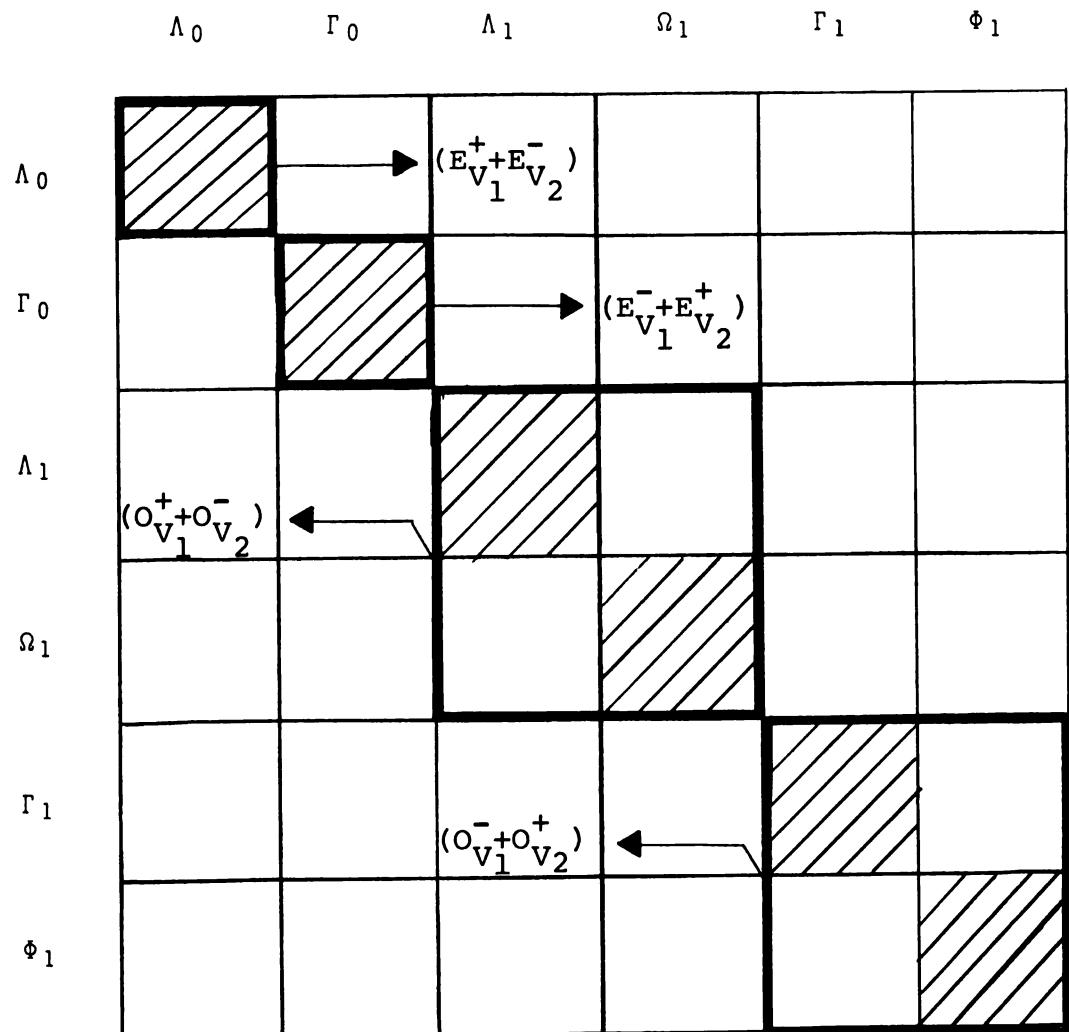
$$W^{-1} H_{trs} W = H_{trs} \quad (\text{IV-6})$$

is a similarity transformation which leaves the trace of the matrix unchanged. Fortunately, odd and even values of  $K$  are not connected in the untransformed Hamiltonian. Therefore, (IV-6) brings about a final matrix form very similar to that given by the ordinary Wang transformation acting on the vibrational state described by (IV-3).

The transformed matrix  $H_{trs}$  is shown in Fig. 10 for  $J = 1$ . Using (IV-6) rapidly becomes very tedious as  $J$  grows larger, since determinant manipulations performed with insight are required to achieve the neat form shown in Fig. 10. Usually it is much easier to go to the set of modified Wang linear combination wave functions constructed by Wilson and calculate the transformed elements directly (14). The combination wave functions are given for an interaction between vibrational states  $V_1$  and  $V_2$ .

Fig. 9. The Double Wang Transformation for  $J = 1$ 
$$W = \frac{1}{\sqrt{2}}$$

1		1			
	$\sqrt{2}$				
1		-1			
			1		1
				$\sqrt{2}$	
			1		-1

Fig. 10. The Transformed Hamiltonian for  $J = 1$ 

$$\Lambda_K = 2^{-\frac{1}{2}} (\psi_{JKM} + \psi_{J-KM}) \psi_{V_1} \quad (K>0)$$

$$\Lambda_O = \psi_{JOM} \psi_{V_1}$$

$$\Gamma_K = 2^{-\frac{1}{2}} (\psi_{JKM} + \psi_{J-KM}) \psi_{V_2} \quad (K>0)$$

$$\Gamma_O = \psi_{JOM} \psi_{V_2}$$

$$\Phi_K = 2^{-\frac{1}{2}} (\psi_{JKM} - \psi_{J-KM}) \psi_{V_1} \quad (K>0)$$

$$\Omega_K = 2^{-\frac{1}{2}} (\psi_{JKM} - \psi_{J-KM}) \psi_{V_2} \quad (K>0)$$

(IV-7)

The use of (IV-7) to calculate the matrix elements of the Hamiltonian is entirely equivalent to calculating the untransformed matrix (IV-3) and (IV-5) and then applying the double Wang transformation as in (IV-6). Wilson originally used the wave functions (IV-7) to calculate the effect of a pure Coriolis perturbation on a rigid asymmetric rotor. The four submatrices generated by the wavefunctions applied to (III-18), (III-19) and (III-20) are classified in Table X for the interacting vibrational states  $V_1$  and  $V_2$ . By the convention used for the ordinary Wang submatrix, E or 0 gives the oddness or evenness of K and no negative values of

Table X. The Coupled Wang Submatrices

Classification	Values of K to J or (J-1)	Generating Elements
$E_{V_1}^+ + E_{V_2}^-$	0, 2, 4, . . . .	$(\Lambda   \Lambda)$ , $(\Lambda   \Omega)$ , $(\Omega   \Omega)$
$E_{V_1}^- + E_{V_2}^+$	0, 2, 4, . . . .	$(\Gamma   \Gamma)$ , $(\Gamma   \Phi)$ , $(\Phi   \Phi)$
$O_{V_1}^+ + O_{V_2}^-$	1, 3, 5, . . . .	$(\Lambda   \Lambda)$ , $(\Lambda   \Omega)$ , $(\Omega   \Omega)$
$O_{V_1}^- + O_{V_2}^+$	1, 3, 5, . . . .	$(\Gamma   \Gamma)$ , $(\Gamma   \Phi)$ , $(\Phi   \Phi)$

$K$  are used. The + or - over  $E$  or 0 gives the sign joining the wave functions in (IV-7). The combination wave functions from (IV-7) are indicated in Fig. 10. Since Fig. 10 displays the  $J = 1$  case, the  $E_{V2}^-$  and  $E_{V1}^-$  contributions are zero even though their positions are indicated.

The general Wang submatrices may be generated from the elements (IV-3) and (IV-5). The diagonal matrix elements are given by

$$\begin{aligned}
 & \frac{[f-K^2]}{2} [A(V) + B(V) - \tau_9 + \frac{K^2 R}{2}] \\
 & + [f^2 - 2(K^2 - 1)f + K^2(K^2 - 5)] \frac{Y}{16} \\
 & + [3f^2 - 2(3K^2 + 1)f + K^2(3K^2 + 5)] \frac{X}{32} \\
 & + \frac{TK^4}{4} + [C^*(V) + \frac{3\tau_9}{4}] K^2 + E(V) \\
 & \pm (\delta_{K,1}) \frac{f}{4} [B(V) - A(V) + (f-1) \frac{W}{4} + \frac{S}{2}] \pm (\delta_{K,2}) f(f-2) U
 \end{aligned}
 \tag{IV-8}$$

In (IV-8) the elements  $(\Lambda_K(V_1) | \Lambda_K(V_1))$  and  $(\Gamma_K(V_2) | \Gamma_K(V_2))$ , which include the  $K = 0$  case, are given when the positive sign is chosen for the delta functions. The elements  $(\phi_K(V_1) | \phi_K(V_1))$  and  $(\Omega_K(V_2) | \Omega_K(V_2))$ , which exclude the  $K = 0$  case, are given when the negative sign is chosen. As usual,

$V$  in (IV-8) stands for either set of quantum numbers

$V_1(v_1 v_2 v_3)$  or  $V_2(v_1 v_2 v_3)$ . The off-diagonal terms for either state  $V_1$  or state  $V_2$  are given by (IV-9) and (IV-10).

$$\frac{(1+\delta_{K,0})^{\frac{1}{2}}}{4} F(K+1) F(K+2) [B(V) - A(V) + (f-K^2-2K-2) \frac{W}{4} + (K^2+2K+2) \frac{S}{2}] \\ \pm (\delta_{K,1}) f [(f-2)(f-6)]^{\frac{1}{2}} U \quad (IV-9)$$

In (IV-9) the elements  $(\Lambda_K(v_1) | \Lambda_{K+2}(v_1))$  and  $(\Gamma_K(v_2) | \Gamma_{K+2}(v_2))$ , which include the  $K = 0$  case, are given when the positive sign is chosen for  $\delta_{K,1}$ . The elements  $(\phi_K(v_1) | \phi_{K+2}(v_1))$  and  $(\Omega_K(v_2) | \Omega_{K+2}(v_2))$  are given when the negative sign is chosen. The remaining elements within a vibrational block  $V_1$  or  $V_2$  are

$$(\Lambda_K | \Lambda_{K+4}) = (\Gamma_K | \Gamma_{K+4}) = (\phi_K | \phi_{K+4}) = (\Omega_K | \Omega_{K+4}) \\ = (1+\delta_{K,0})^{\frac{1}{2}} F(K+1) F(K+2) F(K+3) F(K+4) U \quad (IV-10)$$

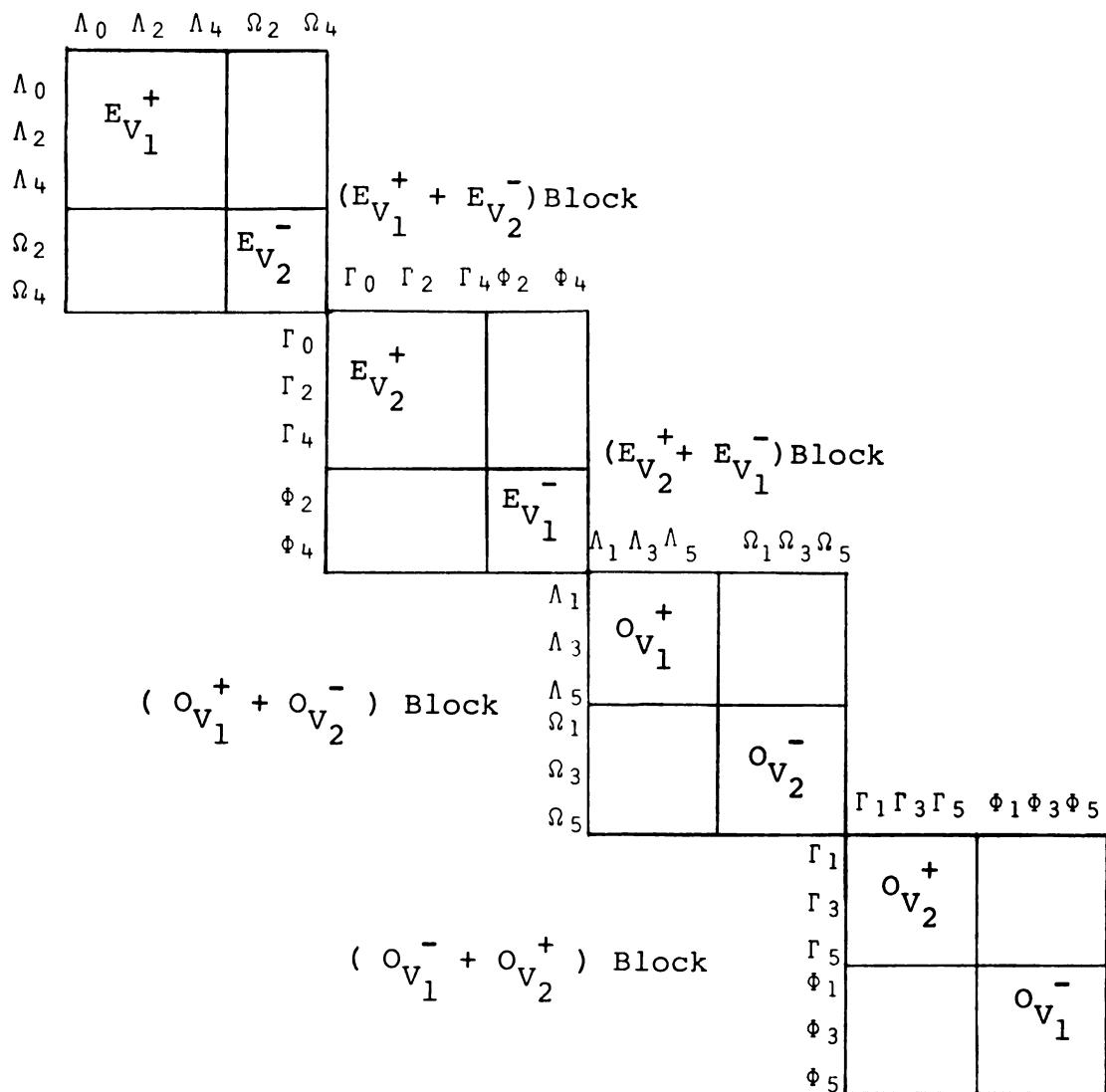
The elements coupling the two vibrational states are due to the higher-order stretching term  $G_{xy}$

$$(\Lambda_K | \Omega_{K+2}) = (\Gamma_K | \phi_{K+2}) = - (\Gamma_{K+2} | \phi_K) = - (\Lambda_{K+2} | \Omega_K) \\ = i \frac{G_{xy}}{4} (1+\delta_{K,0})^{\frac{1}{2}} F(K+1) F(K+2) \quad (IV-11)$$

and to the mixing of the pure Coriolis term  $G_z$  with  $G_{xy}$

$$\begin{aligned}
 (\Lambda_K | \Omega_K) &= -i[G_z K - (\delta_{K,1}) G_{xy} \frac{f}{4}] \\
 (K \neq 0) \\
 (\Gamma_K | \Phi_K) &= i[G_z K + (\delta_{K,1}) G_{xy} \frac{f}{4}]
 \end{aligned} \tag{IV-12}$$

The equations (IV-8) through (IV-12) describe the Hamiltonian in terms of the four Wang submatrices for the case when one vibrational state interacts with another. These equations, with some small empirical modifications, were used to analyze the (110) and (011) absorptions bands of hydrogen sulfide. The form of the array generated by these equations is shown in Fig. 11 for the  $J = 5$  case. However, Fig. 11 may be used as a model for generating an array using other values of  $J$  and equations (IV-8) through (IV-12). It should be noted that if  $G_z = G_{xy} = 0$ , the  $O$  and  $E$  blocks stand alone and Fig. 11 then describes the unperturbed case.

Fig. 11. Form of the Wang Transformed Hamiltonian for  $J = 5$ 

## CHAPTER V

### OBSERVED SPECTRA

#### History

One of the first detailed rotational analyses of hydrogen sulfide using an early quantum-mechanical energy expression was published by Cross in 1935 (29). Cross analyzed the (301) absorption band of  $H_2S$  at about  $10,000\text{ cm}^{-1}$  and was able to identify 84 absorption lines. His values for ground state energy levels and inertial constants were used successfully by infrared spectroscopists in analyzing many other  $H_2S$  bands. A summary of these analyses was published by Allen and Plyler in 1956 (12).

In recent years, additional information about the ground state of  $H_2S$  has been obtained from pure rotational transitions measured by microwave spectroscopy. Frequencies for two  $H_2S^{32}$  microwave lines were first published by Burrus and Gordy in 1953 (30). Since then several other microwave lines of  $H_2S$  have been found and measured by various researchers. Because microwave transitions can be measured very accurately, they are a useful supplement to infrared data for determining ground state structural parameters.

The main bands studied in this work are the (110) band (type B) and the (011) band (type A), both at about

3800 cm<sup>-1</sup>. The first proper analysis of these two bands was published by Savage and Edwards in 1957 (31). They correctly determined the presence of two absorption bands in this region rather than only one as was reported by earlier investigators.

Two other bands were investigated to supplement this work. These are the (210) band (type B) and the (111) band (type A) at about 6300 cm<sup>-1</sup>. The first rotational study of these two bands was published by Allen and Plyler in 1954 (32).

#### Procurement and Measurement of Data

The hydrogen sulfide spectra were obtained on the Michigan State University high-resolution infrared vacuum recording spectrometer. The basic components of this instrument were described in 1964 by Aubel (33) and subsequent improvements will be described by Keck (34).

In the initial work a 300 watt commercial zirconium arc was used as the infrared radiation source. Later, a water-cooled carbon rod source (35) with greater energy was successfully utilized to obtain improved spectra. Two different multiple traverse cells were used during the course of this work. The 80 cm cell was useful for low pressure runs but was initially limited because the infrared beam had to pass through several inches of air (containing H<sub>2</sub>O vapor) before entering it. This problem was later eliminated by the construction of an all-vacuum path for the beam (35). The other cell is a small volume coolable

multiple-traverse cell usually designated as a J. U. White type cell (36,37). Since the air space around this cell could be completely evacuated, it was used for initial data runs.

Two Bausch and Lomb echelle gratings are mounted on a turntable in the main tank of the spectrometer so that either may be readily used. One has 600 rulings per mm and a ruled area of 212 x 158 mm; the other has 300 rulings per mm and a ruled area of 254 x 128 mm. An Eastman-Kodak N-type lead sulfide cell operated at liquid nitrogen temperature was used as a detector for the hydrogen sulfide spectra.

The calibration and data processing used in our laboratory have been reported in Wavelength Standards in the Infrared (38) and also described in detail by Barnett (39); so only the main points will be described here. Calibration lines were recorded both immediately before and immediately after the hydrogen sulfide trace on each chart. The calibration gases used were HCN, CO, HCl and N<sub>2</sub>O which have frequencies measured so accurately that they may be used as standards. The H<sub>2</sub>S spectra were calibrated by means of Edser-Butler bands (or fringes) which were recorded simultaneously with both calibration gases and the H<sub>2</sub>S trace. Edser-Butler bands are used because the consecutive positions of their peaks vary linearly with frequency; thus there is a constant frequency separation between adjacent peaks.

After running a spectrum, the fringes were numbered

and the entire chart photographed for measurement on a Hydel digitized film reader connected to an IBM 526 card punch. A Hydel operator scanning the filmstrip of the chart measured the appropriate coordinates of the fringes and calibration gases for punched-card input to the computer program SCAN (40). The first SCAN computer output gave the relative fringe number of each calibration line. Next, the known frequency and fringe number of each calibration line on the chart was input to the computer in a least-squares routine, CALFIT (40). The CALFIT output gave the slope and intercept parameters necessary to establish the linear equation between the fringe number and frequency of an individual calibration line. These two parameters along with the measured fringe number (from the Hydel) were input to the computer in SCAN. The resulting output gave the frequency of each  $H_2S$  line from its fringe number through the linear equation between frequency and fringe number.

The entire procedure was repeated several times for each chart and the resulting measurements averaged together in order to minimize operator error. The averaging of several hundred data points per chart was done using ASHAFT (41), another computer program developed in this laboratory. Since several runs were made in each region, it was possible to combine the average frequencies from each run by using weighted averaging. The weights assigned to each frequency measurement on a given chart were based on the quality of

the least-squares calibration fit between fringe number and calibration frequency for that chart and on the estimated reproducibility of the frequency measurement for that particular line.

#### Further Experimental Technique

More details about the experimental techniques used in each region are outlined as follows:

(a)  $6300 \text{ cm}^{-1}$  region

This region was calibrated using the (301) band of  $\text{N}_2\text{O}$  (42) with bandcenter at  $5974.8504 \text{ cm}^{-1}$  and the (002) band of HCN (43) with bandcenter  $6519.6145 \text{ cm}^{-1}$ . Two runs,  $\text{H}_2\text{S}$  1 and  $\text{H}_2\text{S}$  2, were made in this region using the 600 line/mm grating in 1st order in a double-pass configuration. A zirconium arc was used as the infrared energy source and the 80 cm multiple traverse cell as the sample holder on both runs. The gas sample, C.P. grade (99.5% purity), was purchased from the Matheson Company and used without further purification. The standard deviation of the calibration fits was about  $0.004 \text{ cm}^{-1}$ . The experimental conditions are summarized in Table XI.

(b)  $3800 \text{ cm}^{-1}$  region

Five data runs were made in this region with run numbers 8, 9, 10, 15-I and 15-II. Calibration for the first three was obtained using the (101)

band of HCN (43) in 3rd order with bandcenter at  $5393.698\text{ cm}^{-1}$  and the (20) band of CO (43) in 2nd order with bandcenter at  $4260.0646\text{ cm}^{-1}$ . A zirconium arc was used as the infrared source and the small coolable multiple traverse cell as a sample holder on all three runs (8, 9, and 10). The  $\text{H}_2\text{S}$  sample for these runs was C.P. grade (99.5% purity), purchased from Matheson and used without further purification. The next run in this region was divided into two overlapping parts. Run 15-I covered the first half or low frequency side of the absorption region and was calibrated between the (101) band of HCN in 3rd order and the (20) band of HCl (44) in 3rd order with bandcenter at  $5667.9841\text{ cm}^{-1}$ . Run number 15-II overlapped the end of 15-I and covered the second half of the region. It was calibrated between the (20) band of HCl in 3rd order and the (20) band of CO in 2nd order. Both a  $\text{CO}_2$  impurity in the sample and  $\text{H}_2\text{O}$  background lines were a problem in this region. For these runs (15-I and 15-II) the  $\text{H}_2\text{S}$  sample was C.P. grade (99.6% purity) with a  $\text{CO}_2$  impurity content certified to be less than 500 ppm. It was purchased from Air Products and Chemicals Inc. The standard deviation of the calibration fits on runs 8, 9, 10 and 15-I was about  $.003\text{ cm}^{-1}$ . On

run 15-II, the standard deviation was about .0015 cm<sup>-1</sup>. On all five runs the 300 line/mm grating was used and the H<sub>2</sub>S trace was in 2nd order. The experimental conditions are summarized in Table XI. In addition to the data runs, one CO<sub>2</sub> background run and several vacuum background runs were made in this region to identify the absorption lines due to impurities in the sample and H<sub>2</sub>O vapor in the spectrometer.

Table XI. Experimental Conditions

Region, $\text{cm}^{-1}$	6300			3800			
Run Number	1	2	8	9	10	15-I	15-II
$\text{H}_2\text{S}$ Pressure, mm Hg	50	70	4	4	9	3	4
Path Length, m	15.75	18.9	6.6			9.45	
Absorption Cell	80 cm		White			8.0 cm	
$\text{H}_2\text{S}$ Temperature, °C	26		-50			26	
Infrared Source	Zirconium Arc			Carbon Rod			
Grating, lines/mm	600	300					
Ave. Fringe Sep., $\text{cm}^{-1}$	0.5358	0.5358	0.3216	0.3216	0.3216	0.3216	0.3216
Obs. Resolution Limit, $\text{cm}^{-1}$	0.040		0.045			0.035	
Calibration Standards	$\text{N}_2\text{O}$ , $\text{HCN}$	$\text{CO}$		$\text{HCN}, \text{HCl}$	$\text{HCl}, \text{CO}$		

## CHAPTER VI

### DATA ANALYSIS

#### Introductory Remarks

In the past few years, many of the procedures for data analysis in the literature have almost become obsolete because they were not designed for use on the computer. Included among these are interpolation tables and the many other routines that have been published specifically for hand calculator manipulation. In addition, many of the computer techniques used successfully on early machines have been replaced by more accurate methods ideally suited to a high-speed digital computer with large memory capacity. For example, first order perturbation theory is no longer necessary to describe the centrifugal stretching since digital computers can now accurately perform the exact diagonalization of an entire Hamiltonian matrix in seconds. Computer technology is evolving so rapidly that the beginning researcher often spends hours scanning obsolete techniques for data analysis before finding the best method available for a given analysis problem.

In addition, an author's description of the solution to a pertinent problem often assumes a complete knowledge of the steps leading from a matrix formulation of the molecular

Hamiltonian to the analysis of experimental data. Many times this is an unwarranted assumption because constructing an analysis program usually requires a considerable amount of insight and hard work. To help clarify the analysis procedure, simple examples will be used to illustrate much of the discussion that follows and references to specific applications will be made when possible.

The general remarks made in the next two sections are by no means limited to asymmetric molecule analysis. For example, an analysis program for treating perturbations between interacting symmetric top energy levels might be designed using the general outline discussed.

#### Components of a Typical Frequency Fitting Program

It is informative to examine the components of a typical frequency fitting program. To simplify the discussion, in this section it will be assumed that the ground state molecular parameters are well known, starting values for the upper state molecular parameters have been found, and a few absorption lines have been correctly identified. A later discussion will treat the case where this information is not known for the molecule.

The internal operations are outlined as follows:

- (a)        The values for the ground state molecular parameters ( $A(0)$ ,  $B(0)$ ,  $C(0)$ ,  $\tau_{aus}$ , etc.), and starting values for the upper state molecular parameters ( $A(V)$ ,  $B(V)$ ,  $C(V)$ ,  $\tau_{aus}$ , perturbation

terms, etc.) are input and stored in memory followed by the quantum numbers, frequency, and weight of each identified transition. If a perturbation connects two or more excited vibrational states as in Fig. 6, Fig. 7 or Fig. 11, a set of parameters for each upper state will be input along with the ground state parameters.

- (b) A matrix array for each J value is formed using the appropriate Hamiltonian for the ground state and the ground state molecular parameters. For example, a suitable array for the ground state may be generated from (IV-8), (IV-9) and (IV-10) when the ground state molecular parameters are used and E(V) is set equal to zero. The ground state array is then input to a suitable exact diagonalization subroutine which finds the eigenvalues. Then a labeling scheme (such as the one described in Chapter I) is used to assign quantum numbers JK-K+ to each ground state energy level or eigenvalue. The ground state levels and their identifying quantum numbers are then stored in memory for future use. An example of a program that performs these functions is G.S.Ex.D. listed in Appendix VII. The exact diagonalization routine used is JHERMX (45).
- (c) Next an upper state Hamiltonian matrix array for each J value is formed using the input starting

values. For example, a suitable array for two interacting bands may be generated from (IV-8), (IV-9), (IV-10), (IV-11) and (IV-12). The upper state array is then diagonalized preferably using the same exact diagonalization routine used for the ground state. Each energy level is labeled with the appropriate quantum numbers JK\_K+ and stored in memory. The set of eigenvectors diagonalizing the array for each J value is computed and stored in memory for future use. As an example, the program U.S.Ex.D. listed in Appendix VIII will perform all of these functions for the interacting (110) and (011) bands except calculate eigenvectors. However, it can be modified to calculate eigenvectors, too.

- (d) Using the selection rules, appropriate energy levels from the ground state are subtracted from each upper state level to give a set of calculated frequencies which are stored in memory. This set of frequencies would represent the observed spectrum of the molecule if the input upper state parameters were the true values for the molecule. However, this is rarely the case at the beginning of an analysis.
- (e) At this point a least squares subroutine may be used to compare calculated and observed frequencies and make adjustments to minimize the differences between them. The transition from a matrix array to

the least squares subroutine is done by means of the stored eigenvectors and will be treated separately in the next section.

