ANALYSIS OF ASYMMETRIC ROTOR MOLECULAR SPECTRA AND DATA ACQUISITION AND TREATMENT BY A MINICOMPUTER

Thesis for the Degree of Ph. D.

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PAUL DANIEL WILLSON

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