- (f) The new upper state parameters found from least squares may be input again and the steps b, c, and d repeated to find the set of frequencies predicted from them. Using frequencies predicted from the new parameters, more observed frequencies may be input and the whole process repeated. In this general manner all of the absorption lines in a given region may hopefully be identified.

#### Programming the Multiple Regression Subroutine

The main problem in using a least squares subroutine to vary upper state parameters and predict the resulting frequencies (multiple regression analysis) is to get from the  $N \times N$  matrix array containing these parameters into a system of  $N$  equations suitable for a least squares treatment. An understanding of this method is very important for using theoretical Hamiltonian arrays to analyze experimental data.

In general, the difference between an observed frequency  $f_o$  and the calculated frequency  $f_c$  is fit in the least squares subroutine. The calculated frequency is the difference between the upper state eigenvalue  $E_u$  and the ground state eigenvalue  $E_g$ . Since the ground state is not being varied, the discussion will center around the upper state treatment. A particular upper state eigenvalue  $E_{xu}$

may be written in terms of its eigenvector  $X$  and the Hamiltonian matrix as

$$X^T H_u X = E_{xu} \quad (\text{VI-1})$$

where  $X$  is a column vector calculated by the subroutine and stored in memory. In terms of the matrix components; the expression equivalent to (VI-1) is

$$E_{xu} = \sum_{ij} x_i^* H_{ij} x_j \quad (\text{VI-2})$$

where the  $H_{ij}$  may be found from (IV-8), (IV-9), (IV-10), (IV-11) and (IV-12) in the case of a Coriolis-type perturbation between mutually interacting bands. The terms in (VI-2) may be factored into products of molecular parameters and operator expectation values in the representation diagonalizing  $H$ .

The sum in (VI-2) may be better understood by considering the case of the rigid rotor described by (I-1). The Hamiltonian matrix for the case  $J = 1$  may be found using either Appendix VI or by simplifying (IV-3). The resulting matrix equation is

$$\begin{vmatrix} H_{11} & 0 & H_{13} \\ 0 & H_{22} & 0 \\ H_{31} & 0 & H_{33} \end{vmatrix} \quad (\text{VI-3})$$

where  $H_{11} = H_{33} = (A+B)/2+C$ ,  $H_{22} = (A+B)$  and  $H_{13} = H_{31} = (B-A)/2$ . The eigenvalues are found to be  $E_1 = A+C$ ,  $E_2 =$

$(A+B)$  and  $E_3 = B+C$ . The set of eigenvectors that would be found by the computer for (VI-3) are

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}, \quad \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \quad \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix} \quad (\text{VI-4})$$

corresponding to  $E_1$ ,  $E_2$  and  $E_3$  respectively. The choice of phase is arbitrary. Thus using the first vector in (VI-4), the eigenvalue  $E_1$  may be written using (VI-2) as

$$E_1 = \frac{A}{2} (x_1 - x_3)^2 + \frac{B}{2} (x_1 + x_3)^2 + C(x_1^2 + x_3^2) \quad (\text{VI-5})$$

where  $x_1 = 2^{-\frac{1}{2}}$  and  $x_3 = -2^{-\frac{1}{2}}$ . Similar equations corresponding to  $E_2$  and  $E_3$  may also be written. The terms in brackets in (VI-5) are operator expectation values in the representation diagonalizing  $H$  so (VI-5) is often found in the literature written symbolically as

$$E_1 = A\langle P_a^2 \rangle + B\langle P_b^2 \rangle + C\langle P_c^2 \rangle \quad (\text{VI-6})$$

At this point, the eigenvalue equation (VI-5) is in a form suitable for entry into a least squares subroutine.

If (VI-6) describes the upper state of this hypothetical rigid rotor, then the frequency due to a transition from a vibrational ground state energy level  $E_g$  is

$$f_1 = E_1 - E_g = A\langle P_a^2 \rangle + B\langle P_b^2 \rangle + C\langle P_c^2 \rangle + v_o - E_g \quad (\text{VI-7})$$

where  $\nu_0$  is the bandcenter and it is assumed that  $E_g$  is very close to its true value. If the "observed" frequency  $f_o$  is close to the calculated frequency  $f_1$  then to a good approximation.

$$\begin{aligned} f_o &= (A + \Delta A) \langle P_a^2 \rangle + (B + \Delta B) \langle P_b^2 \rangle + (C + \Delta C) \langle P_c^2 \rangle \\ &+ (\nu_0 + \Delta \nu_0) - E_g \end{aligned} \quad (VI-8)$$

where the difference between  $f_o$  and  $f_1$  is assumed to be due to small changes in  $A, B, C$  and the bandcenter which don't affect the expectation values of the operators. Thus (VI-7) and (VI-8) are combined to give

$$f_o - f_1 = \Delta A \langle P_a^2 \rangle + \Delta B \langle P_b^2 \rangle + \Delta C \langle P_c^2 \rangle + \Delta \nu_0 \quad (VI-9)$$

Systems of equations of this form may now be input to a least square subroutine since  $\Delta A, \Delta B, \Delta C$ , and  $\Delta \nu_0$  will be common to all equations. The changes found from the fit then are added to get the new values of  $A, B, C$ , and the bandcenter. Several detailed examples applying equations of the form (VI-9) to more complicated Hamiltonian matrix equations have been given by Moncur (46).

#### Method of Analysis

So far, for purposes of illustration it has been assumed that good estimates for the molecular parameters were available to aid in identifying transitions. If this

is not true the method of Hill and Edwards (47) may be used to start the analysis. By this method the nearly symmetric rigid rotor approximation

$$E_O = \frac{1}{2}(A+B)J(J+1) + [C - \frac{1}{2}(A+B)]K^2 \quad (VI-10)$$

is used where  $K$  is the quantum number corresponding to  $K_+$  in the oblate limit. Individual absorption lines are identified by the notation  ${}^{\Delta K} \Delta J_K (J)$  where the changes  $\Delta K$  and  $\Delta J$  are represented by P, Q, and R which stand for -1, 0, and 1 respectively. Using (VI-10) the ground state combination differences formed from the "zero series" lines, ( ${}^R_R$  and  ${}^P_P$  lines for which  $J'' = K''$ ) may be written

$${}^R_R_J (J) - {}^P_P_{J+2} (J+2) = A'' + B'' + 4C'' (J+1) \quad (VI-11)$$

where the double prime is used for the ground state. The zero series lines are used because they are least affected by the asymmetry and are among the strongest observed. If the ground state combination differences are plotted, against  $J(J+1)$ ,  $(A''+B'')$  is the intercept and  $4C''$  the slope.

To get an estimate for the upper state A, B, and C, the upper state combination differences are found from the zero series as

$${}^R_R_J (J) - {}^P_P_J (J) = A' + B' + 4C'J \quad (VI-12)$$

and the plotting procedure repeated. The starting values thus obtained are cycled through the least squares fit of the Hamiltonian to help predict more lines and obtain better values of the molecular parameters. Finally the molecular parameters should converge to a final set of values when all possible lines have been assigned.

#### The (210) and (111) Bands

The observed absorptions bands in the  $6300 \text{ cm}^{-1}$  region are the (210) and the (111) which are type B and type A, respectively. It is believed that a three band Coriolis-type interaction (such as the one illustrated in Fig. 7) is present between the (210), (111), and (012) upper state energy levels. Unfortunately the (012) band is not observed to be infrared active; thus so far only the least perturbed lines have been fit to a Hamiltonian expression with no perturbation terms included.

The details of this analysis are given by us (25) and the weighted lines used in the spectrum fitting are listed in Appendix IX.

The values of  $A_e$  and  $B_e$  found from this analysis were used in the analysis of the two band interaction between the (110) and (011) bands. Using

$$A_e = 10.3491 \text{ cm}^{-1}$$

$$B_e = 9.0426 \text{ cm}^{-1}$$

the r and s values for (IV-8) and (IV-9) were calculated. This is thought to be a better estimate than using the ground state values. At present, these two bands are being reanalyzed for "effective" perturbation terms but the values found for  $A_e$  and  $B_e$  are not expected to change significantly.

The ground state molecular parameters found from these bands were used as starting values in the fit of the (110) and (011) bands.

#### The (110) and (011) Bands

The two bands located in the  $3800 \text{ cm}^{-1}$  region are the (110) and (011) bands which mutually interact through a Coriolis-type perturbation as shown in Fig. 6. Initial frequency assignments were made from the lines reported by Savage and Edwards (31). The ground state parameters from the (110) and (011) bands were used to begin the analysis. An unperturbed fit of each band assuming no interaction was tried but was unsuccessful, since many lines remained unassigned.

A successful fit of both bands was obtained by taking into account the perturbations between them. This was done using SPECFIT, a program written by Moncur (46) which inputs equations (IV-8), (IV-9), (IV-10), (IV-11) and (IV-12) into an exact diagonalization subroutine and a least squares subroutine in the manner previously discussed. This program and the details for using it are given by Moncur.

Two slight empirical modifications were added to the equations derived in Chapter IV. These were the addition of a small term,  $H_K K^6$ , and permitting the centrifugal stretching terms to change from their ground state values in order to get a better fit of the data.

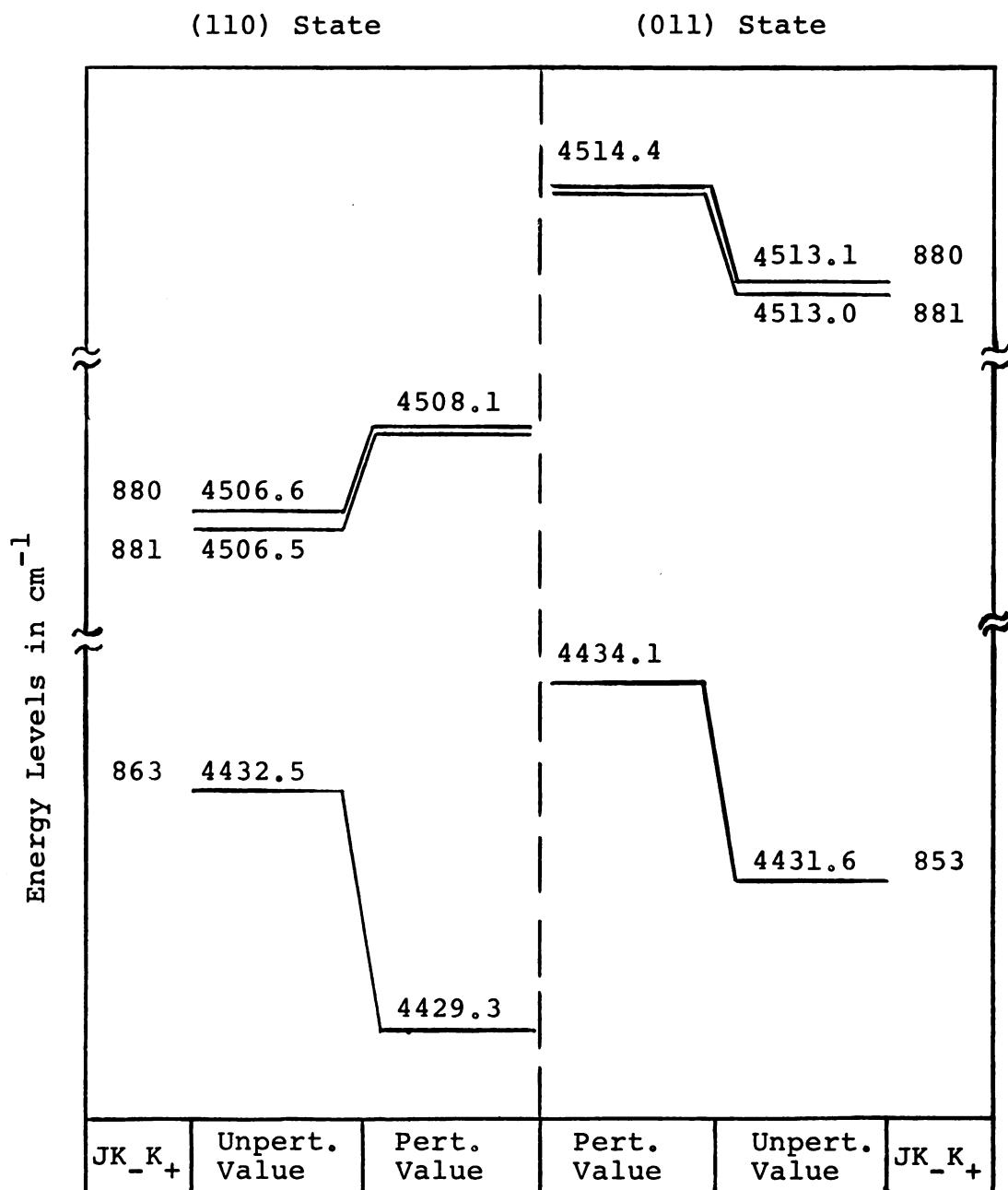
The  $H_K K^6$  is one of several empirical terms suggested in the literature (48); the fourth order Hamiltonian of Chung and Parker as treated by Kneizys, Freedman, and Clough (49) also contains a term with this quantum dependence. The fourth order correction to the equilibrium centrifugal stretching terms as listed by Chung and Parker also shows a vibrational dependence. Thus there is some justification for these empirical modifications.

In the (110) band, 356 lines were identified of which 279 were given nonzero weights. Zero weights were assigned when the shape of a line was very poor, two or more transitions were unresolved, or the line was masked by either an impurity or the isotope  $H_2^{34}S$ . In the (011) band 391 lines were identified of which 316 were given nonzero weights. After all the assignments were made, all possible ground state combination differences were formed and combined with those from the (210) and (111) bands and seven microwave lines to reanalyze the ground state. Then the new ground state parameters were used to refit the upper state of the (011) and (110) bands. The observed and calculated values of the line identifications are listed in Appendix X

Table XII. Molecular Parameters of  $H_2^{3/2}S$  for the States  
(110) and (011)

State	(110)	(011)
$v_0$	$3779.176 \pm 0.011 \text{ cm}^{-1}$	$3789.279 \pm 0.011 \text{ cm}^{-1}$
A	$10.5469 \pm 0.0023$	$10.4828 \pm 0.0019$
B	$9.1057 \pm 0.0020$	$9.1515 \pm 0.0018$
C*	$4.6049 \pm 0.0014$	$4.6109 \pm 0.0014$
$\tau_{aaaa}$	$-0.00971 \pm 0.00014$	$-0.00973 \pm 0.00012$
$\tau_{bbbb}$	$-0.00575 \pm 0.00015$	$-0.00579 \pm 0.00010$
$\tau_{aabb}$	$+0.00678 \pm 0.00017$	$+0.00676 \pm 0.00010$
$\tau_{abab}$	$-0.00213 \pm 0.00010$	$-0.00227 \pm 0.00009$
$H_K$	$-204 \times 10^{-9} \pm 24 \times 10^{-9}$	$-118 \times 10^{-9} \pm 12 \times 10^{-9}$
$G_Z$	$0.261 \pm 0.028 \text{ cm}^{-1}$	
$G_{XY}$	$-0.3603 \pm 0.0079 \text{ cm}^{-1}$	
No. of Points	595	
Standard Deviation	0.0139	

Fig. 12. Energy Level Shifts Due to the Perturbations



and the results of the analysis in Table XII. The tolerance of each parameter is for a confidence interval of 95% which is about 6 times the standard error for this fit.

The shift of several of the more perturbed upper state energy levels from the position predicted by an unperturbed Hamiltonian is shown in Fig. 12. These shifts were calculated using the program NEW CORIKORR listed in Appendix XI.

#### Reanalysis of the Ground State

When the assignments from the (110) and (011) bands were completed the transitions within each band were used to form as many observed ground state combination difference as possible by taking the differences between the appropriate frequencies. Whenever the same combination difference was found within a band or from several bands a weighted average was formed. In all 317 different ground state combination differences were formed from the four bands. In addition, the following seven microwave lines found by Gallagher (50) were included with large weights approximately in proportion to the relative precision of measurement with respect to the infrared combination differences.

$$4_o \rightarrow 4_2 \quad 369,126.912 \text{ MHz}$$

$$2_{-2} \rightarrow 2_o \quad 393,450.40$$

$$3_1 \rightarrow 3_3 \quad 300,505.56$$

$^3_{-1} \rightarrow ^3_1$	369,101.56
$^1_{-1} \rightarrow ^1_1$	168,762.762
$^2_0 \rightarrow ^2_2$	216,710.46
$^4_2 \rightarrow ^4_4$	424,315.45

The conversion used is  $1\text{Mc/sec} = 3.3356382 \times 10^{-5} \text{ cm}^{-1}$ .

Using CD-FIT, a program written by Moncur (46), a set of combination differences  $\Delta f_{\text{calc}}$  (the appropriate differences between the calculated energy levels of the ground state) was formed using the molecular parameters found in our previous analysis. The equation input to the least squares subroutine is

$$\begin{aligned} \Delta f_{\text{obs}} - \Delta f_{\text{calc}} &= (\alpha_1'' - \alpha_2'') \Delta A'' + (\beta_1'' - \beta_2'') \Delta B'' \\ &\quad + (\gamma_1'' - \gamma_2'') \Delta C'' \\ &\quad + \sum_{i=1}^4 [(x_i'')_1 - (x_i'')_2] \Delta \tau_i'' + [(x_8'')_1 - (x_8'')_2] \Delta H_K'' \end{aligned} \quad (\text{VI-13})$$

where  $\Delta f_{\text{obs}}$  stands for the observed ground state combination difference and the coefficients of the molecular parameters are the average values of the operators for the two rotational states involved. The results of the analysis are given in Table XIII. The tolerance of each parameters is for a 95% simultaneous confidence interval which in this case is about 4 times the standard error.

Table XIII. Ground-State Parameters of  $H_2^{32}S$ 

A	$10.3601 \pm 0.0003 \text{ cm}^{-1}$
B	$9.0156 \pm 0.0003$
C	$4.7318 \pm 0.0002$
$\tau_{aaaa}$	$-0.00811 \pm 0.00002$
$\tau_{bbbb}$	$-0.00485 \pm 0.00002$
$\tau_{aabb}$	$+0.00473 \pm 0.00004$
$\tau_{abab}$	$-0.00138 \pm 0.00002$
$H_K$	$-73 \times 10^{-9} \pm 12 \times 10^{-9}$
No. of Points	324
Standard Deviation	0.006      Excludes Microwave Lines

These values lie within the confidence intervals of those reported earlier from our analysis of the (210) and (111) bands. The observed and calculated values of the ground state combination differences are listed in Appendix XII.

## CHAPTER VII

### CONCLUSION

The second-order quantum mechanical Hamiltonian expression for the nonlinear XYX asymmetric molecule has been extended to include Coriolis-type perturbations between pairs of mutually interacting absorption bands. New expressions have been found for the coupled Wang energy matrices which include the perturbation coefficients and centrifugal stretching terms.

The results from the analysis of two calibrated high resolution spectra of the (210) and (111) bands of  $H_2^{3/2}S$  (near  $6300\text{ cm}^{-1}$ ) were used to evaluate terms in the Hamiltonian expression and make order of magnitude estimates.

Five calibrated high resolution spectra of the (110) and (011) bands of  $H_2^{3/2}S$  (which mutually interact through a Coriolis-type perturbation) were run near  $3800\text{ cm}^{-1}$ . In order to minimize measurement error, measured frequencies from each recording were combined using a weighted averaging technique which took into account the precision of measurement of each line and the quality of calibration of each record.

The (110) and (011) bands of  $H_2^{3/2}S$  were simultaneously analyzed using the derived Hamiltonian expression

which takes into account their mutual interaction. It was possible to identify most of the observed  $H_2^{32}S$  absorption lines in the  $3800 \text{ cm}^{-1}$  region by means of this analysis.

Using data from the (210), (111), (110) and (011) bands along with seven microwave lines, the ground state of  $H_2^{32}S$  was refit by means of ground state combination differences. Improved values were obtained for the ground state A, B, C, taus and  $H_K$  term. Then the upper states of the (110) and (011) bands were fit again using the new ground state values. This fit yielded final upper state values of A, B, C, four taus,  $H_K$  and the perturbation coefficients  $G_{xy}$  and  $G_z$ . The revised values of the ground state parameters make no appreciable change in the values for the equilibrium molecular constants and structure published earlier by us (25).

The favorable comparison of the standard deviation of the ground state combination difference fit and of the upper state fit with the standard deviation of the calibration fit is interpreted to mean that the equations used are essentially correct. However, the improved results given by the slight empirical modifications of allowing the taus to differ in different vibrational states and adding the  $H_K$  term indicate that a higher-order expression might be useful for analyzing the  $3800 \text{ cm}^{-1}$  region. The molecular parameters found in this analysis should be directly applicable to such an extension of the energy equations.



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## APPENDIX I

$\Omega_{ss'}^{(2)\alpha\beta}$  FOR THE NONLINEAR XYX MOLECULE

From the definition in (II-8)

$$\Omega_{ss'}^{(2)\alpha\beta} = -A_{ss'}^{\alpha\beta} + \sum_{s''} \zeta_{ss''}^\alpha \zeta_{s's''}^\beta + \sum_{\delta=x,y,z} \frac{a_s^\alpha a_{s'}^\beta}{I_\delta}$$

The  $A_{ss'}^{\alpha\beta}$  are defined as (15)

$$A_{ss'}^{\alpha\alpha} = \sum_i (l_{is}^\beta l_{is'}^\beta + l_{is}^\gamma l_{is'}^\gamma)$$

$$A_{ss'}^{\alpha\beta} = - \sum_i l_{is}^\alpha l_{is'}^\beta$$

When the values for the  $l_{in}^\alpha$  (17) are substituted into this definition, the following non-zero terms result:

$$A_{11}^{xx} = (l_{11}^y)^2 + (l_{21}^y)^2 + (l_{31}^y)^2 = \sin^2 \gamma$$

$$A_{22}^{xx} = (l_{12}^y)^2 + (l_{22}^y)^2 + (l_{32}^y)^2 = \cos^2 \gamma$$

$$A_{33}^{xx} = (l_{23}^y)^2 + (l_{33}^y)^2 = \frac{I_x}{I_z}$$

$$A_{21}^{xx} = l_{12}^y l_{11}^y + l_{22}^y l_{21}^y + l_{32}^y l_{31}^y = \cos \gamma \sin \gamma$$

$$A_{11}^{yy} = (l_{21}^x)^2 + (l_{31}^x)^2 = \cos^2 \gamma$$

$$A_{22}^{yy} = (l_{22}^x)^2 + (l_{32}^x)^2 = \sin^2 \gamma$$

$$A_{33}^{YY} = (l_{13}^X)^2 + (l_{23}^X)^2 + (l_{33}^X)^2 = \frac{I_Y}{I_z}$$

$$A_{21}^{YY} = l_{22}^X l_{21}^X + l_{32}^X l_{31}^X = -\sin\gamma \cos\gamma$$

$$A_{11}^{ZZ} = \sum_i [l_{i1}^X l_{i1}^X + (l_{i1}^Y)^2] = 1$$

$$A_{22}^{ZZ} = \sum_i [(l_{i2}^X)^2 + (l_{i2}^Y)^2] = 1$$

(See p. 110 for

$$A_{33}^{ZZ} = \sum_i [(l_{i3}^X)^2 + (l_{i3}^Y)^2] = 1 \quad \text{nonzero } xy \text{ terms}$$

All other  $A_{ss'}^{\alpha\beta}$  terms were found to be zero. It was necessary to carry out this calculation since many of the terms in similar calculations found in the literature contain typographical errors. It was heartening to find that the above values agreed with those found earlier by Parker (51). By using Table V the possible values of  $\Omega_{ss'}^{(2)\alpha\beta}$  are

$$\Omega_{ss'}^{(2)\alpha\beta} = -A_{ss'}^{\alpha\beta} + \sum_s \zeta_{ss''}^\alpha \zeta_{s's''}^\beta + \sum_{\delta=x,y,z} \frac{a_s^{\alpha\delta} a_{s'}^{\beta\delta}}{I_\delta}$$

By carrying out the sum over the  $\alpha\beta$  components in the first sum of (II-7) the nonzero values are found as follows:

$$\Omega_{ss'}^{(2)XX} = -A_{ss'}^{XX} + \frac{a_s^{XX} a_{s'}^{XX}}{I_X} + \frac{a_s^{XY} a_{s'}^{XY}}{I_Y}$$

$$\Omega_{ss'}^{(2)XY} = -A_{ss'}^{XY} + \frac{a_s^{XX} a_{s'}^{YX}}{I_X} + \frac{a_s^{XY} a_{s'}^{YY}}{I_Y}$$

$$\Omega_{ss'}^{(2)yx} = -A_{ss'}^{yx} + \frac{a_s^{yx} a_{s'}^{xx}}{I_x} + \frac{a_s^{yy} a_{s'}^{xy}}{I_y}$$

$$\Omega_{ss'}^{(2)yy} = -A_{ss'}^{yy} + \frac{a_s^{yx} a_{s'}^{yx}}{I_x} + \frac{a_s^{yy} a_{s'}^{yy}}{I_y}$$

$$\Omega_{ss'}^{(2)zz} = -A_{ss'}^{zz} + \sum_{s''} \zeta_{ss''}^z \zeta_{s's''}^z + \frac{a_s^{zz} a_{s'}^{zz}}{I_z}$$

Therefore the first sum in (II-7) is:

$$\begin{aligned} & \frac{\pi}{2} \sum_{ss'} \frac{q_s q_{s'}}{(\lambda_s \lambda_{s'})^{\frac{1}{4}}} \left[ \begin{array}{l} \frac{\Omega_{ss'}^{(2)xx} p_x^2}{I_x^2} + \frac{\Omega_{ss'}^{(2)xy} p_x p_y}{I_x I_y} + \frac{\Omega_{ss'}^{(2)yx} p_y p_x}{I_y I_x} \\ + \frac{\Omega_{ss'}^{(2)yy} p_y^2}{I_y^2} + \frac{\Omega_{ss'}^{(2)zz} p_z^2}{I_z^2} \end{array} \right] \\ &= \frac{1}{2} \sum_{ss'} \sum_{\alpha \beta} \frac{\Omega_{ss'}^{(2)\alpha \beta}}{I_\alpha I_\beta} \left( \frac{\pi}{\lambda_s \lambda_{s'}} \right)^{\frac{1}{4}} q_s q_{s'} p_\alpha p_\beta \end{aligned}$$


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Nonzero xy terms:

$$A_{13}^{xy} = -\cos\gamma \left( I_x / I_z \right)^{\frac{1}{2}} = A_{31}^{yx}$$

$$A_{23}^{xy} = \sin\gamma \left( I_x / I_z \right)^{\frac{1}{2}} = A_{32}^{yx}$$

$$A_{31}^{xy} = -\left( I_y / I_z \right)^{\frac{1}{2}} \sin\gamma = A_{13}^{yx}$$

$$A_{32}^{xy} = -\left( I_y / I_z \right)^{\frac{1}{2}} \cos\gamma = A_{23}^{yx}$$

## APPENDIX II

### USING ISOTOPIC SUBSTITUTION TO FIND FORCE CONSTANT ESTIMATES

Isotopic substitution is useful for estimating the force constants in (II-28) since the three normal frequencies of hydrogen sulfide do not constitute enough information. By including the normal frequencies of deuterium sulfide, (II-28) may be solved for estimates of the force constants. The method of isotopic substitution is detailed in the literature (19) so only the important steps are covered here.

Using the same geometry and mass-adjusted symmetry coordinates as Chung and Parker (17), the symmetry coordinates without the mass adjustment are denoted by primes on  $u$ ,  $v$ , and  $w$ .

$$\sqrt{\frac{2}{m}} u = (x_2' - x_3') = u'$$

$$\frac{v}{\sqrt{\mu}} = y_1' - \frac{(y_2' + y_3')}{2} = v'$$

$$\frac{w}{\sqrt{\mu_3}} = x_1' - \frac{(x_2' + x_3')}{2} = w'$$

Then the harmonic potential energy is

$$\begin{aligned} 2V &= k_{11}u^2 + k_{22}v^2 + k_{33}w^2 + 2k_{12}uv \\ &= k_{11}'u'^2 + k_{22}'v'^2 + k_{33}'w'^2 + 2k_{12}'u'v' \end{aligned}$$

The harmonic force constants in this system are given by

$$k_{11}' = \frac{m}{2} k_{11}$$

$$k_{33}' = \mu_3 k_{33}$$

$$k_{22}' = \mu k_{22}$$

$$k_{12}' = \sqrt{\frac{m\mu}{2}} k_{12}$$

From (II-28) and the force constants, it is found that

$$\lambda_1 + \lambda_2 = k_{11} + k_{22} = \frac{2}{m} k_{11}' + \frac{k_{22}'}{\mu}$$

To find  $k_{22}'$  from hydrogen sulfide and deuterium sulfide data, respectively, the expression for  $\lambda_1 + \lambda_2$  is written

$$\frac{m_H}{2} (\lambda_1 + \lambda_2)^H = k_{11}' + \left(\frac{m}{2\mu}\right)^H k_{22}'$$

$$\frac{m_D}{2} (\lambda_1 + \lambda_2)^D = k_{11}' + \left(\frac{m}{2\mu}\right)^D k_{22}'$$

Solving for  $k_{22}'$ ,  $k_{22}'$  may be immediately found.

$$k_{22}' = \frac{(2m_H + M) [m_H (\lambda_1 + \lambda_2)^H - m_D (\lambda_1 + \lambda_2)^D]}{2m_H (m_H - m_D)}$$

To find  $k_{11}'$ , arrange the equation for  $\lambda_1 + \lambda_2$  as

$$\mu^H (\lambda_1 + \lambda_2)^H = 2(\frac{\mu}{m})^H k_{11}' + k_{22}'$$

$$\mu^D (\lambda_1 + \lambda_2)^D = 2(\frac{\mu}{m})^D k_{11}' + k_{22}'$$

Solving for  $k_{11}'$ ,  $k_{11}$  may be found.

$$k_{11} = \frac{m_H(2m_D + M)(\lambda_1 + \lambda_2)^H - m_D(2m_H + M)(\lambda_1 + \lambda_2)^D}{2m_H(m_D - m_H)}$$

### APPENDIX III

#### THE VANISHING COMPONENTS OF $H'_1$

$$H'_1, _{11} = \sum_{n=1}^3 (a_{1n} q_n - i[H_O, S_{1n}]) = \sum_{n=1}^3 (a_{1n} q_n + \frac{ia_{1n} 2i\hbar q_n}{2\hbar}) = 0$$

$$H'_1, _{33} = \sum_{n=1}^2 (a_{3n} q_n^3 - i[H_O, S_{3n}]) = \sum_{n=1}^2 a_{3n} (q_n^3 + \frac{i}{\hbar} (i\hbar q_n^3)) = 0$$

$$H'_1, _{72} = a_{72} \left[ \left( \frac{\lambda_2}{\lambda_3} \right)^{\frac{1}{4}} p_2 q_3 - \left( \frac{\lambda_3}{\lambda_2} \right)^{\frac{1}{4}} q_2 p_3 \right] - i[H_O, S_{72}]$$

$$= a_{72} \left[ \left( \frac{\lambda_2}{\lambda_3} \right)^{\frac{1}{4}} p_2 q_3 - \left( \frac{\lambda_3}{\lambda_2} \right)^{\frac{1}{4}} q_2 p_3 \right]$$

$$- a_{72} \left[ \left( \frac{\lambda_2}{\lambda_3} \right)^{\frac{1}{4}} p_2 q_3 - \left( \frac{\lambda_3}{\lambda_2} \right)^{\frac{1}{4}} q_2 p_3 \right] = 0$$

$$H'_1, _{55} = \sum_{n=1}^2 (a_{51n_2} q_1 q_2 + a_{5n_3 3} q_3^2) q_n$$

$$- i[H_O, \sum_{n=1}^2 (S_{51n_2} + S_{5n_3 3})]$$

$$= \sum_{n=1}^2 (a_{51n_2} q_1 q_2 + a_{5n_3 3} q_3^2) q_n$$

$$- \sum_{n=1}^2 a_{51n_2} \sum_{j=1}^2 D_{nj} q_n^2 q_j - \sum_{n=1}^2 a_{5n_3 3} q_3^2 q_n = 0$$

where  $D_{nj} \equiv (1 - \delta_{nj})$

## APPENDIX IV

### THE COMMUTATORS IN $H_2'$

The following notation is used for the commutators in (III-8) :

$$\begin{aligned} N_1 &= \frac{1}{2} \left[ 3 \left( \frac{\lambda_1}{\lambda_3} \right)^{\frac{1}{4}} + \left( \frac{\lambda_3}{\lambda_1} \right)^{\frac{1}{4}} \right] & N_2 &= \left( \frac{\lambda_2}{\lambda_3} \right)^{\frac{1}{4}} \\ M_1 &= \left( \frac{\lambda_3}{\lambda_2} \right)^{\frac{1}{4}} & M_2 &= \frac{1}{2} \left[ 3 \left( \frac{\lambda_3}{\lambda_1} \right)^{\frac{1}{4}} + \left( \frac{\lambda_1}{\lambda_3} \right)^{\frac{1}{4}} \right] \end{aligned}$$

The commutators are:

$$\begin{aligned} \left( \frac{i}{2} \right) \left[ \sum_{n=1}^3 S_{nn'} (H_1 + H_1') \right] &= - \frac{i}{2\hbar^2} \left[ \sum_{n=1}^3 \frac{a_{1n} p_n}{\lambda_n^{\frac{1}{2}}} (H_1 + H_1') \right] \\ &= - \frac{1}{2\hbar} \sum_{n=1}^3 \frac{a_{1n}^2}{\lambda_n^{\frac{1}{2}}} - \frac{3}{2\hbar} \sum_{n=1}^3 \frac{a_{1n} a_{3n} q_n^2}{\lambda_n^{\frac{1}{2}}} - \sum_{n=1}^3 \frac{a_{5n} q_3}{\hbar} \left( \frac{a_{1n} q_3}{2\lambda_n^{\frac{1}{2}}} + \frac{a_{13} q_n}{\lambda_3^{\frac{1}{2}}} \right) q_3 \\ &\quad - \sum_{n,j=1}^2 \frac{D_{nj} a_{1n}}{\hbar \lambda_n^{\frac{1}{2}}} \left( a_{51n_2} q_n + \frac{a_{51j_2} q_j}{2} \right) q_j \\ &\quad + \sum_{n=2,3}^{n \neq 1} \frac{(-1)^n a_{1n}}{2\hbar} \sum_{j=2,3}^{j \neq 1} \frac{a_{72} D_{nj}}{\lambda_n^{\frac{1}{2}}} \left( \frac{\lambda j}{\lambda n} \right)^{\frac{1}{4}} p_j \\ &\quad - \sum_{n=1,3}^{n \neq 2} \frac{(-1)^{n+1} a_{1n} a_{71}}{4\hbar \lambda_n^{\frac{1}{2}}} \sum_{j=1,3}^{j \neq 2} D_{nj} \left[ 3 \left( \frac{\lambda j}{\lambda n} \right)^{\frac{1}{4}} + \left( \frac{\lambda n}{\lambda j} \right)^{\frac{1}{4}} \right] p_j \end{aligned}$$

$$\frac{i}{2} \left[ \sum_{n=1}^2 S_{3n}, (H_1 + H_1') \right] = -\frac{1}{4} \sum_{n=1}^2 \frac{a_{3n}}{\lambda_n^2} \left[ \begin{array}{l} [a_{1n} + a_{5n33}q_3^2 + \sum_{j=1}^2 D_{nj} (a_{51j2}q_j^2 - a_{7nM_j}p_3)] p_n^2 \\ + a_{3n} (\frac{3}{2} [p_n^2, q_n^2] + \lambda_n^2) + a_{51n2} \sum_{j=1}^2 D_{nj} [p_n^2, q_n] + q_j \end{array} \right]$$

$$-\frac{1}{4} \sum_{n=1}^2 \frac{a_{3n}}{2\lambda_n^2} \left[ \begin{array}{l} \sum_{j=1}^2 D_{nj} (a_{51n2} (q_j^2 + 2q_n q_j) - a_{7nM_j} p_3) q_n^2 \\ - a_{7nN_n} [q_n, p_n] + q_3 + (a_{1n} + a_{5n33}q_3^2 + 3a_{3n}q_n^2) q_n^2 \end{array} \right]$$

$$\left( \frac{i}{2} \right) \left[ \sum_{n=1}^2 S_{51n2}, (H_1 + H_1') \right]$$

$$= \frac{-1}{24} \sum_{n,j=1}^2 \frac{D_{nj} a_{51n2}}{\lambda_j^{1/2} (4\lambda_n - \lambda_j)} \left[ \begin{array}{l} (2\lambda_n - \lambda_j) \left[ \begin{array}{l} a_{1j} + a_{51n2}q_n^2 + a_{5j33}q_3^2 \\ - a_{7jM_n}p_3 + 3a_{3j}q_j^2 \\ + 2a_{51j2}q_nq_j \\ - 2a_{7nN_n}q_n p_j q_3 \end{array} \right] q_n^2 \\ + (\lambda_n \lambda_j)^{1/2} \left[ \begin{array}{l} 2 \left[ a_{1n} + a_{51j2}q_j^2 \right] \\ a_{7nM_j}p_3 + a_{5n33}q_3^2 \end{array} \right] q_n q_j \\ + 6a_{3n}^3 q_n q_j + 4a_{51n2} q_j^2 q_n^2 \\ - a_{7jN_j} [p_n, q_n] + q_3 \\ - 2a_{7nN_n} p_n q_j q_3 \end{array} \right]$$

$$+ \frac{-1}{2\kappa} \sum_{n,j=1}^2 \frac{D_{nj} a_{5jn2}}{\lambda_j^2 (4\lambda_n - \lambda_j)} \left( \frac{2\lambda_n}{\kappa^2} \right) \boxed{[a_{1j} + a_{5j33} q_3^2 - a_{7jMn} p_3] p_n^2 + 2[a_{1n} + a_{5n33} q_3^2 - a_{7nMj} p_3] p_n p_j + 3a_{3n} [p_n, q_n]^+ p_j + 3a_{3j} p_n^2 q_j^2 + a_{51n2} [2[p_n, q_n]^+ p_j q_j + q_n^2 p_n^2] + 2a_{51j2} [p_n p_j q_j^2 + q_n p_n^2 q_j]}$$

$$\left(\frac{i}{2}\right) \left[ \sum_{n=1}^2 S_{5n33}, (H_1 + H_1') \right]$$

$$= \left(\frac{-1}{2\kappa}\right) \sum_{n,j=1}^2 \frac{D_{nj} a_{5jn3}}{\lambda_n^2 (4\lambda_3 - \lambda_n)} \left( (2\lambda_3 - \lambda_n) \right) \boxed{[a_{1n} + a_{51j2} q_j^2 + a_{5n33} q_3^2] q_3^2 + 3a_{3n} q_n^2 q_3^2 + 2a_{51n2} q_n q_j q_3^2 + 2a_{7jMn} p_n q_j q_3 + a_{7nMj} (2p_n q_n q_3 - p_3 q_3^2)}$$

$$+ \left(\frac{\lambda_n \lambda_3}{\kappa^2}\right)^{\frac{1}{2}} \boxed{2(a_{13} q_n + a_{7jNj} q_n p_j) q_3 + 4(a_{5133} q_1 q_n + a_{5233} q_2 q_n) q_3^2 - a_{7nNn} (p_3 q_3^2 + q_3 p_3 q_3 - 2p_n q_n q_3) + 2(a_{72M1} q_2 + a_{71M2} q_1) q_n p_3}$$

$$+ \left( \frac{-1}{2\hbar} \right)^2 \sum_{n,j=1}^2 \frac{D_{nj} a_{5n33}}{\lambda_n^2 (4\lambda_3 - \lambda_n)} \left( \frac{2\lambda_3}{\hbar^2} \right) \boxed{(a_{1n} + a_{51j2} q_j^2 - a_{7n} M_j) p_3^2 \\ + 3a_{3n} q_n^2 p_3^2 + 2(a_{51n2}) q_n q_j p_3^2 \\ + a_{5n33} [2[p_3, q_3]^+ p_n q_n + q_3^2 p_3^2] \\ + 2a_{5j33} [p_3, q_3]^+ p_n q_j \\ + 2(a_{13} p_n + a_{71} N_1 p_1 p_n + a_{72} N_2 p_n p_2) p_3}$$

$$\left( \frac{i}{2} \right) [S_{71}^*, (H_1 + H_1')]$$

$$= \frac{a_{71} (\lambda_3^{1/2} - \lambda_1^{1/2}) \hbar}{4(\lambda_1 \lambda_3^{1/4}) (\lambda_1^{1/2} + \lambda_3^{1/2})} \boxed{-a_{72} M_1 q_1 q_2 - a_{71} M_2 q_1^2 + a_{71} N_1 q_3^2 \\ + (a_{11} p_3 + a_{5122} q_2 p_3 - a_{71} M_2 p_3^2) \left( \frac{1}{\hbar^2} \right) \\ + (a_{13} p_1 + a_{72} N_2 p_1 p_2 + a_{71} N_1 p_1^2) \left( \frac{1}{\hbar^2} \right) \\ + 3a_{31} \frac{q_1^2 p_3}{\hbar^2} + 2a_{5112} \frac{q_1 q_2 p_3}{\hbar^2} \\ + \frac{a_{5133}}{\hbar^2} [2p_1 q_1 q_3 + q_3^2 p_3] + \frac{2a_{5233}}{\hbar^2} p_1 q_2 q_3}$$

$$\left( \frac{i}{2} \right) [S_{72}^*, (H_1 + H_1')]$$

$$= \frac{-a_{72} \hbar}{4(\lambda_2 \lambda_3)^{1/4} (\lambda_3 - \lambda_2)} \left( \lambda_2 + \lambda_3 \right) \boxed{a_{72} (M_1 q_2^2 - N_2 q_3^2) + a_{71} \frac{M_2 q_1 q_2}{\hbar}}$$

$$+ \frac{-a_{72} \pi}{4(\lambda_2 \lambda_3)^{\frac{1}{4}} (\lambda_3 - \lambda_2)} \frac{2(\lambda_2 \lambda_3)^{\frac{1}{2}}}{\pi^2} \boxed{a_{12} p_3 + a_{5112} q_1^2 p_3 - a_{72} \overline{M_1 p_3}^2 \\ + a_{13} p_2 + a_{72} N_2 p_2^2 + a_{71} N_1 p_1 p_2 \\ + 3a_{32} q_2^2 p_3 + 2a_{5122} q_1 q_2 p_3 \\ + 2a_{5133} q_1 p_2 q_3 + \\ + a_{5233} (2p_2 q_2 q_3 + q_3^2 p_3)}$$

## APPENDIX V

THE PURELY VIBRATIONAL CONTRIBUTIONS  $E_v'$  AND  $E_v''$

$$E_v' = - \frac{7}{16\hbar} \sum_{n=1}^2 \frac{a_3^2 n}{\lambda_n^{\frac{1}{2}}} - \frac{15}{4\hbar} \sum_{n=1}^2 \frac{a_3^2 n (v_n + \frac{1}{2})^2}{\lambda_n^{\frac{1}{2}}}$$

$$- \frac{3}{2\hbar} \sum_{n=1}^2 \frac{a_3 n a_{5n33} (v_3 + \frac{1}{2}) (v_n + \frac{1}{2})}{\lambda_n^{\frac{1}{2}}}$$

$$- \frac{1}{\hbar} \sum_{n,j=1}^2 \frac{D_{nj} a_{3n}}{\lambda_n^{\frac{1}{2}}} (a_{51j2} + \frac{a_{51n2}}{2}) (v_j + \frac{1}{2}) (v_n + \frac{1}{2})$$

$$- \frac{1}{2\hbar} \sum_{n,j=1}^2 \frac{D_{nj} a_{51n2}}{\lambda_j^{\frac{1}{2}}} \left[ \begin{array}{l} a_{5j33} (v_3 + \frac{1}{2}) + a_{51n2} (v_n + \frac{1}{2}) \\ + (3a_{3j} + \frac{4(\lambda_n \lambda_j)^{\frac{1}{2}}}{(4\lambda_n - \lambda_j)} a_{51n2}) (v_j + \frac{1}{2}) \end{array} \right] (v_n + \frac{1}{2})$$

$$- \frac{1}{2\hbar} \sum_{n,j=1}^2 \frac{D_{nj} a_{5n33}}{\lambda_n^{\frac{1}{2}}} \left[ \begin{array}{l} a_{51j2} (v_j + \frac{1}{2}) + a_{5n33} (v_3 + \frac{1}{2}) \\ + (3a_{3n} + \frac{4(\lambda_n \lambda_3)^{\frac{1}{2}}}{(4\lambda_3 - \lambda_n)} a_{5n33}) (v_n + \frac{1}{2}) \end{array} \right] (v_3 + \frac{1}{2})$$

$$E_v'' = \frac{\pi^2 \zeta_{13}^2}{2I_z} \left[ \left( \frac{\lambda_3}{\lambda_1} \right)^{\frac{1}{2}} + \left( \frac{\lambda_1}{\lambda_3} \right)^{\frac{1}{2}} \right] (v_1 + \frac{1}{2}) (v_3 + \frac{1}{2})$$

$$+ \frac{\pi^2 \zeta_{23}^2}{2I_z} \left[ \left( \frac{\lambda_3}{\lambda_2} \right)^{\frac{1}{2}} + \left( \frac{\lambda_2}{\lambda_3} \right)^{\frac{1}{2}} \right] (v_2 + \frac{1}{2}) (v_3 + \frac{1}{2})$$

$$- \frac{\pi^2}{4I_z} (\zeta_{13}^2 + \zeta_{23}^2) + \frac{3hc}{2} \sum_{i=1}^3 k_{iiii} [(v_i + \frac{1}{2})^2 + \frac{1}{4}]$$

$$+ 3hc \sum_{i,j=1}^3 D_{ij} k_{iiji} (v_i + \frac{1}{2}) (v_j + \frac{1}{2})$$

## APPENDIX VI

### ANGULAR MOMENTUM MATRIX ELEMENTS

Listed here are the angular momentum matrix elements from Posener (19) needed to evaluate (III-18), (III-19) and (III-20) to arrive at (IV-3) and (IV-4) using  $f = J(J+1)$ .

$$\begin{aligned}
 & \langle K | P_z^1 | K \rangle = \hbar K \quad \langle K | P_z^2 | K \rangle = \hbar^2 K^2 \quad \langle K | P_z^4 | K \rangle = \hbar^4 K^4 \\
 & \langle K | P_x^2 | K \rangle = \langle K | P_y^2 | K \rangle = \frac{\hbar^2}{2} [f^2 - K^2] \\
 & \langle K | P_x^4 | K \rangle = \langle K | P_y^4 | K \rangle = \frac{\hbar^4}{8} [3f^2 - 2(3K^2 + 1)f + K^2(3K^2 + 5)] \\
 & \langle K | [P_x^2, P_y^2]^+ | K \rangle = \frac{\hbar^4}{4} [f^2 - 2(K^2 - 1)f + K^2(K^2 - 5)] \\
 & \langle K | [P_x^2, P_z^2]^+ | K \rangle = \langle K | [P_y^2, P_z^2]^+ | K \rangle = \hbar^4 [f - K^2] K^2 \\
 & \langle K | P_x^2 | K \pm 2 \rangle = -\langle K | P_y^2 | K \pm 2 \rangle = -\frac{\hbar^2}{4} [[f - K(K \pm 1)][f - (K \pm 1)(K \pm 2)]]^{\frac{1}{2}} \\
 & \langle K | P_x^4 | K \pm 2 \rangle = -\langle K | P_y^4 | K \pm 2 \rangle \\
 & \qquad \qquad \qquad = -\frac{\hbar^4}{8} [[f - K(K \pm 1)][f - (K \pm 1)(K \pm 2)]]^{\frac{1}{2}} [2f - K - (K+2)^2] \\
 & \langle K | [P_x^2, P_z^2]^+ | K \pm 2 \rangle = -\langle K | [P_y^2, P_z^2]^+ | K \pm 2 \rangle \\
 & \qquad \qquad \qquad = -\frac{\hbar^4}{4} [[f - K(K \pm 1)][f - (K \pm 1)(K \pm 2)]]^{\frac{1}{2}} [K^2 + (K \pm 2)^2] \\
 & \langle K | [P_x, P_y]^+ | K \pm 2 \rangle = \pm i \frac{\hbar^2}{2} [[f - K(K \pm 1)][f - (K \pm 1)(K \pm 2)]]^{\frac{1}{2}} \\
 & \langle K | P_x^4 | K \pm 4 \rangle = \langle K | P_y^4 | K \pm 4 \rangle = -\frac{1}{2} \langle K | [P_x^2, P_y^2]^+ | K \pm 4 \rangle \\
 & \qquad \qquad \qquad = \frac{\hbar^4}{16} [[f - K(K \pm 1)][f - (K \pm 1)(K \pm 2)][f - (K \pm 2)(K \pm 3)][f - (K \pm 3)(K \pm 4)]]^{\frac{1}{2}}
 \end{aligned}$$

APPENDIX VII

LISTING OF PROGRAM G.S.Ex.D.

```

PROGRAM GSEXD
DIMENSION EP(11,11), EM(10,10), OP(10,10), OM(10,10)
COMPLEX EP,EM,OP,OM
COMMON IOPT,RHO,IER
C ARITHMETIC STATEMENT FUNCTIONS
0F1(A,B,CS, J,K)=,5*(J*(J+1,)-K*K)*(A+B*TAN+,5*K*K*R)+(J**2*(J+1,
1 **2 -2,*K*K-1,)*J*(J+1,)*K*K*(K*K-5,))*Y/16,+*(CS+,75*TAN)*K*K
2 +,25*T*K**4+(3,*J**2*(J+1,)**2*2,*+(3,*K*K-1,)*J*(J+1,)*K*K*(3,*K
3*K-5,))*X/32, +HK*K**6
F2(A,B,J)=,25*J*(J+1,)*(B-A*(J*(J+1,)-1,)*,25*V+,5*S)
F3(J)=J*(J+1,)*(J*(J+1,)-2,)
0F4(A,B,J)=,25*SQRT(2,*J*(J+1,)*(J*(J+1,)-2,))*(B=A+,25*V*(J*(J+1,
1=2,)+S)
0F5(J)=SQRT(2,*J*(J+1,)*(J*(J+1,)-2,)*(J*(J+1,)-6,)*(J*(J+1,)-12,))*
1*U
0F6(A,B,J,K)=,25*SQRT((J*(J+1,)-K*(K+1,))*(J*(J+1,)-(K+1,)*(K+2,)))
1*(B-A+,25*(J*(J+1,)-K*K-2,*K-2,)*V+,5*(K*K-2,*K-2,)*S)
F7(J)=J*(J+1,)*SQRT((J*(J+1,)-2,)*(J*(J+1,)-6,))+U
0F8(J,K)=U*SQRT((J*(J+1,)-K*(K+1,))*(J*(J+1,)-(K+1,)*(K+2,))*
1*(J*(J+1,)-(K+2,)*(K+3,))*(J*(J+1,)-(K+3,)*(K+4,)))
READ 12,A,B,C,JRUN,TAO,TAT,TAS,TAN,AEQ,BEQ,HK,IFMAT
12 FORMAT(3F15.7,33X,I2/4F10.7/2F15.7,F15.12,33X,I2)
C ARITHMETIC STATEMENTS
RHO=1,0E-06
IER=0
IOPT=0
CEQ=(AEQ*BEQ)/(AEQ+BEQ)
RS=CEQ**2/AEQ**2
SS=CEQ**2/BEQ**2
R=RS*(TAO+TAS)+SS*(TAT+TAS)
S=TAS*(RS-SS)+TAT*SS-TAO*RS
T=2,*RS*SS*TAS+RS**2*TAO+SS**2*TAT
V=(TAT-TAO)
X=(TAO+TAT)
Y=(TAS+2,*TAN)
U=(,5*X-Y)/32,
PRINT 2000,A,B,C,TAO,TAT,TAS,TAN
2000 FORMAT(// A(V)=*F15.7/* B(V)=*F15.7/* C(V)=*F15.7/
1 * TAAAAA=*F10.7* TBBRB=*F10.7* TAABB=*F10.7* TABAB=*F10.7//)
PRINT 2001,AEQ,BEQ,CEQ,HK
2001 FORMAT(*AEQ=*F15.7* BEQ=*F15.7* CEQ=*F15.7* HK=*F15.12//)
DO 11 J=1,JRUN
DO 13 L=1,11
DO 13 M=1,11
13 EP(L,M)=0.0
DO 113 L=1,10
DO 113 M=1,10
EM(L,M)=0.0
OP(L,M)=0.0
113 OM(L,M)=0.0

```

```

C      MATRIX FOR E PLUS AND E MINUS
KS=J/2-1
KMAX=J/2+1
KMIN=KMAX+1
GO TO (5,6,6,7),J
7 EP(1,3)=F5(J)
6 EP(1,2)=F4(A,B,J)
5 EP(1,1)=F1(A,B,C,J,0)
DO 1 K= 2, KMAX
KK = 2*(K-1)
KM = KMAX + K - 1
GO TO (2,3,4), (KMIN=K)
4 EP(K,K+2)=F8(J,KK)
EM(K-1,K+1)=F8(J,KK)
3 EP(K,K+1)=F6(A,B,J,KK)
EM(K-1,K)=F6(A,B,J,KK)
2 IF(KK,EQ,2) EP(K,K)=F1(A,B,C,J,KK)+F3(J)*U
IF(KK,NE,2) EP(K,K)=F1(A,B,C,J,KK)
IF(KK,EQ,2) EM(K-1,K-1)=F1(A,B,C,J,KK)+F3(J)*U
IF(KK,NE,2) EM(K-1,K-1)=F1(A,B,C,J,KK)
1 CONTINUE
C      MATRIX FOR O PLUS AND OMINUS
KIX=(J+1)/2
DO 101 K=1,KIX
KO=2*K-1
GO TO(102,103,104),(KIX+1-K)
104 OP(K,K+2)=F8(J,KO)
OM(K,K+2)=OP(K,K+2)
103 IF(KO,EQ,1) OP(K,K+1)=F6(A,B,J,KO)+F7(J)
IF(KO,NE,1) OP(K,K+1)=F6(A,B,J,KO)
IF(KO,EQ,1) OM(K,K+1)=F6(A,B,J,KO)+F7(J)
IF(KO,NE,1) OM(K,K+1)=F6(A,B,J,KO)
102 IF(KO,EQ,1) OP(K,K)=F1(A,B,C,J,KO)+F2(A,B,J)
IF(KO,NE,1) OP(K,K)=F1(A,B,C,J,KO)
IF(KO,EQ,1) OM(K,K)=F1(A,B,C,J,KO)+F2(A,B,J)
IF(KO,NE,1) OM(K,K)=F1(A,B,C,J,KO)
101 CONTINUE
C FORMING HERMITIAN CONJUGATES
DO 9 N=1,KMAX
IN=N+1
DO 9 M=IN,KMAX
9 EP(M,N)=EP(N,M)
KX=J/2
DO 19 N=1,KX
IN=N+1
DO 19 M=IN,KX
19 EM(M,N)=EM(N,M)
DO 109 N=1,KIX
IN=N+1
DO 109 M=IN,KIX
OP(M,N)=OP(N,M)
109 OM(M,N)=OM(N,M)

```

```

IF(IFMAT) 517,516
516 CONTINUE
C THIS SECTION PRINTS THE MATRIX ELEMENTS
PRINT 518,J
518 FORMAT(///*EPLUS FOR J=*I3)
DO 14 K=1,KMAX
PRINT 10,( EP(K,L),L=1,KMAX)
10 FORMAT(//(12(F10.4)))
14 CONTINUE
PRINT 519,J
519 FORMAT(///*EMINUS FOR J=*I3)
DO 15 K=1,KX
PRINT 16,(EM(K,L),L=1,KX)
16 FORMAT(//(12(F10.4)))
15 CONTINUE
PRINT 520,J
520 FORMAT(///*OPLUS FOR J=*I3)
DO 114 K=1,KIX
PRINT 110,(OP(K,L),L=1,KIX)
110 FORMAT(//(12(F10.4)))
114 CONTINUE
PRINT 521,J
521 FORMAT(///*OMINUS FOR J=*I3)
DO 115 K=1,KIX
PRINT 116,(OM(K,L),L=1,KIX)
116 FORMAT(//(12(F10.4)))
115 CONTINUE
517 CONTINUE
C EIGENVALUES ARE FOUND IN THIS SECTION
CALL JHERMX (EP,11,KMAX)
CALL JHERMX (EM,10,KX)
CALL JHERMX (OP,10,KIX)
CALL JHERMX (OM,10,KIX)
C PRINTING EIGENVALUES WITH J,K*,K* LABELS
PRINT 312,J
312 FORMAT(///*GROUND STATE ENERGY LEVELS FOR J=*I3//)
DO 313 I=1,KMAX
KPLUS=2*(I-1)
TAUP=J=2*KPLUS
KMINUS=TAUP+KPLUS
PRINT 314,J,KMINUS,KPLUS,EP(I,I)
314 FORMAT(313,F15.4)
313 CONTINUE
DO 320 I=1,KX
KPLUS =2*I
TAUP=J=2*KPLUS+1
KMINUS=TAUP+KPLUS
PRINT 314,J,KMINUS,KPLUS,EM(I,I)
320 CONTINUE
DO 330 I=1,KIX
KPLUS =2*I-1
TAUP=J=2*KPLUS

```



```

KMINUS=TAUP*KPLUS
PRINT 314,J,KMINUS,KPLUS,OP(I,I)
330 CONTINUE
DO 340 I=1,KIX
KPLUS =2*I-1
TAUP=J-2*KPLUS+1
KMINUS=TAUP*KPLUS
PRINT 314,J,KMINUS,KPLUS,OM(I,I)
340 CONTINUE
11 CONTINUE
END
SUBROUTINE JHFRMX(A,NM,N)
COMMON JOPT,RHO,IER
DIMENSION A(NM,NM), S(21,21)
COMPLEX A, S, V1, V2, V3, CSNT, SNT, TEMP
IOC = 0
IER = 0
EPI2=0.000000000001
EN = FLOAT(N)
DO 1 I=1,N
DO 1 J=1,N
S(I,J) = (0,0,0,0)
IF(I,EQ,J)S(I,J) =(1,0,0,0)
1 CONTINUE
IF(N,LE,1)GO TO 12
SOFFD = 0,0
NM1 = N-1
DO 2 I=1,NM1
IJ = I+1
DO 2 J=IJ,N
X1=A(I,J)
X2=A(I,J)*(0,0,-1,0)
2 SOFFD=SOFFD+2,0*(X1*X1+X2*X2)
IF(SOFFD ,LT, 0,1E-10)GO TO 12
THR = SQRTF(SOFFD)
FTHR = RHO*THR / EN
IND = 0
3 THR = THR / EN
4 DO 10 L=2,N
LM1 = L-1
DO 10 K=1,LM1
X1=A(L,K)
X2=A(L,K)*(0,0,1,0)
IF(SQRT(X1*X1+X2*X2),LT,THR) GO TO 10
IND = 1
V1 = A(K,K)
V2 = CONJG( A(L,K) )
V3 = A(L,L)
C = -A*IMAG( A(L,K) )
B = REAL( A(L,K) )
E = REAL( A(L,L) )
D = REAL( A(K,K) )

```

```

THET = 0,0
IF(ABSF(C),LT, EPI2)GO TO 13
THET = 1,5707963
IF(ABSF(B),LT, EPI2)GO TO 13
T = C / B
THET = ATANF(T)
13 CONTINUE
PHI = 0,78539818
ED = ABSF(E=D)
IF(ED ,LT, EPI2)GO TO 15
TAO = 2,0*(B*COSF(THET) + C*SINF(THET)) / (E=D)
PHI = 0,5 * ATANF(TAO)
15 CONTINUE
CSNT = COSF(PHI) + (0,0,0,0)
CS = COSF(THET) * SINF(PHI)
SS = SINF(THET) * SINF(PHI)
SNT = CS + (0,0,1,0) * SS
DO 8 I=1,N
TEMP = A(I,K)*CSNT - A(I,L)*CONJG(SNT)
A(I,L) = A(I,K)*SNT + A(I,L)*CSNT
A(I,K) = TEMP
IF(LOPT ,EQ, 0)GO TO 8
TEMP = S(I,K)*CSNT - S(I,L)*CONJG(SNT)
S(I,L) = S(I,K)*SNT + S(I,L)*CSNT
S(I,K) = TEMP
8 CONTINUE
DO 9 I=1,N
A(K,I) = CONJG( A(I,K) )
A(L,I) = CONJG( A(I,L) )
9 CONTINUE
A(K,K) = SNT*CONJG(SNT)*V3 + CSNT*CSNT*V1 - SNT*CSNT*CONJG(V2)
1 = CSNT*CONJG(SNT)*V2
A(L,L) = CSNT*CSNT*V3 + CONJG(SNT)*SNT*V1 + SNT*CSNT*
2 CONJG(V2) + CONJG(SNT)*CSNT*V2
A(K,L) = CSNT*CSNT*V2 - SNT*SNT*CONJG(V2) + CSNT*SNT*V1
1 = CSNT*SNT*V3
A(L,K) = CONJG( A(K,L) )
10 CONTINUE
IOC = IOC + 1
IF(IOC ,GE, 100)GO TO 21
IF(IND ,LE, 0)GO TO 11
IND = 0
GO TO 4
11 IF(THR=FTHR)12,12,3
12 RETURN
21 IER = 1
RETURN
END
RUN,5,1200

```

APPENDIX VIII

LISTING OF PROGRAM U.S.Ex.D.

```

PROGRAM USEXP
DIMENSION FPV1(21,21),FPV2(21,21),OPV1(20,20),OPV2(20,20),
1 A(2),B(2),CS(2),E(82,3),TAO(2),TAT(2),TAS(2),TAN(2),EN(2),HK(2)
COMPLEX FPV1,FPV2,OPV1,OPV2
COMMON IOPT,RHO,IER
C ARITHMETIC STATEMENT FUNCTIONS
0 F1(A,B,CS,EN,TAN,R,X,Y,T,J,K)=.5*(J*(J+1.)-K*K)*
1 (A+B-TAN+.5*K*K*R)+(J**2*(J+1.)*2-2.*K*K-1.)*J*(J+1.)*
2 +K*K*(K*K-5.))*Y/16.+ (CS+.75*TAN)*K*K+EN+.25*T*K**4 +
3 (3.*J**2*(J+1.)*2-2.* (3.*K*K-1.)*J*(J+1.) +
4 K*K*(3.+K*K-5.))*X/32.+HK*K**6
F2(A,B,J,V,S)=.25*J*(J+1.)*(B-A+(J*(J+1.)-1.)*V/4.+S/2.)
F3(J)=J*(J+1.)*(J*(J+1.)-2.)
F4(A,B,J,V,S)=.25*SQRTF(.+J*(J+1.)*(J*(J+1.)-2.))*
1 (B-A+.25*V*(J*(J+1.)-2.))+S
0 F5(J)=SQRTF(.+J*(J+1.)*(J*(J+1.)-2.)*(J*(J+1.)-6.)*(J*(J+1.)-12.))
0 F6(A,B,J,K,V,S)=.25*SQRTF((J*(J+1.)-K*(K+1.))*(J*(J+1.)-(K+1.)*
1 (K+2.)))*(H-A+.25*(J*(J+1.)-K*K-2.*K-2.)*V
2 +.5*(K*K+2.*K+2.)*S)
F7(J)=J*(J+1.)*SQRTF((J*(J+1.)-2.)*(J*(J+1.)-6.))
0 F8(J,K)=SQRTF((J*(J+1.)-K*(K+1.))*(J*(J+1.)-(K+1.)*(K+2.))*
1 (J*(J+1.)-(K+2.)*(K+3.))*(J*(J+1.)-(K+3.)*(K+4.)))
F9(J)=.25*w*SQRTF(.+J*(J+1.)*(J*(J+1.)-2.))
F10(J,K)=.25*w*SQRTF((J*(J+1.)-K*(K+1.))*(J*(J+1.)-(K+1.)*(K+2.)))
C INPUT INSTRUCTIONS FOR PERTURBATION TERMS... G= -GZ AND W= -GXY
READ 12,(A(I),B(I),CS(I),TAO(I),TAT(I),TAS(I),TAN(I),EN(I),HK(I),
1 I=1,2),G,W,1FMAT,AEQ,REQ,IRJN
12 FORMAT(3F15.7/4F10.7/F10.4,F15.12/3F15.7/4F10.7/F10.4,F15.12/
1 2F10.4,58X,I2/2F15.7,48X,I2)
C ARITHMETIC STATEMENTS
RHO = 1.0E-06
IER=0
IOPT=0
CEQ=(AEQ+BEQ)/(AEQ+BEQ)
RS=BFQ**2/(AEQ+BEQ)**2
SS=AFQ**2/(AFQ+BFQ)**2
R1=RS*(TAO(1)+TAS(1))+SS*(TAT(1)+TAS(1))
R2=RS*(TAO(2)+TAS(2))+SS*(TAT(2)+TAS(2))
S1=TAS(1)*(RS-SS)+TAT(1)*SS-TAO(1)*RS
S2=TAS(2)*(RS-SS)+TAT(2)*SS-TAO(2)*RS
T1=2.*RS*SS*TAS(1)+RS**2*TAO(1)+SS**2*TAT(1)
T2=2.*RS*SS*TAS(2)+RS**2*TAO(2)+SS**2*TAT(2)
V1=TAT(1)-TAO(1)
V2=TAT(2)-TAO(2)
X1=TAT(1)+TAO(1)
X2=TAT(2)+TAO(2)
Y1=TAS(1)+2.*TAN(1)
Y2=TAS(2)+2.*TAN(2)
U1=(.5*X1-Y1)/32.
U2=(.5*X2-Y2)/32.

```

```

PRINT 2000,A(1),B(1),CS(1),TAO(1),TAT(1),TAS(1),TAN(1),EN(1),HK(1)
2001 FORMAT(//*(110) BAND PARAMETERS*/
 1 *A(V1)=*F15.7*   B(V1)=*F15.7*   CS(V1)=*F15.7/
 2*TAAAAA=*F10.7*   TRBRB=*F10.7*   TAARB=*F10.7*   TABAB=*F10.7/
 3 *(110) BAND CENTER =*F10.4/*HK1=*F15.12//)
 PRINT 2001,A(2),B(2),CS(2),TAO(2),TAT(2),TAS(2),TAN(2),EN(2),HK(2)
2001 FORMAT(//*(011) BAND PARAMETERS*/
 1 *A(V2)=*F15.7*   B(V2)=*F15.7*   CS(V2)=*F15.7/
 2*TAAAAA=*F10.7*   TRBRB=*F10.7*   TAARB=*F10.7*   TABAB=*F10.7/
 3 *(011) BAND CENTER =*F10.4/*HK2=*F15.12//)
 PRINT 2002,G,W
2002 FORMAT(//*PERTURRATION COEFFICIENTS*/*G=*F10.4/*W=*F10.4/)
 PRINT 2003,AEQ,BEQ,CEQ
2003 FORMAT(//*EQUILIBRIUM CONSTANTS USED IN O,D. MATRIX ELEMENTS*/
 1 *AEQ=*F15.7/*REQ=*F15.7/*CEQ=*F15.7//)
 DO 11 J= 1,JRUN
 DO 13 L=1,21
 DO 13 M=1,21
 EPV2(L,M)=0.0
13 EPV1(L,M)=0.0
 DO 113 L=1,20
 DO 113 M=1,20
 DPV1(L,M)=0.0
113 DPV2(L,M)=0.0
  MATRIX FOR EVP1PLUS+EPV2MINUS AND EVP2PLUS+EPV1MINUS
 KMAX = J/2 + 1
 KMIN = KMAX + 1
 JEWD = 2*(J/2 + 1)-1
 GO TO (5,6,6,7),J
 7 EPV1 (1,3) = F5(J)*U1
 EPV2(1,3)=F5(J)*U2
 4 EPV1(1,KMIN) = (0.,-1.)*F9(J)
 EPV2(1,KMIN)=EPV1(1,KMIN)
 EPV1 (1,2) = F4( A(1), B(1), J,V1,S1)
 EPV2(1,2)=F4(A(2),B(2),J,V2,S2)
 5 FPV1(1,1)=F1(A(1),B(1),CS(1),EV(1),TAN(1),R1,Y1,T1,X1,HK(1),J,0)
 EPV2(1,1)=F1(A(2),B(2),CS(2),EV(2),TAN(2),R2,Y2,T2,X2,HK(2),J,0)
 DO 1 K= 2, KMAX
 KK = 2*(K-1)
 KM = KMAX + K - 1
 GO TO (2,3,4), (KMIN-K)
 1 EPV1 (K,K+2) = FP(J,KK)*U1
 FPV2 (K,K+2) = FP(J,KK)*U2
 EPV1 (KM, KMIN + K) = F8 (J,KK)*U2
 FPV2 (KM, KMIN + K) = F8 (J,KK)*U1
 3 EPV1 (K,K+1) = F6 ( A(1), B(1), J, KK ,V1,S1)
 EPV2(K,K+1)=F6(A(2),B(2),J,KK,V2,S2)
 EPV1 (KM, KMAX + K) = F6 ( A(2), B(2), J, KK,V2,S2)
 FPV2(KM,KMAX+K)=F6(A(1),B(1),J,KK,V1,S1)
 EPV1 ( K, KMAX + K ) = (0.,-1. )*F10 (J,KK)
 FPV2(K,KMAX+K)=EPV1(K,KMAX+K)
 EPV1 ( K+1 ,KM ) = (0. , 1. )* F10( J, KK)

```

```

    EPV2(K+1,KM)=EPV1(K+1,KM)
2 IF(KK,FQ,2) FPV1(K,K)=F1(A(1),B(1),CS(1),EN(1),TAN(1),R1,Y1,T1,
1 X1,HK(1),J,KK) +F3(J)*U1
1 IF(KK,NE,2) FPV1(K,K)=F1(A(1),B(1),CS(1),EN(1),TAN(1),R1,Y1,T1,
1 X1,HK(1),J,KK)
1 IF(KK,FQ,2)EPV2(K,K)=F1(A(2),B(2),CS(2),EN(2),TAN(2),R2,Y2,T2,X2,
1 HK(2),J,KK) +F3(J)*U2
1 IF(KK,NE,2)EPV2(K,K)=F1(A(2),B(2),CS(2),EN(2),TAN(2),R2,Y2,T2,X2,
1 HK(2),J,KK)
    EPV1 (K, KM) = (n.,1.)*G*KK
    EPV2(K,KM)=-EPV1(K,KM)
    IF(KK,FQ,2) EPV1(KM,KM)=F1(A(2),B(2),CS(2),EN(2),TAN(2),R2,Y2,T2,
1 X2,HK(2),J,KK) -F3(J)*U2
    IF(KK,NE,2) EPV1(KM,KM)=F1(A(2),B(2),CS(2),EN(2),TAN(2),R2,Y2,T2,
1 X2,HK(2),J,KK)
    IF(KK,FQ,2)EPV2(KM,KM)=F1(A(1),B(1),CS(1),EN(1),TAN(1),R1,Y1,T1,
1 X1,HK(1),J,KK) -F3(J)*U1
    IF(KK,NE,2)EPV2(KM,KM)=F1(A(1),B(1),CS(1),EN(1),TAN(1),R1,Y1,T1,
1 X1,HK(1),J,KK)
1 CONTINUE
C MATRIX FOR OV1PLUS+OV2MINUS AND OV1MINUS+OV2PLUS
    KIX=(J+1)/2
    IMP=2*KIX
    DO 101 K=1,KIX
    KAT=KIX+K
    KO=2*K-1
    GO TO (102,103,104),(KIX+1-K)
104 OPV1(K,K+2)=F8(J,KO)*U1
    OPV1(KAT,KAT+2)=F8(J,KO) *U2
    OPV2(K,K+2)=F8(J,KO) *U2
    OPV2(KAT,KAT+2)=F8(J,KO) *U1
103 IF(KO,FQ,1) OPV1(K,K+1)=F6(A(1),B(1),J,KO,V1,S1)+F7(J)*U1
    IF(KO,NE,1) OPV1(K,K+1)=F6(A(1),B(1),J,KO,V1,S1)
    IF(KO,FQ,1)OPV1(KAT,KAT+1)=F6(A(2),B(2),J,KO,V2,S2)-F7(J)*U2
    IF(KO,NE,1)OPV1(KAT,KAT+1)=F6(A(2),B(2),J,KO,V2,S2)
    OPV1(K,KAT+1)=(0.,-1.)*F10(J,KO)
    OPV1(K+1,KAT)=-OPV1(K,KAT+1)
    IF(KO,FQ,1)OPV2(K,K+1)=F6(A(2),B(2),J,KO,V2,S2)+F7(J)*U2
    IF(KO,NE,1)OPV2(K,K+1)=F6(A(2),B(2),J,KO,V2,S2)
    IF(KO,FQ,1)OPV2(KAT,KAT+1)=F6(A(1),B(1),J,KO,V1,S1)-F7(J)*U1
    IF(KO,NE,1)OPV2(KAT,KAT+1)=F6(A(1),B(1),J,KO,V1,S1)
    OPV2(K,KAT+1)=OPV1(K,KAT+1)
    OPV2(K+1,KAT)=-OPV1(K,KAT+1)
102n IF(KO,FQ,1)OPV1(K,K)=F1(A(1),B(1),CS(1),EN(1),TAN(1),R1,Y1,T1,
1 X1,HK(1),J,KO)+F2(A(1),B(1),J,V1,S1)
n IF(KO,NE,1)OPV1(K,K)=F1(A(1),B(1),CS(1),EN(1),TAN(1),R1,Y1,T1,
1 X1,HK(1),J,KO)
n IF(KO,FQ,1)OPV1(KAT,KAT)=F1(A(2),B(2),CS(2),EN(2),TAN(2),R2,Y2,
1 T2,X2,HK(2),J,KO)- F2(A(2),B(2),J,V2,S2)
n IF(KO,NE,1)OPV1(KAT,KAT)=F1(A(2),B(2),CS(2),EN(2),TAN(2),R2,Y2,
1 T2,X2,HK(2),J,KO)
IF(KO,FQ,1)OPV1(K,KAT)=(n.,1.)*(G*KO-.25*W*J*(J+1))

```

```

IF(K0.NE.1)OPV1(K,KAT)=(0.,1.)*(G*K0)
IF(K0.EQ.1)OPV2(K,K)=F1(A(2),B(2),CS(2),EN(2),TAN(2),R2,Y2,T2,X2,
1 HK(2),J,K0)+F2(A(2),B(2),J,V2,S2)
IF(K0.NE.1)OPV2(K,K)=F1(A(2),B(2),CS(2),EN(2),TAN(2),R2,Y2,T2,X2,
1 HK(2),J,K0)
IF(K0.EQ.1)OPV2(KAT,KAT)=F1(A(1),B(1),CS(1),EN(1),TAN(1),R1,Y1,
1 T1,X1,HK(1),J,K0)-F2(A(1),B(1),J,V1,S1)
IF(K0.NE.1)OPV2(KAT,KAT)=F1(A(1),B(1),CS(1),EN(1),TAN(1),R1,Y1,
1 T1,X1,HK(1),J,K0)
IF(K0.EQ.1)OPV2(K,KAT)=(0.,-1.)*(G*K0+.25*W*J*(J+1))
IF(K0.NE.1)OPV2(K,KAT)=(0.,-1.)*(G*K0)

101 CONTINUE
C FORMING HERMITIAN CONJUGATES OF EPV1,EPV2,OPV1,OPV2
DO 9 N=1,JEMD
IN=N+1
DO 9 M=IN,JEMD
FPV2(M,N)=CONJG(FPV2(N,M))
9 EPV1(M,N)=CONJG(FPV1(N,M))
DO 109 N=1,IMD
IN=N+1
DO 109 M=IN,IMD
OPV2(M,N)=CONJG(OPV2(N,M))
109 OPV1(M,N)=CONJG(OPV1(N,M))
IF(IFMAT) 517,514
514 CONTINUE
C THIS SECTION PRINTS MATRIX ELEMENTS ,SET IFMAT =1 IF NOT DESIRED
PRINT 519,J
519 FORMAT(//'*EV1PLUS+FV2MINUS FOR J=*13)
DO 14 K=1,JEMD
PRINT 10,(FPV1(K,L),L=1,JEVD)
10 FORMAT(/(6C(F10.4,F10.4)))
14 CONTINUE
PRINT 519,J
519 FORMAT(//'*EV2PLUS+FV1MINUS FOR J=*13)
DO 15 K=1,JEMD
PRINT 16,(FPV2(K,L),L=1,JEVD)
15 FORMAT(/(6C(F10.4,F10.4)))
13 CONTINUE
PRINT 520,J
520 FORMAT(//'*OPV1PLUS+OPV2MINUS FOR J=*13)
DO 114 K=1,IMD
PRINT 110,(OPV1(K,L),L=1,IMD)
110 FORMAT(/(6C(F10.4,F10.4)))
114 CONTINUE
PRINT 521,J
521 FORMAT(//'*OPV2PLUS+OPV1MINUS FOR J=*13)
DO 115 K=1,IMD
PRINT 116,(OPV2(K,L),L=1,IMD)
115 FORMAT(/(6C(F10.4,F10.4)))
517 CONTINUE
C THIS SECTION CALLS JHERMY

```

```

CALL JHERMX(EPV1,21,JEND)
CALL JHERMX(FPV2,21,JEND)
CALL JHERMX(OPV1,20,IMD)
CALL JHERMX(OPV2,20,IMD)
C PRINTING EIGENVALUES WITH J,K+,K- LABELS
PRINT 523
523 FORMAT(//*EV1PLUS+EV2MINUS F.LEVELS          EV2PLUS+EV1MINUS E.LEVE
1LS*/)
DO 313 I=1,KMAX
KPLUS=2*(I-1)
TAUP=J-2*KPLUS
KMINUS=TAUP+KPLUS
PRINT 314,J,KMINUS,KPLUS,EPV1(I,I),J,KMINUS,KPLUS,FPV2(I,I)
314 FORMAT(2(313,F15.5,10X))
313 CONTINUE
IMIN1=KMAX+1
DO 315 I=IMIN1,JFMP
KPLUS=2*(I-KMAX)
TAUP=J-2*KPLUS+1
KMINUS=TAUP+KPLUS
PRINT 314,J,KMINUS,KPLUS,EPV1(I,I),J,KMINUS,KPLUS,FPV2(I,I)
315 CONTINUE
PRINT 522
522 FORMAT(//*OV1PLUS+OV2MINUS F.LEVELS          OV2PLUS+OV1MINUS E.LEVE
1LS*/)
DO 316 I=1,KIX
KPLUS=2*I-1
TAUP=J-2*KPLUS
KMINUS=TAUP+KPLUS
PRINT 314,J,KMINUS,KPLUS,OPV1(I,I),J,KMINUS,KPLUS,OPV2(I,I)
316 CONTINUE
IMIN2=KIX+1
DO 317 I=IMIN2,IMD
KPLUS=2*(I-KIX)-1
TAUP=J-2*KPLUS+1
KMINUS=TAUP+KPLUS
PRINT 314,J,KMINUS,KPLUS,OPV1(I,I),J,KMINUS,KPLUS,OPV2(I,I)
317 CONTINUE
11 CONTINUE
END

SUBROUTINE JHERMX(A,NM,N)
COMMON INPT,RHO,IER
DIMENSION A(NM,NM), S(21,21)
COMPLEX A, S, V1, V2, V3, CSNT, SNT, TEMP
IOC = 0
IER = 0
EP12=0.000000000001
EN = FLOAT(E)
DO 1 I=1,N
DO 1 J=1,N
S(I,J) = (0.0,0.0)
IF(I.EQ.J)S(I,J) =(1.0,0.0)

```

```

1 CONTINUE
IF(N,LF,1)GO TO 12
SOFFD = 0.0
NM1 = N-1
DO 2 I=1,NM1
IJ = I+1
DO 2 J=IJ,N
X1=A(I,J)
X2=A(I,J)*(0.0,-1.0)
2 SOFFD=SOFFD+2.0*(X1*X1+X2*X2)
IF(SOFFD .LT. 0.1E-10)GO TO 12
THR = SQRTF(SOFFD)
FTHR = RHO*THR / EN
IND = 0
3 THR = THR / EN
4 DO 10 L=2,N
LM1 = L-1
DO 10 K=1,LM1
X1=A(L,K)
X2=A(L,K)*(0.0,1.0)
IF(SQRT(X1*X1+X2*X2).LT.THR)GO TO 10
IND = 1
V1 = A(K,K)
V2 = CONJG(A(L,K))
V3 = A(L,L)
C = -AIMAG(A(L,K))
R = REAL(A(L,K))
E = REAL(A(L,L))
D = REAL(A(K,K))
THET = 0.0
IF(ARSF(C).LT. EPI2)GO TO 13
THET = 1.5707963
IF(ARSF(R).LT. EPI2)GO TO 13
T = C / R
THET = ATANF(T)
13 CONTINUE
PHI = 0.78539818
ED = ARSF(E-D)
IF(ED .LT. EPI2)GO TO 15
TAO = 2.0*(B*COSF(THET) + C*SINF(THET)) / (E-D)
PHI = 0.5 * ATANF(TAO)
15 CONTINUE
CSNT = COSF(PHI) + (0.0,0.0)
CS = COSF(THET) + SINF(PHI)
SS = SINF(THET) * SINF(PHI)
SNT = CS + (0.0,1.0) * SS
DO 8 I=1,N
TEMP = A(I,K)*CSNT - A(I,L)*CONJG(SNT)
A(I,L) = A(I,K)*SNT + A(I,L)*CSNT
A(I,K) = TEMP
IF(IOPT .EQ. 0)GO TO 8
TEMP = S(I,K)*CSNT - S(I,L)*CONJG(SNT)

```

```

S(I,L) = S(I,K)*SNT + S(I,L)*CSNT
S(I,K) = TFMP
9 CONTINUE
DO 9 I=1,N
A(K,I) = CONJG( A(I,K) )
A(L,I) = CONJG( A(I,L) )
10 CONTINUE
A(K,K) = SNT*CONJG(SNT)*V3 + CSNT*CSNT*V1-SNT*CSNT*CONJG(V2)
1 -CSNT*CONJG(SNT)*V2
A(L,L) = CSNT*CSNT*V3 + CONJG(SNT)*SNT*V1 + SNT*CSNT*
2 CONJG(V2) + CONJG(SNT)*CSNT*V2
A(K,L) = CSNT*CSNT*V2 - SNT*SNT*CONJG(V2) + CSNT*SNT*V1
1 -CSNT*SNT*V3
A(L,K) = CONJG( A(K,L) )
11 CONTINUE
IOC = IOC + 1
IF(IOC .GE. 100)GO TO 21
IF(IND .LE. 0)GO TO 11
IND = 0
GO TO 4
11 IF(THR-FTHR)12,12,3
12 RETURN
21 IER = 1
RETURN
END
RUN,5,1200

```

APPENDIX IX

FREQUENCY ASSIGNMENTS FOR THE  
(210) AND (111) BANDS OF  $H_2^{3\ 2}S$

## ASSIGNED FREQUENCIES FOR THE (210) BAND

UPPER		GROUND		OBSERVED	DIFFERENCE	WEIGHT	
1	0	1	-	2 1 2	6263.355	-0.005	0.03
2	0	2	-	3 1 3	6253.924	0.024	0.08
3	0	3	-	4 1 4	6243.439	0.004	0.70
4	1	4	-	5 0 5	6232.867	-0.003	0.90
5	0	5	-	6 1 6	6221.717	0.018	1.00
4	1	6	-	7 0 7	6210.193	0.030	0.60
7	0	7	-	8 1 8	6198.301	0.039	0.30
8	1	8	-	9 0 9	6186.045	0.045	0.40
9	0	9	-	10 1 10	6173.425	0.043	0.10
10	1	10	-	11 0 11	6161.424	0.013	0.02
11	0	11	-	12 1 12	6147.098	0.008	0.03
1	1	0	-	2 2 1	6252.360	0.000	0.50
5	1	4	-	6 2 5	6213.476	0.019	0.50
4	2	5	-	7 1 6	6202.328	0.002	0.70
7	1	6	-	8 2 7	6190.810	0.024	0.30
8	2	7	-	9 1 8	6178.937	0.047	0.01
9	1	8	-	10 2 9	6166.490	0.053	0.01
10	2	9	-	11 1 10	6154.111	0.077	0.03
3	2	1	-	4 3 2	6220.938	-0.018	0.06
4	3	4	-	7 2 5	6194.149	-0.065	0.20
4	2	4	-	7 3 5	6193.967	0.043	0.10
7	2	5	-	8 3 6	6182.929	0.030	0.04
8	3	6	-	9 2 7	6171.408	0.003	0.10
3	3	7	-	4 4 1	6209.885	-0.023	0.50
2	0	2	-	1 1 1	6310.285	0.014	0.20
3	0	3	-	2 1 2	6319.518	0.005	1.00
3	1	3	-	2 0 2	6319.816	-0.023	0.40
4	1	4	-	3 0 3	6327.783	-0.006	0.80
5	0	5	-	4 1 4	6335.471	0.002	1.00
4	1	6	-	5 0 5	6342.810	0.014	1.00
7	0	7	-	6 1 6	6349.749	0.015	1.00
8	1	8	-	7 0 7	6356.311	0.023	1.00
9	0	9	-	8 1 8	6362.487	0.032	1.00
11	1	10	-	9 0 9	6368.249	0.015	0.80
11	0	11	-	10 1 10	6373.648	0.028	1.00
13	0	13	-	12 1 12	6383.250	0.058	0.10
11	1	14	-	13 0 13	6387.457	0.097	0.02
2	2	1	-	1 1 0	6323.901	0.039	1.00
3	1	2	-	2 2 1	6327.104	0.039	0.70
5	2	4	-	4 1 3	6346.940	-0.029	0.12
4	2	5	-	5 1 4	6354.459	-0.004	0.70
7	1	6	-	6 2 5	6361.696	0.011	1.00
8	2	7	-	7 1 6	6368.594	0.031	0.20
9	1	8	-	8 2 7	6375.103	0.050	0.30
11	2	9	-	9 1 8	6381.926	0.067	0.20

12	2	11	-	11	1	10	6392.316	0.104	0.02
3	3	1	-	2	2	0	6345.179	0.024	0.60
4	2	2	-	3	3	1	6341.993	0.039	0.10
7	2	5	-	6	3	4	6373.069	0.014	0.60
7	3	5	-	6	2	4	6373.301	-0.028	0.03
11	3	8	-	9	2	7	6393.510	0.047	0.20
11	2	9	-	10	3	8	6399.481	0.023	0.10
4	4	1	-	3	3	0	6366.429	0.012	1.00
5	4	2	-	4	3	1	6375.428	0.094	0.30
8	3	3	-	5	4	2	6370.868	0.044	0.30
2	4	5	-	7	3	4	6392.110	-0.091	0.06
5	5	1	-	4	4	0	6387.818	-0.061	0.40
4	5	2	-	5	4	1	6397.505	0.029	0.70
7	4	3	-	6	5	2	6384.051	0.021	0.40
1	0	1	-	1	1	0	6282.270	-0.011	0.90
2	1	1	-	2	2	0	6280.535	-0.000	0.30
3	2	1	-	3	3	0	6277.507	-0.022	1.00
4	3	1	-	4	4	0	6273.110	-0.034	0.25
4	5	1	-	6	6	0	6261.790	-0.065	0.20
7	6	1	-	7	7	0	6256.123	-0.159	0.50
2	0	2	-	2	1	1	6274.236	0.013	0.15
2	1	2	-	2	2	1	6270.437	-0.075	0.10
3	1	2	-	3	2	1	6274.895	0.036	0.80
4	2	2	-	4	3	1	6274.570	0.024	0.60
5	3	2	-	5	4	1	6272.800	-0.012	1.00
4	4	2	-	6	5	1	6269.352	-0.035	0.14
4	5	2	-	6	6	1	6258.268	0.015	1.00
7	5	2	-	7	6	1	6264.256	-0.030	0.60
9	7	2	-	8	8	1	6250.224	-0.068	0.03
7	0	3	-	3	1	2	6262.752	-0.003	0.30
4	1	3	-	4	2	2	6264.054	0.034	0.10
4	3	3	-	6	4	2	6266.536	0.038	0.20
7	4	3	-	7	5	2	6266.164	0.000	1.00
4	1	6	-	6	2	5	6227.560	0.022	0.15
7	1	6	-	7	2	5	6227.826	0.018	0.08
7	0	7	-	7	1	6	6215.343	0.014	0.03
9	2	7	-	8	3	6	6215.648	0.034	0.03
9	2	7	-	9	3	6	6215.877	-0.013	0.01
9	1	8	-	8	2	7	6202.790	0.026	0.02
1	1	9	-	1	0	1	6293.750	-0.023	0.50
2	2	0	-	2	1	1	6295.324	-0.037	0.06
1	3	0	-	3	2	1	6298.180	-0.021	0.90
2	1	1	-	2	0	2	6300.880	-0.008	0.03
2	2	1	-	3	1	2	6299.850	-0.015	0.50
6	4	1	-	5	3	2	6300.400	-0.032	0.25
2	2	1	-	3	3	0	6225.878	0.031	0.80
3	3	1	-	4	4	0	6206.752	0.029	0.10
2	2	0	-	1	1	1	6331.352	-0.058	0.20
1	3	0	-	2	2	1	6350.373	-0.034	1.00

## ASSIGNED FREQUENCIES FOR THE (111) BAND

UPPER		GROUND		OBSERVED	DIFFERENCE	WEIGHT
1	1	1	-	6265.785	-0.006	0.60
2	1	2	-	6255.210	-0.006	0.80
3	1	3	-	6244.722	0.007	0.10
4	0	4	-	6233.965	0.028	0.80
5	1	5	-	6222.849	0.030	0.80
6	0	6	-	6211.379	0.037	0.60
8	0	8	-	6187.365	0.033	0.60
9	1	9	-	6174.824	0.019	0.80
10	1	10	-	6161.937	0.003	1.00
11	1	11	-	6148.685	-0.033	0.50
12	0	12	-	6135.103	-0.053	0.60
13	1	13	-	6121.173	-0.070	0.20
14	0	14	-	6106.905	-0.066	0.30
1	1	0	-	6257.388	0.021	0.80
2	2	1	-	6247.782	0.001	1.00
2	1	1	-	6244.797	-0.066	0.02
3	2	2	-	6236.205	-0.038	1.00
4	2	3	-	6225.369	-0.032	0.10
5	2	4	-	6214.566	0.017	0.50
6	1	5	-	6203.458	0.051	0.70
7	2	6	-	6191.980	0.048	1.00
8	1	7	-	6180.159	0.052	1.00
9	2	8	-	6167.989	0.050	0.90
10	1	9	-	6155.486	0.054	0.70
11	2	10	-	6142.608	0.018	0.02
12	1	11	-	6129.445	0.031	0.30
13	2	12	-	6115.925	0.021	0.08
2	2	0	-	6240.111	0.025	1.00
3	3	1	-	6230.434	0.019	1.00
3	2	1	-	6225.568	-0.030	0.60
4	3	2	-	6217.642	-0.035	0.30
7	3	5	-	6184.032	0.018	0.90
8	2	6	-	6172.575	0.044	1.00
9	3	7	-	6160.764	0.046	0.30
11	2	8	-	6148.610	0.048	0.10
11	3	9	-	6136.212	0.138	0.06
7	3	0	-	6223.841	0.037	0.70
4	4	1	-	6213.671	0.011	0.40
4	3	1	-	6207.175	-0.021	1.00
4	4	3	-	6187.208	-0.076	0.10
9	4	5	-	6153.113	-0.021	0.60
10	3	7	-	6141.323	-0.001	0.02
11	4	8	-	6129.190	0.005	0.02
4	4	0	-	6208.576	0.020	1.00
5	5	1	-	6197.403	-0.037	0.80

5	4	1	-	6	4	2	6189.877	0.013	0.50
5	5	2	-	7	5	3	6182.123	0.012	0.20
7	5	3	-	8	5	4	6168.648	-0.054	0.20
2	4	4	-	9	4	5	6155.283	0.003	0.20
8	5	1	-	7	5	2	6173.756	0.029	0.80
7	6	2	-	8	6	3	6165.160	0.021	0.50
2	5	3	-	9	5	4	6144.283	0.030	0.08
8	6	0	-	7	6	1	6179.421	-0.166	0.50
2	1	2	-	1	1	1	6311.565	-0.023	0.40
3	1	3	-	2	1	2	6320.600	0.008	0.30
3	0	3	-	2	0	2	6320.868	0.035	0.40
4	0	4	-	3	0	3	6328.875	0.021	0.30
5	1	5	-	4	1	4	6336.622	0.033	0.30
4	0	6	-	5	0	5	6344.002	0.028	1.00
7	1	7	-	6	1	6	6351.001	0.018	0.70
2	0	8	-	7	0	7	6357.630	0.011	0.80
2	1	9	-	8	1	8	6363.898	0.019	1.00
11	1	11	-	10	1	10	6375.247	-0.002	1.00
12	0	12	-	11	0	11	6380.349	0.007	1.00
13	1	13	-	12	1	12	6385.093	0.068	0.60
4	2	3	-	3	2	2	6339.248	-0.023	1.00
5	2	4	-	4	2	3	6347.743	0.010	0.70
5	1	4	-	4	1	3	6348.016	0.049	1.00
4	1	5	-	5	1	4	6355.568	0.024	0.60
7	2	6	-	6	2	5	6362.876	0.044	1.00
2	2	8	-	8	2	7	6376.399	0.045	0.90
11	1	9	-	9	1	8	6382.402	0.045	1.00
11	2	10	-	10	2	9	6388.388	0.003	0.06
12	1	11	-	11	1	10	6393.886	0.054	1.00
13	2	12	-	12	2	11	6398.974	0.085	0.30
14	1	13	-	13	1	12	6403.688	0.145	0.20
3	2	1	-	2	2	0	6337.522	-0.042	0.40
4	3	2	-	3	3	1	6346.657	-0.070	0.60
5	3	4	-	5	3	3	6366.291	-0.024	0.50
7	3	5	-	6	3	4	6374.180	0.010	1.00
7	2	5	-	6	2	4	6374.404	0.042	0.70
8	2	6	-	7	2	5	6381.529	0.052	0.20
9	3	7	-	8	3	6	6388.324	0.034	0.10
11	2	8	-	9	2	7	6394.791	0.025	1.00
11	3	9	-	10	3	8	6400.989	0.119	0.50
4	3	1	-	3	3	0	6353.519	-0.025	1.00
5	4	2	-	4	4	1	6363.313	-0.010	1.00
8	4	3	-	5	4	2	6374.753	-0.094	0.30
9	4	5	-	7	4	4	6392.420	-0.060	0.12
9	4	6	-	8	4	5	6399.703	-0.022	0.60
9	3	6	-	8	3	5	6399.895	0.012	0.04
10	3	7	-	9	3	6	6406.584	0.089	0.04
11	4	8	-	10	4	7	6412.783	-0.010	0.40
5	4	1	-	4	4	0	6368.477	-0.016	0.10
5	5	2	-	5	5	1	6379.395	0.018	0.10
7	5	3	-	6	5	2	6391.493	-0.041	0.60
9	4	4	-	7	4	3	6405.896	0.007	0.40

1	4	6	-	9	4	5	6418.096	0.001	0.60
8	5	1	-	5	5	0	6382.838	0.036	0.60
8	6	2	-	7	6	1	6414.011	0.011	0.50
1	1	1	-	1	1	0	6284.710	-0.002	0.80
2	2	1	-	2	2	0	6285.812	0.009	1.00
3	3	1	-	3	3	0	6287.005	0.017	1.00
4	4	1	-	4	4	0	6287.981	0.018	0.50
5	5	1	-	5	5	0	6288.596	-0.053	1.00
6	6	1	-	6	6	0	6289.171	0.018	0.80
3	2	2	-	3	2	1	6277.242	-0.048	0.90
4	3	2	-	4	3	1	6279.379	-0.040	0.40
5	4	2	-	5	4	1	6281.623	-0.023	0.70
6	5	2	-	6	5	1	6283.597	0.006	0.50
7	6	2	-	7	6	1	6284.950	0.008	1.00
8	7	2	-	8	7	1	6285.439	0.006	0.10
9	1	3	-	3	1	2	6263.848	0.013	0.30
4	2	3	-	4	2	2	6265.299	-0.028	0.20
5	3	3	-	5	3	2	6267.547	-0.079	0.20
6	5	3	-	7	5	2	6273.404	-0.064	0.30
4	6	3	-	8	6	2	6276.453	0.030	0.04
1	4	4	-	4	1	3	6252.177	0.032	0.20
1	0	4	-	4	2	3	6251.885	0.022	0.70
5	5	2	-	5	2	3	6252.819	0.013	0.80
6	1	4	-	5	3	3	6251.741	0.026	0.10
7	4	4	-	8	6	3	6246.671	0.007	0.01
8	2	5	-	6	2	4	6240.885	0.037	0.14
7	3	5	-	7	3	4	6241.444	0.007	0.50
3	4	5	-	8	4	4	6242.540	-0.059	0.03
2	3	5	-	8	5	4	6240.331	0.052	0.50
8	0	6	-	6	2	5	6228.748	0.031	0.20
7	2	6	-	7	2	5	6228.991	0.037	0.30
3	3	6	-	8	3	5	6229.291	0.026	0.01
2	2	6	-	8	4	5	6229.099	0.026	0.10
2	4	6	-	9	4	5	6229.730	-0.039	0.04
7	1	7	-	7	1	6	6216.601	0.023	0.40
2	1	7	-	8	3	6	6216.881	0.050	0.30
0	3	7	-	9	3	6	6217.121	0.020	0.02
2	0	8	-	8	2	7	6204.119	0.024	0.20
0	2	8	-	9	2	7	6204.484	0.054	0.30
1	2	8	-	10	4	7	6204.747	0.029	0.05
2	1	9	-	9	1	8	6191.287	0.015	0.10
1	1	9	-	10	3	8	6191.771	0.062	0.04
1	1	0	-	1	1	1	6293.437	0.021	0.60
2	2	0	-	2	2	1	6292.310	0.018	0.80
3	3	0	-	3	3	1	6291.140	0.027	0.90
4	4	0	-	4	4	1	6290.247	0.014	0.80
5	5	0	-	5	5	1	6289.733	-0.041	1.00
2	1	1	-	2	1	2	6301.583	-0.038	0.80
2	2	1	-	2	0	2	6306.164	0.009	0.30
3	2	1	-	3	2	2	6299.518	-0.025	0.40
3	3	1	-	3	1	2	6309.345	0.021	0.50
4	3	1	-	4	3	2	6296.950	-0.021	0.80

4	4	1	-	4	2	2	6314.440	0.011	0.01
5	4	1	-	5	4	2	6294.200	0.010	0.60
8	5	1	-	6	5	2	6291.622	0.029	1.00
2	2	2	-	3	7	3	6313.193	-0.042	1.00
4	3	2	-	4	1	3	6313.884	-0.044	0.80
5	4	2	-	5	2	3	6315.524	-0.017	1.00
4	5	2	-	6	3	3	6318.268	0.003	0.10
7	5	2	-	7	5	3	6298.590	-0.099	0.30
7	6	2	-	7	4	3	6324.361	-0.002	0.10
4	2	3	-	4	0	4	6321.485	-0.007	0.30
5	2	4	-	5	0	5	6329.819	0.013	1.00
2	4	4	-	8	4	5	6325.247	0.011	0.04
8	1	5	-	6	1	6	6337.964	0.052	0.40
7	3	5	-	7	1	6	6336.078	0.015	0.40
9	3	5	-	8	3	6	6335.780	0.083	0.02
7	2	6	-	7	0	7	6345.501	0.044	0.70
9	2	6	-	8	2	7	6344.493	0.038	0.70
0	4	6	-	9	2	7	6343.165	-0.018	0.10
10	4	6	-	10	4	7	6341.460	-0.000	0.04
9	1	7	-	8	1	8	6352.770	0.057	0.15
0	3	7	-	9	1	8	6351.604	0.038	0.20
11	3	7	-	10	3	8	6350.110	-0.002	0.01
0	2	8	-	9	0	9	6359.642	0.051	0.20
11	2	8	-	10	2	9	6358.304	0.029	0.20
2	1	1	-	3	3	0	6222.488	-0.039	0.20
7	2	2	-	4	4	1	6188.981	-0.016	0.20
4	0	4	-	5	2	3	6156.054	0.018	0.04
2	2	0	-	1	0	1	6333.734	0.028	0.90
4	4	0	-	3	2	1	6378.562	0.036	0.20
5	5	0	-	4	3	1	6403.201	-0.027	0.04
8	6	0	-	5	4	1	6428.940	0.042	0.20
2	2	1	-	2	0	2	6357.896	-0.021	0.01
3	3	1	-	2	1	2	6366.133	0.051	0.20
4	3	1	-	3	1	2	6375.868	-0.012	1.00
5	5	1	-	4	3	2	6411.324	-0.035	0.30
4	5	1	-	5	3	2	6415.773	0.035	1.00
5	4	2	-	4	2	3	6410.550	-0.018	0.40
8	5	2	-	5	3	3	6431.088	-0.001	0.04
7	6	2	-	6	4	3	6452.254	0.028	0.50
8	6	2	-	7	4	3	6453.442	0.021	0.40
7	5	3	-	6	3	4	6454.229	-0.046	0.30

APPENDIX X

FREQUENCY ASSIGNMENTS FOR THE  
(110) AND (011) BANDS OF  $H_2^{32}S$

## ASSIGNED FREQUENCIES FOR THE (110) BAND

UPPER		GROUND		OBSERVED	DIFFERENCE	WEIGHT	
1	0	0	-	1 1 1	3764.081	-0.006	4.81
1	0	1	-	2 1 2	3754.565	-0.007	6.25
1	1	1	-	2 0 2	3755.294	-0.015	0.00
2	1	2	-	3 0 3	3745.783	-0.001	0.69
2	0	2	-	3 1 3	3745.435	-0.001	4.56
3	1	3	-	4 0 4	3735.661	0.006	0.02
3	0	3	-	4 1 4	3735.618	0.013	1.25
4	1	4	-	5 0 5	3725.406	0.014	0.64
5	0	5	-	6 1 6	3714.925	0.035	0.00
5	1	6	-	7 0 7	3704.174	0.030	0.00
7	0	7	-	8 1 8	3693.172	0.021	0.02
8	1	8	-	9 0 9	3681.929	0.013	5.50
9	0	9	-	10 1 10	3670.423	-0.020	0.00
11	1	10	-	11 0 11	3658.701	-0.032	0.81
11	0	11	-	12 1 12	3646.728	-0.055	1.52
1	1	0	-	2 2 1	3743.662	-0.006	1.25
2	2	1	-	3 1 2	3739.983	0.007	1.25
2	1	1	-	3 2 2	3734.280	-0.019	0.00
3	2	2	-	4 1 3	3727.947	-0.008	0.00
3	1	2	-	4 2 3	3725.224	-0.005	7.00
4	2	3	-	5 1 4	3717.595	0.010	0.11
4	1	3	-	5 2 4	3717.244	0.004	0.83
5	2	4	-	6 1 5	3707.519	0.012	0.09
5	1	4	-	6 2 5	3707.465	0.016	0.25
8	2	5	-	7 1 6	3697.303	0.018	6.25
7	1	6	-	8 2 7	3686.860	0.028	0.64
8	2	7	-	9 1 8	3676.167	0.021	0.00
9	1	8	-	10 2 9	3665.245	0.021	5.06
11	2	9	-	11 1 10	3654.082	0.009	0.77
11	1	10	-	12 2 11	3642.683	-0.012	0.05
12	2	11	-	13 1 12	3631.066	-0.024	0.52
2	0	0	-	3 3 1	3723.083	-0.002	0.87
3	3	1	-	4 2 2	3725.567	0.021	0.02
3	2	1	-	4 3 2	3713.595	-0.014	5.50
4	3	2	-	5 2 3	3711.334	0.007	1.06
4	2	2	-	5 3 3	3706.371	-0.012	0.34
5	3	3	-	6 2 4	3700.081	0.003	0.55
5	2	3	-	6 3 4	3698.720	-0.003	0.64
8	3	4	-	7 2 5	3689.975	0.014	0.20
8	2	4	-	7 3 5	3689.688	0.015	0.09
7	3	5	-	8 2 6	3679.985	0.019	0.02
7	2	5	-	8 3 6	3679.935	0.024	0.64
8	3	6	-	9 2 7	3669.824	0.021	0.19
9	2	7	-	10 3 8	3659.442	0.028	0.58
11	3	8	-	11 2 9	3648.822	0.023	0.03



1	2	9	-	12	3	10	3637.970	0.011	0.00	
3	3	0	-	4	4	1	3702.783	0.002	1.25	
4	3	1	-	5	4	2	3692.662	-0.014	0.14	
5	4	2	-	6	3	3	3695.171	0.000	0.00	
5	3	2	-	6	4	3	3685.784	-0.018	0.62	
8	4	3	-	7	3	4	3683.442	-0.006	1.02	
6	3	3	-	7	4	4	3679.813	-0.003	0.08	
7	4	4	-	8	3	5	3672.863	0.005	0.03	
7	3	4	-	8	4	5	3671.836	0.007	0.00	
8	4	5	-	9	3	6	3662.950	0.007	0.14	
8	3	5	-	9	4	6	3662.723	0.019	0.03	
9	0	3	6	-	10	4	7	3653.001	0.025	0.08
1	1	4	7	-	11	3	8	3642.044	0.015	0.00
1	1	3	8	-	12	4	9	3632.619	0.015	0.02
1	4	4	0	-	5	5	1	3683.158	-0.002	0.83
5	4	1	-	6	5	2	3671.836	-0.013	0.00	
5	5	1	-	6	4	2	3705.004	-0.042	0.00	
8	5	2	-	7	4	3	3685.652	-0.035	0.00	
8	4	2	-	7	5	3	3664.439	-0.025	0.00	
7	5	3	-	8	4	4	3667.982	-0.043	0.00	
7	4	3	-	8	5	4	3659.549	-0.000	0.09	
8	5	4	-	9	4	5	3656.395	-0.031	0.00	
5	5	0	-	6	6	1	3664.343	-0.018	0.87	
4	5	1	-	7	6	2	3651.581	-0.022	0.08	
7	5	2	-	8	6	3	3643.338	0.011	0.00	
7	6	1	-	8	7	2	3632.261	-0.044	0.08	
1	1	1	-	0	0	0	3794.329	0.005	0.39	
2	0	2	-	1	1	1	3801.813	0.004	0.00	
2	1	2	-	1	0	1	3803.463	0.004	3.25	
3	0	3	-	2	1	2	3811.494	0.010	4.00	
3	1	3	-	2	0	2	3811.819	0.010	3.25	
4	0	4	-	3	1	3	3820.281	0.017	0.03	
4	1	4	-	3	0	3	3820.325	0.015	0.16	
5	0	5	-	4	1	4	3828.486	0.025	2.50	
8	1	6	-	5	0	5	3836.798	0.021	3.25	
7	0	7	-	6	1	6	3844.633	0.011	1.00	
9	1	8	-	7	0	7	3852.200	-0.004	1.00	
9	0	9	-	8	1	8	3859.505	-0.011	4.00	
1	1	10	-	9	0	9	3866.529	-0.027	3.25	
1	0	11	-	10	1	10	3873.290	-0.023	0.81	
1	1	12	-	11	0	11	3879.767	-0.009	1.56	
1	0	13	-	12	1	12	3885.973	0.046	0.75	
2	2	1	-	1	1	0	3815.665	0.011	3.25	
7	1	2	-	2	2	1	3819.479	-0.004	1.00	
3	2	2	-	2	1	1	3824.957	0.005	0.00	
4	1	3	-	3	2	2	3831.117	0.005	1.56	
4	2	3	-	3	1	2	3832.756	0.012	3.25	
5	1	4	-	4	2	3	3840.651	0.018	4.00	
5	2	4	-	4	1	3	3840.978	0.018	0.62	
8	1	5	-	5	2	4	3849.386	0.020	0.11	
6	2	5	-	5	1	4	3849.442	0.021	0.62	
7	1	6	-	6	2	5	3857.759	0.028	4.00	



8	2	7	-	7	1	6	3865.838	0.019	4.00
9	1	8	-	8	2	7	3873.649	0.009	1.75
10	2	9	-	9	1	8	3881.200	0.001	0.00
11	1	10	-	10	2	9	3888.483	-0.007	3.02
12	2	11	-	11	1	10	3895.496	-0.012	0.02
13	1	12	-	12	2	11	3902.255	0.016	0.00
14	2	13	-	13	1	12	3908.755	0.086	0.56
15	1	14	-	14	2	13	3914.863	0.089	0.37
3	3	1	-	2	2	0	3837.533	0.022	0.11
4	4	2	-	3	3	1	3835.416	-0.017	0.00
4	3	2	-	3	2	1	3847.311	0.010	3.25
5	2	3	-	4	3	2	3849.903	-0.000	2.50
5	3	3	-	4	2	2	3854.665	0.006	0.81
6	2	4	-	5	3	3	3860.817	0.012	2.31
6	3	4	-	5	2	3	3862.106	0.011	3.25
7	2	5	-	6	3	4	3870.086	0.019	0.02
7	3	5	-	6	2	4	3870.355	0.013	0.62
8	2	6	-	7	3	5	3878.717	0.022	0.09
8	3	6	-	7	2	5	3878.766	0.017	0.62
9	2	7	-	8	3	6	3887.003	0.018	3.06
10	3	8	-	9	2	7	3895.005	0.001	3.06
11	2	9	-	10	3	8	3902.751	-0.005	0.20
12	3	10	-	11	2	9	3910.224	-0.023	0.75
13	2	11	-	12	3	10	3917.440	-0.028	0.14
14	4	1	-	3	3	0	3861.007	-0.010	4.00
5	3	2	-	4	4	1	3849.481	-0.025	0.00
6	3	3	-	5	4	2	3867.174	-0.004	0.16
6	4	3	-	5	3	2	3877.583	-0.003	3.25
7	3	4	-	6	4	3	3880.350	0.007	0.00
7	4	4	-	6	3	3	3884.039	0.001	0.58
8	3	5	-	7	4	4	3890.584	0.018	0.05
8	4	5	-	7	3	4	3891.558	0.003	0.02
9	3	6	-	8	4	5	3899.585	0.019	0.77
9	4	6	-	8	3	5	3899.813	0.016	0.37
10	3	7	-	9	4	6	3908.073	0.025	0.00
10	4	7	-	9	3	6	3908.110	0.011	0.00
11	3	8	-	10	4	7	3916.217	0.004	1.50
12	4	9	-	11	3	8	3924.094	-0.015	1.50
13	3	10	-	12	4	9	3931.702	-0.034	0.00
5	5	1	-	4	4	0	3883.671	-0.004	3.25
4	4	2	-	5	5	1	3861.904	-0.025	0.02
5	5	2	-	5	4	1	3895.462	-0.015	0.44
7	4	3	-	6	5	2	3882.391	0.010	1.56
7	5	3	-	6	4	2	3901.117	-0.026	0.03
8	4	4	-	7	5	3	3898.619	0.040	0.00
8	5	4	-	7	4	3	3907.015	-0.020	0.02
9	4	5	-	8	5	4	3910.541	0.040	0.00
9	5	5	-	8	4	4	3913.335	0.005	0.33
10	4	6	-	9	5	5	3920.218	0.051	0.05
10	5	6	-	9	4	5	3920.982	0.029	0.00
11	4	7	-	10	5	6	3928.938	0.040	0.37
12	5	8	-	11	4	7	3937.260	0.028	0.03

1	4	9	-	12	5	8	3945.185	0.028	0.02
8	6	1	-	5	5	0	3905.295	-0.016	0.44
7	5	2	-	6	6	1	3873.196	-0.021	0.06
7	6	2	-	6	5	1	3918.984	-0.018	0.06
8	6	3	-	7	5	2	3923.465	-0.038	0.00
9	6	4	-	8	5	3	3930.016	-0.047	0.00
10	6	5	-	9	5	4	3935.025	0.001	0.14
7	7	1	-	6	6	0	3928.791	-0.012	2.31
8	7	2	-	7	6	1	3942.482	-0.003	2.50
9	7	3	-	8	6	2	3952.430	0.033	0.56
2	8	1	-	7	7	0	3951.137	0.008	1.56
3	8	2	-	8	7	1	3965.530	0.038	0.52
1	0	1	-	1	1	0	3773.487	-0.005	8.00
2	1	1	-	2	2	0	3772.314	-0.007	3.00
2	2	1	-	3	3	0	3770.172	-0.011	7.25
4	3	1	-	4	4	0	3766.965	-0.014	5.56
5	4	1	-	5	5	0	3763.040	-0.018	1.12
6	5	1	-	6	6	0	3759.058	-0.053	0.00
2	0	2	-	2	1	1	3765.763	0.003	0.00
2	1	2	-	2	2	1	3762.045	-0.000	7.25
2	1	2	-	3	2	1	3767.270	-0.006	7.25
3	2	2	-	3	3	1	3760.756	0.003	1.81
4	2	2	-	4	3	1	3768.116	-0.009	4.81
4	3	2	-	4	4	1	3759.021	0.012	0.16
5	3	2	-	5	4	1	3767.812	-0.017	6.50
4	4	2	-	5	5	1	3756.593	0.009	0.00
4	4	2	-	6	5	1	3766.119	-0.024	0.00
4	5	2	-	6	6	1	3756.213	-0.040	0.59
7	5	2	-	7	6	1	3763.114	-0.016	0.94
7	6	2	-	7	7	1	3754.007	-0.029	0.00
2	6	2	-	8	7	1	3759.300	-0.001	0.00
2	7	2	-	9	8	1	3755.453	-0.018	0.12
3	0	3	-	3	1	2	3754.734	0.008	6.25
1	1	3	-	3	2	2	3753.437	0.003	0.00
1	1	3	-	4	2	2	3757.174	0.007	1.62
2	2	3	-	4	3	2	3753.843	0.008	0.25
2	2	3	-	5	3	2	3760.131	0.003	6.25
3	3	3	-	5	4	2	3753.894	0.005	0.02
3	3	3	-	6	4	2	3762.847	-0.005	0.00
4	4	3	-	6	5	2	3753.437	-0.003	0.00
4	4	3	-	7	5	2	3764.516	0.000	2.06
5	5	3	-	7	6	2	3752.219	-0.014	0.00
5	5	3	-	8	6	2	3764.591	0.027	0.05
6	6	3	-	9	7	2	3762.947	0.043	0.00
7	7	3	-	9	8	2	3751.544	0.035	0.00
0	0	4	-	4	1	3	3743.608	0.018	0.02
1	1	4	-	4	2	3	3743.331	0.013	0.69
1	1	4	-	5	2	3	3745.725	0.019	0.11
2	2	4	-	5	3	3	3744.720	0.012	0.02
2	2	4	-	6	3	3	3748.694	0.013	0.64
3	3	4	-	6	4	3	3746.083	0.010	4.52
3	3	4	-	7	4	3	3752.498	0.017	0.03

7	4	4	-	7	5	3	3747.192	0.008	0.00
5	4	4	-	8	5	3	3747.798	-0.013	0.81
4	5	5	-	5	1	4	3756.593	0.023	0.00
0	1	5	-	5	2	4	3732.439	0.017	0.11
1	1	5	-	6	2	4	3732.400	0.024	0.02
1	2	5	-	6	3	4	3734.730	0.019	0.05
2	2	5	-	7	3	4	3734.512	0.022	0.87
2	3	5	-	7	4	4	3737.351	0.018	0.83
2	3	5	-	8	4	4	3736.612	0.021	0.03
2	4	5	-	8	5	4	3740.492	0.006	0.05
2	4	5	-	9	5	4	3738.720	0.006	1.00
2	4	5	-	9	5	4	3744.901	-0.010	0.14
8	1	6	-	6	2	5	3721.532	0.013	0.00
7	1	6	-	7	2	5	3723.973	0.020	0.87
9	3	6	-	8	4	5	3726.360	0.014	0.14
2	3	6	-	9	4	5	3729.405	-0.005	0.05
2	4	6	-	9	5	5	3729.039	-0.002	0.03
7	0	7	-	7	1	6	3710.227	0.009	0.81
9	2	7	-	8	3	6	3712.888	0.018	0.05
2	2	7	-	9	3	6	3715.902	0.005	0.05
1	4	7	-	10	5	6	3718.813	-0.016	5.00
9	1	8	-	8	2	7	3698.484	0.004	0.02
2	1	8	-	9	2	7	3701.739	0.024	0.00
1	3	8	-	10	4	7	3704.959	0.003	0.00
1	2	9	-	10	3	8	3699.360	0.010	0.02
1	2	9	-	11	3	8	3693.961	-0.007	0.02
1	1	0	-	1	0	1	3785.078	-0.004	0.39
2	2	0	-	2	1	1	3787.283	-0.001	1.00
3	3	0	-	3	2	1	3791.076	0.002	3.02
4	4	0	-	4	3	1	3795.611	-0.003	1.33
5	5	0	-	5	4	1	3803.578	-0.006	0.39
4	6	0	-	6	5	1	3811.301	-0.000	0.09
7	7	0	-	7	5	1	3819.073	-0.002	0.03
2	1	1	-	2	0	2	3792.666	-0.007	0.62
2	2	1	-	2	1	2	3796.738	0.005	3.25
2	2	1	-	3	1	2	3792.512	-0.007	3.25
3	3	1	-	3	2	2	3799.515	0.025	1.75
4	3	1	-	4	2	2	3793.433	-0.012	1.56
4	4	1	-	4	3	2	3804.431	-0.013	0.16
5	4	1	-	5	3	2	3795.979	-0.015	0.62
5	5	1	-	5	4	2	3809.364	-0.009	0.03
5	5	1	-	6	4	2	3800.494	-0.018	0.14
8	6	1	-	6	5	2	3815.095	-0.006	0.05
7	6	1	-	7	5	2	3806.978	-0.017	0.00
3	1	2	-	3	0	3	3803.216	-0.005	3.25
3	2	2	-	3	1	3	3804.626	-0.003	0.02
4	2	2	-	4	1	3	3802.626	-0.008	0.03
4	3	2	-	4	2	3	3806.262	0.009	4.00
5	3	2	-	5	2	3	3801.813	-0.012	0.00
5	4	2	-	5	3	3	3808.305	0.009	0.62
8	4	2	-	6	3	3	3801.493	-0.024	0.08
8	5	2	-	6	4	3	3813.483	0.034	0.00

7	5	2	-	7	4	3	3802.534	-0.016	0.39
7	6	2	-	7	5	3	3817.508	-0.013	0.02
7	6	2	-	8	5	3	3805.573	-0.014	0.14
7	7	2	-	8	6	3	3822.679	-0.003	0.00
7	4	2	3	4	1	4	3813.643	0.019	0.00
7	5	2	3	5	1	4	3813.643	-0.010	0.00
7	3	3	-	5	2	4	3814.736	0.003	0.00
7	3	3	-	6	2	4	3813.410	0.043	0.00
7	4	3	-	6	3	4	3816.174	-0.007	0.11
7	4	3	-	7	3	4	3812.395	0.006	2.31
7	5	5	-	7	4	4	3817.885	-0.021	0.39
7	5	5	-	8	4	4	3811.222	0.034	0.09
7	6	3	-	8	5	4	3818.488	-0.048	1.52
7	1	4	-	5	0	5	3822.722	0.016	0.44
7	2	4	-	5	1	5	3822.769	0.013	0.02
7	2	4	-	6	1	5	3823.634	0.031	0.00
7	3	4	-	6	2	5	3823.861	0.023	0.00
7	3	4	-	7	2	5	3824.251	0.019	0.25
7	4	4	-	7	3	5	3825.030	-0.001	0.09
7	4	4	-	8	3	5	3824.287	0.035	0.00
7	5	4	-	8	4	5	3826.371	-0.011	0.56
7	5	4	-	9	4	5	3823.403	0.057	0.00
7	6	4	-	9	5	5	3827.865	-0.024	0.05
10	7	4	-	10	6	5	3828.762	-0.052	0.03
7	2	5	-	6	1	6	3831.705	0.015	0.00
7	2	5	-	7	1	6	3832.878	0.018	0.58
7	3	5	-	7	2	6	3832.918	0.012	0.02
7	3	5	-	8	2	6	3833.967	0.024	0.05
7	4	5	-	8	3	6	3834.145	0.013	0.58
7	4	5	-	9	3	6	3834.789	0.059	0.00
7	5	5	-	9	4	6	3835.381	0.033	0.00
7	1	6	-	7	0	7	3840.386	0.030	2.31
7	3	6	-	8	2	7	3841.743	0.016	0.39
7	3	6	-	9	2	7	3843.054	0.029	0.14
7	4	6	-	9	3	7	3843.087	0.019	0.00
11	5	6	-	10	4	7	3844.364	0.046	0.09
7	2	7	-	8	1	8	3848.778	0.025	2.08
7	2	7	-	9	1	8	3850.279	0.018	1.31
11	4	7	-	10	3	8	3851.743	0.027	0.00
11	4	7	-	11	3	8	3853.005	0.008	0.00
7	1	8	-	9	0	9	3856.898	0.022	0.56
11	3	8	-	10	2	9	3858.520	0.008	0.37
11	3	8	-	11	2	9	3860.078	0.021	0.02
11	2	9	-	10	1	10	3864.740	0.008	0.52
11	2	9	-	11	1	10	3866.486	0.007	0.00
12	4	9	-	12	3	10	3868.116	0.016	0.00
12	3	10	-	12	2	11	3874.139	-0.025	0.03
12	2	11	-	12	1	12	3879.611	-0.025	0.00
1	1	1	-	2	2	0	3735.957	-0.000	0.16
2	2	1	-	3	3	0	3717.645	0.006	0.06
3	3	1	-	4	4	0	3699.096	0.017	0.08
4	4	1	-	5	5	0	3681.721	-0.012	5.31

5	1	-	6	6	0	3663.420	-0.024	0.14
7	1	-	8	8	0	3628.859	-0.003	0.06
2	2	-	3	3	1	3701.545	-0.016	0.00
2	1	2	-	3	2	3709.841	0.002	0.05
3	1	2	-	4	4	3678.991	0.008	0.03
3	2	2	-	4	3	3693.451	0.006	0.08
4	1	3	2	-	5	3677.344	0.013	0.06
4	5	2	2	-	7	3646.141	-0.025	0.05
4	0	3	3	-	4	3675.823	0.007	0.02
4	1	3	3	-	5	3656.395	-0.002	0.00
4	2	3	3	-	5	3664.073	0.013	0.03
2	2	0	0	-	1	3823.330	-0.002	0.81
3	3	0	0	-	2	3843.281	0.001	4.00
4	4	0	0	-	3	3863.928	0.006	0.25
5	5	0	0	-	4	3885.260	-0.001	0.25
6	6	0	0	-	5	3907.075	-0.012	0.20
7	7	0	0	-	6	3929.151	-0.011	4.00
8	8	0	0	-	7	3951.299	0.009	2.25
9	9	0	0	-	8	3973.326	0.006	0.09
3	3	1	1	-	2	3857.887	0.022	0.09
2	2	1	1	-	2	3849.267	-0.010	0.02
3	3	1	1	-	3	3867.376	-0.014	0.25
4	4	1	1	-	4	3885.750	-0.018	0.25
5	5	1	1	-	5	3904.816	-0.023	0.00
6	6	1	1	-	6	3924.847	-0.013	2.50
7	7	1	1	-	7	3945.745	-0.001	0.58
8	8	1	1	-	8	3967.215	0.045	0.39
3	3	2	2	-	3	3983.265	0.019	0.00
2	2	2	2	-	3	3879.299	-0.010	0.03
4	4	2	2	-	4	3904.558	0.010	0.34
3	3	2	2	-	4	3896.733	-0.019	1.52
4	4	2	2	-	5	3913.419	-0.022	0.16
5	5	2	2	-	6	3930.404	-0.009	0.81
6	6	2	2	-	7	3947.614	0.019	0.14
3	3	3	3	-	4	3910.829	0.006	0.03
2	2	3	3	-	4	3909.692	0.000	0.14
4	4	3	3	-	5	3931.114	0.003	0.00
3	3	3	3	-	5	3928.015	-0.007	0.05
4	4	3	3	-	6	3945.129	0.007	0.37
5	5	3	3	-	7	3961.113	0.045	0.02
6	6	3	3	-	7	3971.332	-0.044	2.08
2	2	4	4	-	5	3938.854	0.002	0.00
3	3	4	4	-	5	3939.110	0.014	0.06
4	4	4	4	-	6	3953.961	0.000	0.03
3	3	4	4	-	6	3958.120	0.010	0.52
5	5	4	4	-	7	3978.778	-0.009	0.33
4	4	4	4	-	7	3976.445	0.020	0.14
6	6	4	4	-	8	3998.436	-0.009	0.02
2	2	5	5	-	6	3967.283	0.018	0.02
4	4	5	5	-	7	3987.092	0.011	0.14
3	3	5	5	-	7	3986.902	0.020	0.02

## ASSIGNED FREQUENCIES FOR THE (011) BAND

UPPER		GROUND		OBSERVED	DIFFERENCE	WEIGHT
0	0	0	-	3775.526	-0.007	1.50
1	1	1	-	3766.089	-0.001	0.50
1	0	1	-	3765.030	0.005	0.00
2	1	2	-	3755.991	-0.001	7.00
2	0	2	-	3755.683	0.001	2.75
3	1	3	-	3745.909	-0.008	0.00
1	0	4	-	3735.903	0.012	0.87
5	1	5	-	3725.478	0.014	0.64
4	0	6	-	3714.925	0.006	0.00
7	1	7	-	3704.174	0.009	0.00
9	0	8	-	3693.210	0.006	0.02
0	1	9	-	3682.035	-0.006	5.12
10	0	10	-	3670.651	-0.030	0.64
11	1	11	-	3659.061	-0.067	5.25
1	1	0	-	3757.767	-0.007	6.25
2	2	1	-	3748.592	-0.005	4.56
2	1	1	-	3745.909	-0.012	0.00
3	2	2	-	3737.740	0.001	7.00
3	1	2	-	3736.808	-0.007	0.59
4	2	3	-	3727.776	0.002	0.44
4	1	3	-	3727.598	-0.001	5.50
5	2	4	-	3717.888	-0.002	0.06
4	1	5	-	3707.850	0.012	7.00
7	2	6	-	3697.409	0.019	6.25
9	1	7	-	3687.156	0.021	5.31
0	2	8	-	3676.499	0.019	5.27
10	1	9	-	3665.642	0.009	4.31
11	2	10	-	3654.590	-0.007	1.56
12	1	11	-	3643.338	-0.042	0.00
13	2	12	-	3631.989	0.006	0.52
2	2	0	-	3741.043	-0.006	6.25
3	3	1	-	3731.087	-0.001	7.00
3	2	1	-	3727.947	-0.012	0.00
4	3	2	-	3720.254	0.003	5.31
4	2	2	-	3717.992	-0.016	4.56
5	3	3	-	3710.013	-0.008	0.00
9	2	3	-	3709.406	0.007	0.00
4	3	4	-	3700.291	-0.001	4.33
4	2	4	-	3700.173	0.003	1.25
7	3	5	-	3690.517	0.003	0.05
9	2	6	-	3680.565	0.017	0.64
0	3	7	-	3670.416	0.025	0.00
11	2	8	-	3660.052	0.019	0.37
11	3	9	-	3649.498	0.010	0.05
12	2	10	-	3638.758	-0.003	0.00

3	3	0	-	4	3	1	3725.537	-0.001	0.08
4	4	1	-	5	4	2	3716.194	-0.004	0.00
5	5	2	-	6	3	2	3709.970	0.014	0.00
6	6	4	-	6	4	3	3499.941	-0.024	0.14
7	7	4	-	7	4	4	3703.555	0.004	4.56
8	8	3	-	7	3	4	3492.755	-0.009	0.93
9	9	3	-	8	3	5	3491.190	-0.013	0.87
0	0	7	-	8	4	5	3482.612	-0.003	0.19
1	1	7	-	9	3	6	3483.006	-0.012	4.56
2	2	5	-	9	4	6	3473.377	-0.001	0.62
3	3	4	-	9	4	6	3473.458	-0.006	0.09
4	4	6	-	10	4	7	3463.777	-0.005	1.12
5	5	3	-	11	3	8	3453.905	0.003	0.02
6	6	4	-	12	4	9	3443.835	0.001	0.08
7	7	3	-	13	3	10	3433.572	-0.002	0.02
8	8	4	-	5	4	1	3711.227	-0.007	4.75
9	9	5	1	-	6	5	3701.105	-0.002	1.81
0	0	5	4	1	6	4	3494.186	-0.000	4.52
1	1	5	2	-	7	5	3487.680	0.009	0.81
2	2	4	-	7	4	3	3480.625	-0.017	0.64
3	3	5	3	-	8	5	3476.144	-0.014	0.00
4	4	4	-	8	4	4	3473.316	-0.016	0.08
5	5	4	4	-	9	4	3465.071	-0.011	4.08
6	6	5	4	-	9	5	3466.093	-0.035	0.05
7	7	5	5	-	10	5	3453.653	-0.035	0.58
8	8	5	0	-	6	5	3497.749	-0.008	0.14
9	9	5	1	-	7	5	3479.697	-0.006	5.31
0	0	6	1	-	7	6	3486.547	-0.001	0.05
1	1	7	5	-	8	5	3464.639	0.002	0.00
2	2	7	2	-	8	6	3472.570	0.011	0.81
3	3	6	3	-	9	6	3460.289	-0.036	0.09
4	4	5	3	-	9	5	3457.786	0.017	0.03
5	5	6	4	-	10	6	3449.762	0.005	0.03
6	6	6	0	-	7	6	3484.547	-0.009	0.05
7	7	6	1	-	8	6	3466.442	-0.007	0.05
8	8	7	1	-	8	7	3472.343	0.011	0.09
9	9	7	2	-	9	7	3458.108	0.021	0.03
0	0	7	7	-	8	7	3471.268	0.008	0.03
1	1	7	7	-	8	7	3403.036	-0.003	0.62
2	2	1	0	-	0	0	3412.266	0.001	4.00
3	3	0	2	-	1	1	3413.355	-0.003	3.25
4	4	1	3	-	2	1	3421.785	-0.009	0.00
5	5	0	3	-	2	0	3422.049	0.005	3.25
6	6	1	4	-	3	1	3430.681	0.008	0.00
7	7	0	4	-	3	0	3430.708	-0.002	0.05
8	8	1	5	-	4	1	3439.250	0.016	3.25
9	9	0	6	-	5	0	3447.565	0.014	3.25
0	0	1	7	-	6	1	3455.442	0.006	4.00
1	1	0	8	-	7	0	3463.491	0.001	4.00
2	2	1	9	-	8	1	3471.102	-0.012	3.25
3	3	0	10	-	9	0	3479.478	-0.027	4.00
4	4	1	11	-	10	1	3485.622	-0.035	0.03

12	0	12	-	11	0	11	3892.523	-0.045	3.06
13	1	13	-	12	1	12	3899.217	-0.013	0.06
14	0	14	-	13	0	13	3905.407	-0.023	0.77
15	1	15	-	14	1	14	3911.795	0.039	1.31
2	1	1	-	1	1	0	3821.593	-0.006	2.50
3	2	2	-	2	2	1	3830.999	0.006	3.25
3	1	2	-	2	1	1	3833.809	-0.004	4.00
4	2	3	-	3	2	2	3841.646	0.001	2.50
4	1	3	-	3	1	2	3842.759	0.002	4.00
5	2	4	-	4	2	3	3851.079	0.006	0.81
5	1	4	-	4	1	3	3851.325	0.008	4.00
5	2	5	-	5	2	4	3859.944	0.012	0.02
6	1	5	-	5	1	4	3859.986	0.011	0.20
7	2	6	-	6	2	5	3868.504	0.015	4.00
2	1	7	-	7	1	6	3876.819	0.011	4.00
2	2	8	-	8	2	7	3884.909	0.013	0.81
10	1	9	-	9	1	8	3892.759	0.002	3.25
11	2	10	-	10	2	9	3900.384	-0.008	3.02
12	1	11	-	11	1	10	3907.784	-0.013	3.00
14	1	13	-	13	1	12	3921.885	-0.012	0.56
15	2	14	-	14	2	13	3928.603	0.027	0.19
3	2	1	-	2	2	0	3839.911	-0.013	0.06
4	3	2	-	3	3	1	3849.304	0.003	0.11
4	2	2	-	3	2	1	3853.969	-0.013	0.00
5	3	3	-	4	3	2	3861.202	0.002	0.81
5	2	3	-	4	2	2	3863.978	-0.002	0.25
5	3	4	-	5	3	3	3871.427	0.003	1.00
4	2	4	-	5	2	3	3872.311	0.006	4.00
7	2	5	-	6	2	4	3880.875	0.007	3.06
7	3	5	-	6	3	4	3880.677	0.007	4.00
2	3	6	-	7	3	5	3889.476	0.021	0.00
3	2	6	-	7	2	5	3889.497	0.003	0.11
3	3	7	-	8	3	6	3897.971	0.008	2.31
10	2	8	-	9	2	7	3906.238	0.000	0.06
11	3	9	-	10	3	8	3914.272	-0.012	2.27
12	2	10	-	11	2	9	3922.090	-0.019	2.27
13	3	11	-	12	3	10	3929.695	-0.012	0.56
14	2	12	-	13	2	11	3936.996	-0.081	0.14
15	3	13	-	14	3	12	3944.149	-0.062	0.03
4	3	1	-	3	3	0	3854.309	0.005	3.25
5	4	2	-	4	4	1	3867.262	0.007	1.00
5	3	2	-	4	3	1	3873.803	-0.029	1.75
4	4	3	-	5	4	2	3880.326	-0.001	0.00
4	3	3	-	5	3	2	3885.332	-0.009	0.25
7	4	4	-	6	4	3	3891.526	-0.007	0.20
7	3	4	-	6	3	3	3893.789	-0.006	1.56
2	3	5	-	7	3	4	3901.989	-0.001	1.75
2	4	5	-	7	4	4	3901.321	-0.006	3.02
2	4	6	-	8	4	5	3910.369	-0.005	3.06
2	3	6	-	8	3	5	3910.541	0.009	0.00
10	3	7	-	9	3	6	3919.057	-0.016	0.06
11	4	8	-	10	4	7	3927.428	-0.015	2.27

12	3	9	-	11	3	8	3035.595	-0.025	0.56
12	4	11	-	12	4	9	3943.541	-0.030	0.09
5	4	1	-	4	4	0	3972.815	-0.000	1.37
4	4	2	-	5	4	1	3990.527	-0.005	0.62
4	5	2	-	5	5	1	3984.936	-0.001	0.00
7	5	3	-	6	5	2	3998.981	-0.010	3.25
7	4	3	-	6	4	2	3906.446	-0.004	2.50
8	5	4	-	7	5	3	3911.188	-0.022	1.31
8	4	4	-	7	4	3	3915.698	0.007	3.25
9	5	5	-	8	5	4	3921.719	-0.011	0.00
9	4	5	-	8	4	4	3923.465	-0.000	0.00
11	5	6	-	9	5	5	3931.114	-0.018	0.00
11	4	6	-	9	4	5	3931.645	0.006	0.56
11	5	7	-	10	5	6	3939.952	0.001	0.75
11	4	7	-	10	4	6	3940.077	-0.006	0.00
12	5	8	-	11	5	7	3948.431	-0.008	0.00
12	4	8	-	11	4	7	3948.465	-0.007	0.08
13	5	9	-	12	5	8	3956.485	0.006	0.00
4	5	1	-	5	5	0	3888.780	0.001	3.25
7	5	2	-	6	5	1	3908.110	-0.014	0.00
7	6	2	-	6	6	1	3902.452	0.003	0.58
8	6	3	-	7	6	2	3917.220	-0.003	0.03
8	5	3	-	7	5	2	3928.348	0.022	3.25
9	6	4	-	8	6	3	3930.321	-0.020	0.39
9	5	4	-	8	5	3	3937.459	0.058	0.56
11	6	5	-	9	4	4	3941.482	0.005	0.03
11	5	5	-	9	5	4	3945.411	0.051	1.50
11	5	6	-	10	5	5	3952.957	0.044	0.03
7	6	1	-	6	6	0	3904.816	0.026	0.00
9	7	2	-	7	7	1	3919.902	0.004	0.03
9	6	2	-	7	6	1	3924.396	-0.008	0.56
9	7	3	-	8	7	2	3935.081	0.009	0.14
9	7	1	-	7	7	0	3921.193	0.001	0.34
9	8	2	-	8	8	1	3937.382	0.006	0.03
9	7	2	-	8	7	1	3940.077	0.037	0.00
11	1	1	-	1	1	0	3785.010	-0.001	0.44
9	2	1	-	2	2	0	3786.620	0.001	3.25
3	3	1	-	3	3	0	3788.562	0.001	2.50
4	4	1	-	4	4	0	3790.499	-0.002	1.75
5	5	1	-	5	5	0	3792.312	-0.004	0.44
4	6	1	-	6	6	0	3794.047	-0.009	3.25
7	7	1	-	7	7	0	3795.777	-0.017	2.50
9	9	1	-	9	9	0	3799.397	0.003	0.56
9	0	2	-	2	2	1	3771.940	-0.004	6.50
9	1	2	-	2	1	1	3776.214	-0.002	5.56
4	2	2	-	4	4	1	3765.676	-0.014	0.89
5	3	2	-	5	5	1	3760.353	-0.025	0.14
5	4	2	-	5	4	1	3785.588	0.010	4.00
4	5	2	-	6	5	1	3789.160	0.009	1.56
7	6	2	-	7	6	1	3792.375	0.013	0.34
8	7	2	-	8	7	1	3795.122	0.030	0.37
9	8	2	-	9	8	1	3797.489	0.066	0.00

3	3	-	3	2	2	3763.661	-0.009	0.00
1	3	-	3	1	2	3765.030	-0.006	0.00
2	3	-	4	2	2	3767.704	0.004	0.94
1	3	-	4	3	2	3763.849	0.000	7.25
3	3	-	5	3	2	3771.428	0.003	8.00
5	3	-	5	4	2	3763.204	-0.007	0.89
5	3	-	6	5	2	3761.184	-0.013	0.20
5	3	-	6	4	2	3775.996	-0.004	0.89
7	4	-	7	6	2	3757.533	-0.007	0.14
7	5	-	8	7	2	3753.643	0.006	0.19
7	5	-	7	5	2	3781.106	-0.019	6.31
6	3	-	8	6	2	3786.363	-0.028	0.14
7	3	-	9	7	2	3791.299	0.004	0.00
1	8	-	10	8	2	3795.447	-0.001	0.02
1	4	-	4	1	3	3754.007	0.008	0.00
1	0	-	4	2	3	3753.724	0.006	1.25
2	4	-	5	2	3	3756.155	0.008	0.69
1	4	-	5	3	3	3755.071	0.006	5.27
2	4	-	6	4	3	3756.294	0.012	0.00
3	4	-	6	3	3	3759.300	0.001	0.00
7	3	-	7	5	3	3756.944	0.002	0.05
7	4	-	7	4	3	3763.461	-0.010	0.00
4	4	-	8	6	3	3756.472	0.005	0.77
5	5	-	8	5	3	3769.151	-0.051	0.05
0	5	-	5	2	4	3743.158	0.010	0.02
1	1	-	5	1	4	3743.204	0.008	0.11
1	1	-	6	3	4	3745.077	0.032	0.00
2	2	-	6	2	4	3745.293	0.015	0.19
7	2	-	7	4	4	3747.123	0.007	0.53
7	3	-	7	3	4	3747.942	0.006	0.83
3	4	-	8	5	4	3749.142	-0.007	0.02
4	4	-	8	4	4	3751.437	-0.010	1.00
4	4	-	9	6	4	3750.774	-0.000	0.02
0	6	-	6	2	5	3732.301	0.007	0.05
7	2	-	7	2	5	3734.585	-0.027	0.00
2	6	-	8	4	5	3737.096	0.006	0.19
3	6	-	8	3	5	3737.293	0.011	0.03
4	6	-	9	4	5	3740.392	-0.025	0.03
3	6	-	9	5	5	3739.758	-0.018	0.03
7	1	-	7	1	6	3721.234	0.004	4.37
1	7	-	8	3	6	3723.839	-0.019	0.00
3	7	-	9	3	6	3726.772	-0.003	0.09
1	3	-	10	5	6	3729.765	-0.038	0.00
1	4	-	10	4	6	3729.932	-0.035	0.00
11	5	-	11	5	6	3733.535	0.016	0.02
8	0	-	8	2	7	3709.070	0.004	0.00
2	2	-	9	2	7	3712.983	0.012	0.53
10	2	-	10	4	7	3716.194	0.005	0.00
11	3	-	11	5	7	3719.560	-0.025	0.03
0	1	-	9	1	8	3698.496	-0.012	0.14
1	1	-	10	3	8	3701.918	0.008	0.03
11	2	1	11	2	9	3690.684	0.005	0.02

1	2	1	0	-	1	2	4	9	3894.434	-0.021	0.02
1	1	0	-	-	1	1	1	1	3793.820	-0.003	4.00
2	2	0	-	-	2	2	1	1	3793.252	-0.003	3.25
3	3	0	-	-	3	3	1	1	3792.843	-0.004	0.39
4	4	0	-	-	4	4	1	1	3792.907	-0.005	0.44
5	5	0	-	-	5	5	1	1	3793.538	-0.005	2.50
6	6	0	-	-	6	6	1	1	3794.632	-0.011	4.00
7	7	0	-	-	7	7	1	1	3795.047	-0.020	0.39
8	8	0	-	-	8	8	1	1	3797.482	-0.015	0.39
9	9	0	-	-	9	9	1	1	3799.450	-0.001	0.02
10	10	0	-	-	10	10	1	1	3801.299	0.029	0.14
11	1	1	-	-	2	1	2	2	3802.467	-0.011	0.20
12	2	1	-	-	2	0	2	2	3806.978	0.007	0.00
13	2	1	-	-	3	2	2	2	3801.977	-0.026	0.09
14	3	1	-	-	3	1	2	2	3810.999	0.002	1.75
15	3	1	-	-	4	3	2	2	3799.738	0.007	4.00
16	4	1	-	-	4	2	2	2	3816.964	-0.003	0.39
17	4	1	-	-	5	4	2	2	3798.511	-0.002	2.50
18	5	1	-	-	5	3	2	2	3825.249	-0.003	0.58
19	5	1	-	-	6	5	2	2	3797.567	-0.003	2.50
20	6	1	-	-	7	6	2	2	3797.285	0.004	1.33
21	7	1	-	-	8	7	2	2	3797.758	0.029	0.05
22	8	1	-	-	9	8	2	2	3798.823	0.066	0.00
23	1	2	-	-	3	1	3	3	3813.483	-0.007	0.00
24	2	2	-	-	3	0	3	3	3814.736	0.004	0.00
25	2	2	-	-	4	2	3	3	3812.919	-0.016	3.25
26	3	2	-	-	4	1	3	3	3816.507	0.004	0.44
27	3	2	-	-	5	3	3	3	3812.062	-0.028	0.37
28	4	2	-	-	5	2	3	3	3819.581	0.008	0.81
29	4	2	-	-	6	4	3	3	3809.496	-0.008	2.50
30	5	2	-	-	6	3	3	3	3824.533	0.008	0.56
31	5	2	-	-	7	5	3	3	3806.627	-0.018	0.56
32	6	2	-	-	7	4	3	3	3831.795	0.012	0.05
33	6	2	-	-	8	6	3	3	3804.592	-0.009	0.09
34	7	2	-	-	8	5	3	3	3841.405	0.029	0.00
35	7	2	-	-	9	7	3	3	3803.083	0.048	0.00
36	8	2	-	-	10	8	3	3	3802.361	0.048	0.12
37	1	3	-	-	4	1	4	4	3823.434	-0.003	0.00
38	2	3	-	-	4	0	4	4	3823.861	-0.003	0.00
39	2	3	-	-	5	2	4	4	3824.050	-0.004	1.56
40	3	3	-	-	5	1	4	4	3824.957	0.006	0.00
41	3	3	-	-	6	3	4	4	3823.924	-0.013	0.44
42	4	3	-	-	6	2	4	4	3826.508	-0.007	0.58
43	4	3	-	-	7	4	4	4	3823.210	-0.003	0.08
44	5	3	-	-	7	3	4	4	3828.985	-0.013	0.81
45	5	3	-	-	8	5	4	4	3823.403	0.044	0.00
46	6	3	-	-	8	4	4	4	3832.992	-0.024	0.05
47	6	3	-	-	9	6	4	4	3816.434	-0.002	0.05
48	2	4	-	-	5	0	5	5	3833.150	0.004	0.00
49	2	4	-	-	6	2	5	5	3834.048	0.001	0.81
50	3	4	-	-	6	1	5	5	3834.222	0.000	0.39
51	3	4	-	-	7	3	5	5	3834.789	0.001	0.00

7	4	4	-	7	2	5	3835.416	-0.005	0.00
9	4	4	-	8	4	5	3835.048	0.010	0.02
9	5	4	-	8	3	5	3836.857	-0.026	0.02
9	6	4	-	9	4	5	3838.017	-0.040	0.00
8	1	5	-	6	1	6	3842.260	0.017	4.00
7	3	5	-	7	1	6	3843.464	0.001	0.20
8	3	5	-	8	3	6	3844.578	0.011	0.03
8	4	5	-	8	2	6	3844.696	-0.007	0.02
9	4	5	-	9	4	6	3845.500	0.017	0.03
9	5	5	-	9	3	6	3845.951	-0.007	0.14
7	2	6	-	7	0	7	3851.123	0.008	0.02
8	2	6	-	8	2	7	3852.482	0.010	2.31
9	4	6	-	9	2	7	3853.836	0.005	0.14
10	4	6	-	10	4	7	3855.037	0.032	0.14
11	5	6	-	10	3	7	3855.141	0.021	0.02
8	1	7	-	8	1	8	3859.765	0.023	0.81
9	3	7	-	9	1	8	3861.242	0.003	0.00
10	3	7	-	10	3	8	3862.498	0.008	0.33
9	2	8	-	9	0	9	3868.148	0.016	0.14
11	2	8	-	10	2	9	3869.748	0.002	1.31
11	4	8	-	11	2	9	3871.299	0.011	0.09
10	1	9	-	10	1	10	3876.298	0.007	0.33
11	3	9	-	11	1	10	3877.991	-0.016	0.08
12	3	9	-	12	3	10	3879.611	-0.001	0.00
11	2	10	-	11	0	11	3884.210	-0.011	0.14
1	0	1	-	2	2	0	3744.460	-0.013	0.00
2	1	1	-	3	3	0	3723.576	-0.009	5.50
7	2	1	-	4	4	0	3701.469	-0.023	0.52
2	0	2	-	3	2	1	3710.735	-0.003	0.16
7	1	2	-	4	3	1	3702.301	-0.005	0.16
4	2	2	-	5	4	1	3683.998	-0.014	0.64
5	3	2	-	6	5	1	3664.579	-0.012	0.05
7	1	3	-	4	3	2	3686.132	0.005	0.03
4	1	3	-	5	3	2	3674.078	0.004	0.56
4	2	3	-	5	4	2	3666.033	0.003	0.00
5	2	3	-	6	4	2	3658.980	-0.004	0.03
5	3	3	-	6	5	2	3647.270	-0.011	0.14
4	3	3	-	7	5	2	3643.338	0.007	0.00
4	0	4	-	5	2	3	3658.796	0.005	0.00
5	1	4	-	6	3	3	3642.944	0.003	0.00
5	2	4	-	6	4	3	3640.128	0.005	0.03
4	2	4	-	7	4	3	3628.411	-0.008	0.02
2	2	0	-	1	0	1	3834.463	-0.006	2.50
7	3	0	-	2	1	1	3857.046	0.000	0.77
4	4	0	-	3	2	1	3881.200	-0.005	0.00
5	5	0	-	4	3	1	3907.015	0.018	0.00
4	6	0	-	5	4	1	3933.870	0.003	1.33
7	7	0	-	6	5	1	3961.055	0.022	0.00
7	2	1	-	2	0	2	3860.257	-0.020	0.03
7	3	1	-	2	1	2	3867.646	-0.009	0.03
4	3	1	-	3	1	2	3878.648	0.008	0.44
1	4	1	-	3	2	2	3890.015	0.003	0.11

5	4	1	-	4	2	2	3899.281	-0.000	0.06
5	5	1	-	4	3	2	3915.025	-0.001	0.62
5	5	1	-	5	3	2	3921.719	0.005	0.00
6	6	1	-	5	4	2	3930.785	0.002	0.08
7	6	1	-	6	4	2	3946.205	0.014	0.14
7	7	1	-	6	5	2	3964.922	0.034	0.00
8	7	1	-	7	5	2	3972.457	0.039	1.27
4	2	2	-	3	7	3	3889.012	-0.015	0.58
4	3	2	-	3	1	3	3893.188	0.011	0.06
5	3	2	-	4	1	3	3908.313	-0.028	0.03
5	4	2	-	4	2	3	3914.504	0.004	1.56
5	4	2	-	5	2	3	3924.519	-0.008	2.31
4	5	2	-	5	3	3	3936.657	0.007	0.16
7	5	2	-	6	3	3	3943.484	-0.014	0.14
7	6	2	-	6	4	3	3950.459	0.014	1.33
8	6	2	-	7	4	3	3963.820	-0.005	2.31
9	7	2	-	8	5	3	3986.336	0.012	0.14
5	2	3	-	4	0	4	3920.143	-0.002	0.00
5	3	3	-	4	1	4	3920.982	-0.008	0.00
5	3	3	-	5	1	4	3938.854	-0.013	0.00
4	4	3	-	5	2	4	3941.167	-0.004	0.05
7	5	3	-	6	3	4	3961.718	-0.013	1.33
8	6	3	-	7	4	4	3982.888	-0.007	0.14
9	6	3	-	8	4	4	3989.128	0.002	0.02
4	2	4	-	5	0	5	3949.311	0.005	0.12
4	3	4	-	5	1	5	3949.474	0.004	0.06
7	3	4	-	6	1	5	3968.721	0.003	0.03
7	4	4	-	6	2	5	3969.268	-0.010	0.14
8	4	4	-	7	2	5	3987.455	0.013	0.37
9	5	4	-	7	3	5	3989.036	-0.021	0.02
7	3	5	-	6	1	6	3977.870	0.002	0.03

APPENDIX XI

LISTING OF PROGRAM CORIKORR

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PROGRAM CORIKORR
DIMENSION EPV1(21,21),EPV2(21,21),OPV1(20,20),OPV2(20,20),
1 A(2),B(2),CS(2),E(82,3),TAO(2),TAT(2),TAS(2),TAN(2),EN(2),HK(2)
COMPLEX EPV1,EPV2,OPV1,OPV2
COMMON IOPT,RHO,IER
C ARITHMETIC STATEMENT FUNCTIONS
0 F1(A,B,CS,EN,TAN,R,Y,T,X,HK,J,K)=.5*(J*(J+1.)-K*K)*
1 (A+B-TAN+.5*K*K*H)*(J**2*(J+1.)***2+2.**(K*K-1.)*J*(J+1.)*
2 +K*K*(K*K-5.))*Y/16.+*(CS+.75*TAN)*K*K*EN+.25*T*K**4 +
3 (3.*J**2*(J+1.)***2-2.* (3.*K*K+1.)*J*(J+1.)*
4 K*K*(3.*K*K+5.))*X/32.+HK*K**6
F2(A,B,J,V,S)=.25+J*(J+1.)*(B-A+(J*(J+1.)-1.)*V/4.+S/2.)
F3(J)=J*(J+1.)*(J*(J+1.)-2.)
F4(A,B,J,V,S)=.25*SQRTE((2.*J*(J+1.)*(J*(J+1.)-2.))*
1 (B-A+.25*V*(J*(J+1.)-2.))+S)
0 F5(J)=SQRTE((2*J*(J+1.)*(J*(J+1.)-2.)*(J*(J+1.)-6.)*(J*(J+1.)-12.)))
0 F6(A,B,J,K,V,S)=.25*SQRTE((J*(J+1.)-K*(K+1.))*(J*(J+1.)-(K+1.)*
1 (K+2.)))*(B-A+.25*(J*(J+1.)-K*K-2.*K-2.)*V
2 +.5*(K*K+2.*K+2.)*S)
F7(J)=J*(J+1.)*SQRTE((J*(J+1.)-2.)*(J*(J+1.)-6.))
0 F8(J,K)=SQRTE((J*(J+1.)-K*(K+1.))*(J*(J+1.)-(K+1.)*(K+2.))*
1 (J*(J+1.)-(K+2.)*(K+3.))*(J*(J+1.)-(K+3.)*(K+4.)))
F9(J)=.25*W*SQRTE(.25*J*(J+1.)*(J*(J+1.)-2.))
F10(J,K)=.25*W*SQRTE((J*(J+1.)-K*(K+1.))*(J*(J+1.)-(K+1.)*(K+2.)))
C INPUT INSTRUCTIONS FOR PERTURBATION TERMS,,, G= -GZ AND W= -GX
READ 12,(A(I),R(I),CS(I),TAO(I),TAT(I),TAS(I),TAN(I),EN(I),HK(I)),
1 I=1,2),G,W,AEQ,BEQ,JRUN
12 FORMAT(3F15.7/4F10.7/F10.4,F15.12/3F15.7/4F10.7/F10.4,F15.12/
1 2F10.4/2F15.7,48X,12)
C ARITHMETIC STATEMENTS
RHO = 1.0E-06
IER=0
IOPT=0
CEQ=(AEQ*BEQ)/(AEQ+BEQ)
RS*BEQ**2/(AEQ+BEQ)**2
SS*AEQ**2/(AEQ+BEQ)**2
R1=RS*(TAO(1)+TAS(1))+SS*(TAT(1)+TAS(1))
R2=RS*(TAO(2)+TAS(2))+SS*(TAT(2)+TAS(2))
S1=TAS(1)*(RS-SS)+TAT(1)*SS-TAO(1)*RS
S2=TAS(2)*(RS-SS)+TAT(2)*SS-TAO(2)*RS
T1=2.*RS*SS*TAS(1)+RS**2*TAO(1)+SS**2*TAT(1)
T2=2.*RS*SS*TAS(2)+RS**2*TAO(2)+SS**2*TAT(2)
V1=TAT(1)-TAO(1)
V2=TAT(2)-TAO(2)
X1=TAT(1)+TAO(1)
X2=TAT(2)+TAO(2)
Y1= TAS(1)+2.*TAN(1)
Y2= TAS(2)+2.*TAN(2)
U1=(.5*X1-Y1)/32.
U2=(.5*X2-Y2)/32.

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PRINT 2000,A(1),B(1),CS(1),TAO(1),TAT(1),TAS(1),TAN(1),EN(1),HK(1)
2000 FORMAT(//*(110) BAND PARAMETERS*/
 1 *A(V1)=*F15.7*   B(V1)=*F15.7*   CS(V1)=*F15.7/
 2*TAAAAA=*F10.7*   TB BBBB=*F10.7*   TAABB=*F10.7*   TABAB=*F10.7/
 3 *(110) BAND CENTER =*F10.4/*HK1=*F15.12//)
 PRINT 2001,A(2),B(2),CS(2),TAO(2),TAT(2),TAS(2),TAN(2),EN(2),HK(2)
2001 FORMAT(//*(011) BAND PARAMETERS*/
 1 *A(V2)=*F15.7*   B(V2)=*F15.7*   CS(V2)=*F15.7/
 2*TAAAAA=*F10.7*   TB BBBB=*F10.7*   TAABB=*F10.7*   TABAB=*F10.7/
 3 *(011) BAND CENTER =*F10.4/*HK2=*F15.12//)
 PRINT 2002,G,W
2002 FORMAT(//*PERTURBATION COEFFICIENTS*/ *G=*F10.4/***=*F10.4/)
 PRINT 2003,AEQ,BEQ,CEQ
2003 FORMAT(//*EQUILIBRIUM CONSTANTS USED IN O.U. MATRIX ELEMENTS*/
 1 *AEQ=*F15.7/*REQ=*F15.7/*CEO=*F15.7//)
 DO 11 J= 1,JRUN
 NTMS=0
200 NTMS=NTMS+1
REWIND 51
GO TO (201,202),NTMS
201 DO 13 L=1,21
 DO 13 M=1,21
 EPV2(L,M)=0,0
13 EPV1(L,M)=0,0
 DO 113 L=1,20
 DO 113 M=1,20
 OPV1(L,M)=0,0
113 OPV2(L,M)=0,0
 GO TO 203
202 READ TAPE 51,EPV1,EPV2,OPV1,OPV2
C MATRIX FOR EVP1PLUS+EVP2MINUS AND EVP2PLUS+EVP1MINUS
203 KMAX =J/2+1
 KMIN = KMAX + 1
 JEND = 2*(J/2 + 1)-1
 GO TO (5,6,6,7),J
 7 IF (NTMS,EQ,2) GO TO 249
 EPV1 (1,3) = F5(J)*U1
 EPV2(1,3)=F5(J)*U2
 6 IF (NTMS,EQ,2) GO TO 249
 EPV1 (1,2) = F4( A(1), B(1), J,V1,S1)
 EPV2(1,2)=F4(A(2),B(2),J,V2,S2)
 GO TO 5
249 CONTINUE
 EPV1(1,KMIN) = (0.,-1.)*F9(J)
 EPV2(1,KMIN)=EPV1(1,KMIN)
 GO TO 250
 5 IF (NTMS,EQ,2) GO TO 250
 EPV1(1,1)=F1(A(1),B(1),CS(1),EN(1),TAN(1),R1,Y1,T1,X1,HK(1),J,0)
 EPV2(1,1)=F1(A(2),B(2),CS(2),EN(2),TAN(2),R2,Y2,T2,X2,HK(2),J,0)
250 CONTINUE
 DO 1 K= 2, KMAX
 KK = 2*(K-1)

```

```

KM = KMAX + K - 1
GO TO (2,3,4), (KMIN-K)
4 IF (NTMS,EQ,2) GO TO 251
EPV1 (K,K+2) = F8(J,KK)*U1
EPV2 (K,K+2) = F8(J,KK)*U2
EPV1 (KM, KMIN + K) = F8 (J,KK)*U2
EPV2 (KM, KMIN + K) = F8 (J,KK)*U1
3 IF (NTMS,EQ,2) GO TO 251
EPV1 (K,K+1) = F6 ( A(1), B(1), J, KK ,V1,S1)
EPV2(K,K+1)=F6(A(2),B(2),J,KK,V2,S2)
EPV1 (KM, KMAX + K) = F6 ( A(2), B(2), J, KK,V2,S2)
EPV2(KM,KMAX+K)=F6(A(1),B(1),J,KK,V1,S1)
GO TO 2
251 CONTINUE
EPV1 ( K, KMAX + K ) = (0.,-1.) *F10 ( J, KK )
EPV2(K,KMAX+K)=EPV1(K,KMAX+K)
EPV1 ( K+1 , KM ) = (0., , 1.) * F10( J, KK )
EPV2(K+1,KM)=EPV1(K+1,KM)
2 IF (NTMS,EQ,2) GO TO 252
IF(KK,EQ,2) EPV1(K,K)=F1(A(1),B(1),CS(1),EN(1),TAN(1),R1,Y1,T1,
1 X1, HK(1),J,KK) +F3(J)*U1
IF(KK,NE,2) EPV1(K,K)=F1(A(1),B(1),CS(1),EN(1),TAN(1),R1,Y1,T1,
1 X1, HK(1),J,KK)
IF(KK,EQ,2)EPV2(K,K)=F1(A(2),B(2),CS(2),EN(2),TAN(2),R2,Y2,T2,X2,
1 HK(2),J,KK) +F3(J)*U2
IF(KK,NE,2)EPV2(K,K)=F1(A(2),B(2),CS(2),EN(2),TAN(2),R2,Y2,T2,X2,
1 HK(2),J,KK)
IF(KK,EQ,2) EPV1(KM,KM)=F1(A(2),B(2),CS(2),EN(2),TAN(2),R2,Y2,T2,
1 X2, HK(2),J,KK) +F3(J)*U2
IF(KK,NE,2) EPV1(KM,KM)=F1(A(2),B(2),CS(2),EN(2),TAN(2),R2,Y2,T2,
1 X2, HK(2),J,KK)
IF(KK,EQ,2)EPV2(KM,KM)=F1(A(1),B(1),CS(1),EN(1),TAN(1),R1,Y1,T1,
1 X1, HK(1),J,KK) -F3(J)*U1
IF(KK,NE,2)EPV2(KM,KM)=F1(A(1),B(1),CS(1),EN(1),TAN(1),R1,Y1,T1,
1 X1, HK(1),J,KK)
GO TO 1
252 CONTINUE
EPV1 (K, KM) = (0.,1.) *G*KK
EPV2(K,KM)=EPV1(K,KM)
1 CONTINUE
C MATRIX FOR OV1PLUS+OV2MINUS AND OV1MINUS+OV2PLUS
KIX=(J+1)/2
IMD=2*KIX
DO 101 K=1,KIX
KAT=KIX*K
KO=2*K-1
GO TO (102,103,104),(KIX+1-K)
104 IF (NTMS,EQ,2) GO TO 261
OPV1(K,K+2)=F8(J,KU)*U1
OPV1(KAT,KAT+2)=F8(J,KO) *U2
OPV2(K,K+2)=F8(J,KU) *U2
OPV2(KAT,KAT+2)=F8(J,KO) *U1

```

```

103 IF (NTMS,EQ,2) GO TO 261
  IF(KO,EQ,1) OPV1(K,K+1)=F6(A(1),B(1),J,K0,V1,S1)*F7(J)*U1
  IF(KO,NE,1) OPV1(K,K+1)=F6(A(1),B(1),J,K0,V1,S1)
  IF(KO,FQ,1)OPV1(KAT,KAT+1)=F6(A(2),B(2),J,K0,V2,S2)-F7(J)*U2
  IF(KO,NE,1)OPV1(KAT,KAT+1)=F6(A(2),B(2),J,K0,V2,S2)
  IF(KO,FQ,1)OPV2(K,K+1)=F6(A(2),B(2),J,K0,V2,S2)+F7(J)*U2
  IF(KO,NE,1)OPV2(K,K+1)=F6(A(2),B(2),J,K0,V2,S2)
  IF(KO,EQ,1)OPV2(KAT,KAT+1)=F6(A(1),B(1),J,K0,V1,S1)-F7(J)*U1
  IF(KO,NE,1)OPV2(KAT,KAT+1)=F6(A(1),B(1),J,K0,V1,S1)
  GO TO 102
261 CONTINUE
  OPV1(K,KAT+1)=(0.,-1.)*F10(J,K0)
  OPV1(K+1,KAT)=-OPV1(K,KAT+1)
  OPV2(K,KAT+1)=OPV1(K,KAT+1)
  OPV2(K+1,KAT)=-OPV1(K,KAT+1)
102 IF (NTMS,EQ,2) GO TO 262
  OIF(KO,EQ,1)OPV1(K,K)=F1(A(1),B(1),CS(1),EN(1),TAN(1),R1,Y1,T1,
  1 X1,HK(1),J,K0)+F2(A(1),B(1),J,V1,S1)
  OIF(KO,NE,1)OPV1(K,K)=F1(A(1),B(1),CS(1),EN(1),TAN(1),R1,Y1,T1,
  1 X1,HK(1),J,K0)
  OIF(KO,EQ,1)OPV1(KAT,KAT)=F1(A(2),B(2),CS(2),EN(2),TAN(2),R2,Y2,
  1 T2,X2,HK(2),J,K0)+ F2(A(2),B(2),J,V2,S2)
  OIF(KO,NE,1)OPV1(KAT,KAT)=F1(A(2),B(2),CS(2),EN(2),TAN(2),R2,Y2,
  1 T2,X2,HK(2),J,K0)
  IF(KO,EQ,1)OPV2(K,K)=F1(A(2),B(2),CS(2),EN(2),TAN(2),R2,Y2,T2,X2,
  1 HK(2),J,<0)+F2(A(2),B(2),J,V2,S2)
  IF(KO,NE,1)OPV2(K,K)=F1(A(2),B(2),CS(2),EN(2),TAN(2),R2,Y2,T2,X2,
  1 HK(2),J,<0)
  OIF(KO,EQ,1)OPV2(KAT,KAT)=F1(A(1),B(1),CS(1),EN(1),TAN(1),R1,Y1,
  1 T1,X1,HK(1),J,K0) -F2(A(1),B(1),J,V1,S1)
  OIF(KO,NE,1)OPV2(KAT,KAT)=F1(A(1),B(1),CS(1),EN(1),TAN(1),R1,Y1,
  1 T1,X1,HK(1),J,K0)
  GO TO 101
262 CONTINUE
  IF(KO,FQ,1)OPV1(K,KAT)=(0.,1.)*(G*K0+.25*W*J*(J+1))
  IF(KO,NE,1)OPV1(K,KAT)=(0.,1.)*(G*K0)
  IF(KO,EQ,1)OPV2(K,KAT)=(0.,-1.)*(G*K0+.25*W*J*(J+1))
  IF(KO,NE,1)OPV2(K,KAT)=(0.,-1.)*(G*K0)
101 CONTINUE
C FORMING HERMITIAN CONJUGATES OF EPV1,EPV2,OPV1,OPV2
  DO 9 N=1,JEMD
    IN=N+1
    DO 9 M=IN,JEMD
      EPV2(M,N)=CONJG(EPV2(N,M))
9   FPV1(M,N)=CONJG(EPV1(N,M))
    DO 109 N=1,IMD
      IN=N+1
      DO 109 M=IN,IMD
        OPV2(M,N)=CONJG(OPV2(N,M))
109  OPV1(M,N)=CONJG(OPV1(N,M))
C ALL MATRIX ELEMENTS HAVE BEEN FORMED AT THIS POINT
  IF (NTMS,EQ,1) 270,280

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270 WRITE TAPE 51,EPV1,EPV2,OPV1,OPV2
280 CONTINUE
C EIGENVALUES ARE FOUND IN THIS SECTION
  CALL JHERMX (EPV1,21,JEMD)
  CALL JHERMX (EPV2,21,JEMD)
  CALL JHERMX (OPV1,20,IMD)
  CALL JHERMX (OPV2,20,IMD)
C STORING EIGENVALUES IN E(NCOL,NTMS)
  NCOL=0
  DO 301 I=1,JEMD
    NCOL=NCOL+1
  301 E(NCOL,NTMS)=EPV1(1,I)
    DO 302 I=1,JEMD
      NCOL=NCOL+1
  302 E(NCOL,NTMS)=EPV2(1,I)
    DO 303 I=1,IMD
      NCOL=NCOL+1
  303 E(NCOL,NTMS)=OPV1(1,I)
    DO 304 I=1,IMD
      NCOL=NCOL+1
  304 E(NCOL,NTMS)=OPV2(1,I)
    GO TO (200,311),NTMS
  311 CONTINUE
C PRINTING EIGENVALUES WITH J,K+,K- LABELS
  PRINT 312,J,J
  3120FORMAT(//*(110) STATE FOR J= *I3* V1 OR B BAND*22X
  1*(011) STATE FOR J= *I3* V2 OR A BAND*/*
  22(* J K- <**4X*UNPERTURBED COR,PERTURBED COR=UNP*11X))
  IMIN5=JEMD
  DO 313 I=1,KMAX
    KPLUS=2*(I-1)
    TAUP=J-2*KPLUS
    KMINUS = TAUP+KPLUS
    E(I,3)=E(I,2)-E(I,1)
    IMIN5=IMIN5+1
    E(IMIN5,3)=E(IMIN5,2)-E(IMIN5,1)
    PRINT 314,J,KMINUS,KPLUS,(E(I,K),K=1,3),J,KMINUS,KPLUS,
    1(E(IMIN5,K),K=1,3)
  314 FORMAT(2(3I3,2F15.4,F8.3,10X))
  313 CONTINUE
  IMIN4=KMAX
  IMIN1=JEMD+KMAX+1
  IMAX1=2*JEMD
  DO 320 I=IMIN1,IMAX1
    KPLUS=2*(I-JEMD-KMAX)
    TAUP=J-2*KPLUS+1
    KMINUS = TAUP+KPLUS
    E(I,3)=E(I,2)-E(I,1)
    IMIN4=IMIN4+1
    E(IMIN4,3)=E(IMIN4,2)-E(IMIN4,1)
    PRINT 314,J,KMINUS,KPLUS,(E(I,K),K=1,3),J,KMINUS,KPLUS,
    1(E(IMIN4,K),K=1,3)

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```

320 CONTINUE
IMIN7=2*JEMD+IMD
IMIN2=2*JEMD+1
IMAX2=2*JEMD+KIX
DO 330 I=IMIN2,IMAX2
KPLUS=2*(I-2*JEMD)+1
TAUP=J-2*KPLUS
KMINUS = TAUP+KPLUS
E(I,3)=E(I,2)-F(I,1)
IMIN7=IMIN7+1
E(IMIN7,3)=E(IMIN7,2)-E(IMIN7,1)
PRINT 314,J,KMINUS,KPLUS,(E(I,K),K=1,3),J,KMINUS,KPLUS,
1(E(IMIN7,K),K=1,3)
330 CONTINUE
IMIN6=2*JEMD+KIX
IMIN3=2*JEMD+IMD+KIX+1
IMAX3=2*(2*J+1)
DO 340 I=IMIN3,IMAX3
KPLUS=2*(I-(2*JEMD+IMD+KIX))+1
TAUP=J-2*KPLUS+1
KMINUS = TAUP+KPLUS
E(I,3)=E(I,2)-F(I,1)
IMIN6=IMIN6+1
E(IMIN6,3)=E(IMIN6,2)-E(IMIN6,1)
PRINT 314,J,KMINUS,KPLUS,(E(I,K),K=1,3),J,KMINUS,KPLUS,
1(E(IMIN6,K),K=1,3)
340 CONTINUE
11 CONTINUE
END
SUBROUTINE JHERMX(A,NM,N)
COMMON IOPT,RHO,IER
DIMENSION A(NM,NM), S(21,21)
COMPLEX A, S, V1, V2, V3, CSNT, SNT, TEMP
IOC = 0
IER = 0
FP12=0.000000000001
FN = FLOAT(N)
DO 1 I=1,N
DO 1 J=1,N
S(I,J) = (0,0,0,0)
IF(I,EQ,J)S(I,J) =(1.0,0.0)
1 CONTINUE
IF(N,LE,1)GO TO 12
SOFFD = 0,0
NM1 = N-1
DO 2 I=1,NM1
IJ = I+1
DO 2 J=IJ,N
X1=A(I,J)
X2=A(I,J)*(0.0,-1.0)
2 SOFFD=SOFFD+2,0*(X1*X1+X2*X2)
IF(SOFFD ,_T. 0,1E-10)GO TO 12

```

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THR = SQRTF(SOFFD)
FTHR = RHO*THR / EN
IND = 0
3 THR = THR / EN
4 DO 10 L=2,N
  LM1 = L-1
  DO 10 K=1,LM1
    X1=A(L,K)
    X2=A(L,K)*(0.0,1.0)
    IF(SQRT(X1*X1+X2*X2).LT,THR) GO TO 10
    IND = 1
    V1 = A(K,K)
    V2 = CONJG( A(L,K) )
    V3 = A(L,L)
    C = -AIMAG( A(L,K) )
    B = REAL( A(L,K) )
    E = REAL( A(L,L) )
    D = REAL( A(K,K) )
    THFT = 0.0
    IF(ABSF(C).LT, EPI2)GO TO 13
    THET = 1.5707963
    IF(ABSF(B).LT, EPI2)GO TO 13
    T = C / B
    THFT = ATANF(T)
13 CONTINUE
  PHI = 0.78539818
  ED = ABSF(E-D)
  IF(ED .LT, EPI2)GO TO 15
  TAO = 2.0*(B*COSF(THET) + C*SINF(THET)) / (E-D)
  PHI = 0.5 * ATANF(TAO)
15 CONTINUE
  CSNT = COSF(PHI) + (0.0,0.0)
  CS = COSF(THET) * SINF(PHI)
  SS = SINF(THET) * SINF(PHI)
  SNT = CS + (0.0,1.0) * SS
  DO 8 I=1,N
    TEMP = A(I,K)*CSNT - A(I,L)*CONJG(SNT)
    A(I,L) = A(I,K)*SNT + A(I,L)*CSNT
    A(I,K) = TEMP
    IF(IOPT .EQ, 0)GO TO 8
    TEMP = S(I,K)*CSNT - S(I,L)*CONJG(SNT)
    S(I,L) = S(I,K)*SNT + S(I,L)*CSNT
    S(I,K) = TEMP
8 CONTINUE
  DO 9 I=1,N
    A(K,I) = CONJG( A(I,K) )
    A(L,I) = CONJG( A(I,L) )
9 CONTINUE
  A(K,K) = SVT*CONJG(SNT)*V3 + CSNT*CSNT*V1-SNT*CSVT*CONJG(V2)
1 = CSNT*CONJG(SNT)*V2
  A(L,L) = CSNT*CSNT*V3 + CONJG(SNT)*SNT*V1 + SNT*CSNT*
2 CONJG(V2) + CONJG(SNT)*CSNT*V2

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```
A(K,L) = CSNT★CSNT★V2 - SNT★SNT★CONJG(V2) + CSNT★SNT★V1
1  =CSNT★SNT★V3
A(L,K) = CONJG( A(K,L) )
10 CONTINUE
IOC = IOC + 1
IF(IOC ,GE, 100)GO TO 21
IF(IND ,LE, 0)GO TO 11
IND = 0
GO TO 4
11 IF(THR-FTHR)12,12,5
12 RETURN
21 IER = 1
RETURN
END
```

APPENDIX XII

GROUND STATE COMBINATION DIFFERENCES OF  $H_2^{3\ 2}S$

## GROUND STATE COMBINATION DIFFERENCES

I	K-	K+	J	K-	K+	OBSERVED	OBS-CALC	WEIGHT	
2	2	0	-	2	0	2	20.353	0.000	1.76
2	2	1	-	1	0	1	41.415	0.001	4.44
2	1	1	-	1	1	1	36.051	0.002	1.50
2	1	2	-	1	1	0	18.024	0.003	1.87
2	2	0	-	0	0	0	59.372	0.005	0.23
2	3	0	-	3	1	2	22.341	0.005	9.83
2	3	0	-	1	1	0	98.019	0.004	4.46
2	3	1	-	2	1	1	64.200	0.001	3.70
2	2	1	-	2	2	1	52.206	-0.000	7.08
2	2	1	-	3	0	3	35.947	0.003	6.18
2	2	1	-	1	0	1	93.621	0.001	4.98
2	2	2	-	2	2	0	38.026	0.004	5.48
2	2	2	-	2	0	2	58.379	0.005	0.76
2	1	2	-	2	1	2	56.760	0.002	7.92
2	1	3	-	1	1	1	56.373	0.000	5.69
2	0	3	-	1	0	1	57.674	-0.001	5.02
2	0	3	-	2	2	1	16.258	-0.004	7.45
2	3	1	-	3	1	3	43.879	0.003	0.12
2	3	1	-	1	1	1	100.248	-0.000	0.84
2	1	2	-	1	1	0	75.682	0.003	1.81
2	1	3	-	2	1	1	20.323	-0.001	6.20
2	3	0	-	2	1	2	79.092	-0.002	0.61
4	4	0	-	4	2	2	26.468	0.002	3.24
4	4	0	-	2	2	0	138.433	0.000	0.40
4	4	1	-	4	2	3	47.240	-0.005	3.89
4	4	1	-	3	2	1	88.292	-0.001	3.33
4	1	4	-	2	2	1	140.495	-0.004	2.66
4	3	1	-	3	3	1	67.302	-0.006	2.69
4	3	1	-	4	1	3	34.508	-0.002	1.55
4	3	2	-	3	1	2	78.014	0.005	5.94
4	3	2	-	3	3	0	56.574	0.001	5.83
4	3	2	-	4	1	4	59.794	0.005	0.95
4	2	2	-	3	2	2	73.044	-0.001	4.40
4	2	2	-	2	2	0	111.955	-0.011	0.53
4	2	2	-	2	0	2	132.323	0.004	0.05
4	2	3	-	3	0	3	76.092	-0.000	7.38
4	2	3	-	3	2	1	41.048	0.000	9.73
4	2	3	-	2	2	1	93.257	0.003	7.19
4	1	3	-	2	1	1	97.001	0.003	1.33
4	1	4	-	2	1	2	75.876	-0.002	2.90
4	1	4	-	3	1	2	19.119	-0.001	3.18
4	0	4	-	3	2	2	17.763	-0.017	0.50
4	4	0	-	3	2	2	100.413	0.002	0.99
4	4	0	-	2	0	2	158.789	0.004	0.14
4	3	1	-	3	1	3	111.186	0.002	0.21

4	0	4	-	2	0	2	76.157	0.003	0.04
4	3	1	-	2	1	1	131.509	0.001	0.45
4	4	2	-	4	0	4	56.164	-0.001	0.06
4	4	1	-	3	3	1	32.800	0.001	0.95
4	4	4	-	3	0	3	124.235	-0.002	0.76
4	4	3	-	2	1	2	135.666	-0.001	0.14
4	4	4	-	3	1	3	76.479	0.004	0.16
4	4	1	-	3	2	2	122.716	0.005	1.73
4	5	5	-	4	3	2	32.937	0.001	2.10
4	5	5	-	5	3	3	51.710	-0.002	0.24
4	5	5	-	4	3	1	113.454	0.000	1.38
4	5	4	-	3	0	3	205.914	-0.001	0.81
4	5	4	-	4	2	3	128.018	-0.005	6.89
4	5	4	-	5	2	3	33.093	-0.003	5.56
4	5	4	-	3	2	1	169.967	-0.003	1.02
4	5	4	-	4	4	1	81.678	0.001	5.24
4	5	4	-	4	4	0	74.303	0.000	2.70
4	5	4	-	4	2	2	100.774	0.005	1.02
4	5	3	-	3	1	2	168.688	0.004	2.34
4	5	3	-	3	3	0	146.344	-0.004	1.00
4	5	3	-	4	3	2	89.772	-0.003	8.59
4	5	3	-	5	1	4	53.521	-0.005	2.27
4	5	3	-	4	1	4	149.561	-0.003	0.51
4	5	3	-	4	1	3	96.254	0.002	6.55
4	5	3	-	4	3	1	61.743	0.001	3.89
4	5	2	-	3	0	3	171.920	0.001	1.08
4	5	2	-	5	0	5	77.001	0.001	1.50
4	5	2	-	3	2	1	135.975	0.000	2.40
4	5	2	-	4	2	3	94.925	-0.001	9.65
4	5	2	-	4	4	1	47.485	0.003	3.66
4	5	2	-	3	2	2	113.872	0.001	2.03
4	5	2	-	4	0	4	96.116	0.025	0.20
4	1	1	-	4	3	2	36.250	0.001	8.20
4	1	1	-	3	1	2	115.161	0.003	6.14
4	1	1	-	4	1	4	96.036	-0.002	0.96
4	0	0	-	3	0	3	94.014	-0.005	1.55
4	5	5	-	4	2	3	17.924	-0.003	3.99
4	5	5	-	3	3	0	179.286	0.002	4.56
4	5	5	-	3	3	1	180.771	0.009	0.38
4	4	4	-	5	2	4	60.846	0.003	1.21
4	4	4	-	3	2	2	174.714	0.000	0.18
4	4	4	-	4	0	4	156.035	0.001	0.02
4	3	3	-	3	1	3	172.032	0.006	0.18
4	3	3	-	5	1	5	78.048	0.001	0.13
4	2	2	-	4	2	2	39.929	0.003	2.13
4	1	5	-	4	1	3	18.209	0.005	0.04
4	5	1	-	4	1	3	147.061	-0.003	0.05
4	3	3	-	3	3	1	129.050	-0.000	0.22
4	5	1	-	5	3	3	147.493	-0.005	0.44
4	5	1	-	6	3	3	35.372	-0.002	1.10
4	5	1	-	5	5	1	95.788	0.002	0.66
4	5	2	-	5	5	0	91.209	-0.000	5.32

5	2	-	4	3	2	213.922	0.002	1.56
5	2	-	6	3	4	62.737	-0.003	3.16
4	2	-	5	4	2	104.325	-0.001	3.98
4	3	-	5	2	3	116.026	0.003	9.41
3	3	-	5	3	3	112.122	-0.003	1.91
3	3	-	5	5	1	60.418	0.005	0.27
3	4	-	4	3	2	151.185	0.006	2.02
3	4	-	5	3	2	61.408	0.003	2.89
3	4	-	5	1	4	114.927	-0.003	2.02
3	4	-	4	1	4	210.972	0.003	0.28
2	4	-	4	2	2	154.584	0.003	0.86
2	4	-	5	4	2	53.806	-0.005	0.14
2	5	-	5	2	3	38.260	0.003	2.21
2	5	-	5	0	5	115.255	-0.002	1.93
2	5	-	4	2	3	133.182	-0.002	1.18
1	6	-	4	1	4	113.765	-0.005	2.47
6	0	-	4	4	0	220.051	0.020	0.27
6	0	-	5	4	2	145.740	0.012	0.21
6	1	-	5	4	1	139.239	0.015	3.04
6	1	-	4	4	1	220.017	0.016	0.39
6	1	-	6	4	3	57.207	0.011	0.92
4	3	-	4	2	3	210.950	0.000	3.26
3	3	-	6	1	5	74.927	0.004	0.12
3	4	-	6	1	6	97.194	-0.005	0.08
2	4	-	5	2	4	114.656	0.001	0.20
2	4	-	4	0	4	210.749	0.003	0.06
1	5	-	4	1	3	133.459	0.006	0.16
1	5	-	5	3	3	37.205	0.003	0.59
1	5	-	5	1	5	115.252	0.003	0.13
5	1	-	4	3	1	209.224	-0.016	0.10
5	1	-	4	1	3	243.734	-0.016	0.04
5	2	-	5	3	2	124.147	0.002	1.38
4	2	-	6	2	4	50.512	-0.003	0.70
4	2	-	4	2	2	205.096	0.000	0.17
4	2	-	5	2	4	165.170	0.000	0.15
4	3	-	6	2	5	77.762	-0.004	0.20
4	3	-	4	4	1	163.708	0.003	1.64
3	3	-	4	3	1	173.862	-0.004	0.26
3	3	-	4	1	3	208.373	-0.003	0.05
4	2	-	4	4	0	178.629	-0.000	2.10
4	3	-	5	0	5	193.027	0.004	0.12
1	5	-	5	1	4	17.726	-0.006	0.57
4	3	-	5	4	1	82.032	0.005	6.39
6	1	-	7	4	3	39.424	0.003	2.64
6	1	-	6	4	3	167.293	0.010	2.11
5	2	-	5	5	0	209.083	0.008	4.73
5	2	-	5	3	2	242.017	0.006	0.90
5	2	-	6	5	2	117.874	0.008	1.37
5	2	-	6	3	4	180.613	0.007	3.13
5	3	-	5	3	3	248.974	-0.004	0.32
5	3	-	5	5	1	197.272	0.006	0.10
5	3	-	6	3	3	136.852	-0.001	1.08

7	5	3	-	6	5	1	101.479	-0.001	1.40
7	4	3	-	7	2	5	71.758	0.007	1.19
7	4	3	-	5	4	1	209.901	0.011	1.43
7	4	3	-	6	4	3	127.868	0.006	3.25
7	4	4	-	5	4	2	187.551	-0.012	0.31
7	4	3	-	5	2	3	243.892	0.006	1.84
7	3	4	-	6	3	4	132.734	0.001	5.35
7	3	4	-	7	1	6	95.528	0.002	1.44
7	3	4	-	5	3	2	194.139	0.001	2.84
7	3	4	-	5	1	4	247.656	-0.007	0.60
7	2	5	-	5	0	5	249.138	0.003	0.34
7	2	5	-	6	2	5	133.880	0.003	3.39
7	2	5	-	5	2	3	172.138	0.004	3.58
7	2	5	-	6	4	3	56.109	-0.002	1.98
7	1	5	-	5	1	4	152.131	-0.006	2.82
7	1	5	-	6	1	6	134.408	0.003	1.31
7	1	5	-	6	3	4	37.209	0.002	2.55
7	0	7	-	5	0	5	132.420	-0.012	1.60
7	6	1	-	5	4	1	249.322	0.011	0.19
7	6	1	-	6	6	1	110.079	-0.008	0.79
7	6	2	-	6	4	2	148.916	0.007	0.62
7	5	2	-	7	3	4	47.879	0.006	3.62
7	4	3	-	6	6	1	70.659	-0.007	0.19
7	4	3	-	6	2	5	205.627	-0.001	0.10
7	4	4	-	6	4	2	83.240	0.003	1.07
7	4	4	-	6	2	4	133.752	0.000	1.65
7	4	4	-	5	2	4	248.407	0.001	0.15
7	4	4	-	7	2	6	96.312	-0.003	0.05
7	3	4	-	6	5	2	69.996	0.003	3.48
7	3	4	-	6	1	6	229.930	-0.002	0.10
7	3	5	-	6	3	3	59.007	0.000	0.31
7	3	5	-	6	1	5	133.931	0.001	0.77
7	2	5	-	6	2	4	37.437	0.001	0.04
7	0	7	-	6	2	5	17.373	-0.002	2.97
7	7	0	-	7	5	2	51.264	0.037	0.54
7	6	2	-	6	6	0	107.500	-0.008	0.10
7	6	2	-	5	4	2	253.239	0.003	0.06
7	6	2	-	7	4	4	65.674	0.001	0.15
7	5	3	-	6	1	5	211.777	0.001	0.04
7	4	3	-	5	0	5	320.899	0.013	0.03
7	3	5	-	5	1	5	249.183	0.004	0.12
7	2	5	-	7	0	7	116.512	0.010	1.66
7	3	5	-	5	3	3	171.135	0.003	1.79
7	5	3	-	7	3	5	77.848	0.001	0.04
8	6	3	-	6	4	3	287.091	0.004	1.51
8	6	3	-	7	6	1	119.797	-0.006	1.33
8	5	4	-	6	5	2	222.844	0.011	0.47
8	5	4	-	7	5	2	104.961	-0.006	0.37
8	5	4	-	7	3	4	152.847	0.007	2.71
8	4	4	-	6	3	4	285.581	0.008	0.44
8	4	4	-	7	4	4	149.885	0.005	1.78
8	4	5	-	8	2	7	115.388	0.006	0.76

2	4	5	-	6	4	3	208.512	-0.003	1.28
2	4	5	-	7	4	3	80.634	-0.019	0.68
2	4	5	-	7	2	5	152.399	-0.005	1.42
2	3	6	-	6	3	4	190.148	-0.008	1.14
2	3	6	-	7	3	4	57.415	-0.008	1.54
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2	3	6	-	8	1	8	135.889	0.006	0.30
2	2	7	-	7	0	7	153.521	-0.003	2.22
2	2	7	-	6	2	5	170.896	-0.003	7.48
2	2	7	-	7	2	5	37.017	-0.005	2.37
1	1	8	-	7	1	6	17.058	-0.008	4.18
1	1	8	-	6	1	6	151.449	-0.023	0.54
8	8	0	-	6	6	0	299.932	-0.009	0.12
7	7	2	-	6	5	2	292.582	0.027	0.31
6	6	2	-	8	4	4	46.430	0.006	0.13
6	6	2	-	7	4	4	196.524	0.019	0.17
6	6	3	-	8	4	5	78.574	0.003	0.70
6	6	3	-	7	2	5	230.981	0.006	0.97
5	5	3	-	7	5	3	142.039	0.031	0.24
5	5	4	-	7	1	6	248.372	0.005	0.25
4	4	4	-	8	2	6	93.267	0.011	0.09
4	4	4	-	7	2	6	246.210	0.014	0.03
3	3	5	-	6	3	3	211.177	-0.003	0.40
3	3	5	-	7	3	5	152.170	-0.003	0.07
3	3	5	-	6	1	5	286.105	0.002	0.08
3	3	6	-	6	1	6	287.351	-0.004	0.08
2	2	6	-	6	2	4	190.370	-0.006	0.04
2	2	6	-	7	4	4	56.422	-0.002	0.11
2	2	6	-	7	2	6	152.934	-0.006	0.05
7	7	1	-	7	7	1	124.780	-0.027	0.11
7	7	1	-	6	5	1	289.787	0.014	0.06
7	7	2	-	7	7	0	123.434	-0.028	0.26
7	7	2	-	7	5	2	174.704	0.015	0.46
6	6	2	-	7	6	2	130.848	0.016	0.15
6	6	2	-	6	4	2	279.762	0.021	0.07
6	6	3	-	6	6	1	229.882	-0.008	0.68
5	5	3	-	8	3	5	67.706	0.024	0.03
5	5	3	-	7	3	5	219.885	0.030	0.03
4	4	4	-	6	4	2	233.130	0.013	0.16
4	4	4	-	7	6	2	84.220	0.013	0.14
4	4	5	-	6	2	5	286.282	0.001	0.27
3	3	5	-	7	5	3	74.332	0.005	0.12
6	6	3	-	7	4	3	159.226	0.002	1.55
5	5	4	-	8	3	6	95.425	0.008	0.75
4	4	5	-	7	4	3	250.625	0.017	3.92
4	4	5	-	8	6	3	91.402	0.018	1.76
3	3	6	-	8	3	6	171.198	0.010	0.58
3	3	6	-	8	5	4	75.761	-0.010	0.69
3	3	6	-	9	1	8	134.466	0.002	0.14
2	2	7	-	8	2	7	228.411	-0.000	1.45
2	2	7	-	7	2	5	171.919	-0.005	3.20
2	2	7	-	7	2	5	208.044	-0.002	0.78

2	2	7	-	8	4	5	56.533	-0.009	1.16
2	1	8	-	8	3	6	36.723	-0.001	2.44
2	1	8	-	8	1	8	172.409	0.002	1.97
2	1	8	-	7	1	6	189.663	-0.010	4.58
2	0	9	-	7	0	7	170.269	-0.018	3.03
2	0	9	-	8	2	7	16.753	-0.010	1.46
2	5	5	-	8	3	5	170.771	0.015	0.11
2	4	5	-	8	4	5	169.977	0.021	0.19
2	4	5	-	9	2	7	113.446	0.032	0.12
2	4	6	-	7	4	4	227.862	-0.000	0.21
2	4	6	-	8	4	4	77.976	-0.006	0.21
2	4	6	-	8	2	6	171.241	0.003	0.07
2	4	6	-	7	2	6	324.179	0.001	0.02
2	3	6	-	7	1	6	324.142	0.004	0.14
2	7	3	-	7	7	1	261.795	-0.017	0.03
2	7	3	-	8	7	1	137.014	0.009	0.06
2	6	4	-	7	6	2	256.932	0.034	0.05
2	6	4	-	8	6	2	126.075	0.009	0.11
2	6	4	-	8	4	4	172.700	0.009	0.09
2	6	4	-	7	4	4	322.600	0.029	0.11
2	6	4	-	9	4	6	94.726	0.017	0.02
2	5	4	-	7	5	2	270.562	0.005	0.06
2	5	4	-	8	7	2	95.857	-0.011	0.05
2	5	5	-	7	5	3	245.095	0.012	0.10
2	5	5	-	8	5	3	103.058	-0.016	0.05
2	5	5	-	7	3	5	322.943	0.014	0.03
2	4	5	-	7	2	5	322.383	0.024	0.68
2	2	7	-	9	0	9	155.165	0.004	0.22
11	4	7	-	9	4	5	76.613	-0.022	0.39
11	4	7	-	9	2	7	190.053	0.004	0.65
11	4	7	-	8	4	5	246.590	-0.001	2.38
11	3	8	-	8	3	6	227.561	-0.011	1.18
11	3	8	-	9	3	6	56.359	-0.024	0.22
11	3	8	-	9	1	8	190.838	-0.010	1.06
11	2	9	-	8	2	7	208.407	-0.008	4.90
11	2	9	-	9	2	7	36.487	-0.004	2.24
11	1	10	-	8	1	8	189.068	-0.005	5.08
11	3	8	-	10	1	10	174.380	-0.001	0.10
11	2	9	-	9	0	9	191.652	-0.000	1.28
11	6	5	-	8	6	3	280.559	-0.025	0.06
11	5	6	-	9	3	6	189.298	0.028	0.23
11	1	10	-	9	1	8	16.461	-0.006	0.87
11	3	8	-	10	3	8	208.791	0.004	0.09
11	2	9	-	10	4	7	56.133	-0.022	0.31
11	2	9	-	9	2	7	246.183	-0.021	0.36
11	1	10	-	9	1	8	227.118	-0.007	4.56
11	0	11	-	9	0	9	207.828	0.005	2.44
11	2	9	-	10	2	9	209.696	-0.017	0.68
11	1	10	-	10	3	8	36.280	0.003	0.25
11	5	6	-	10	5	6	206.416	-0.015	0.04
11	2	9	-	11	0	11	193.526	-0.016	0.04

11	0	11	-	10	2	9	16.174	0.003	0.27
11	3	8	-	9	3	6	265.152	-0.019	0.03
12	3	10	-	10	3	8	264.775	-0.021	0.20
12	1	12	-	10	1	10	226.562	0.032	1.88
12	4	9	-	10	4	7	283.594	-0.015	0.22
12	4	9	-	11	2	9	227.461	0.008	0.14
12	2	11	-	10	2	9	245.794	-0.001	2.16
12	2	11	-	11	2	9	36.088	0.006	0.10
12	3	10	-	11	1	10	228.493	-0.026	0.06
12	2	11	-	11	0	11	229.620	-0.004	0.26
13	1	12	-	11	1	10	264.440	0.023	0.54
13	3	10	-	11	3	8	302.024	-0.022	0.04

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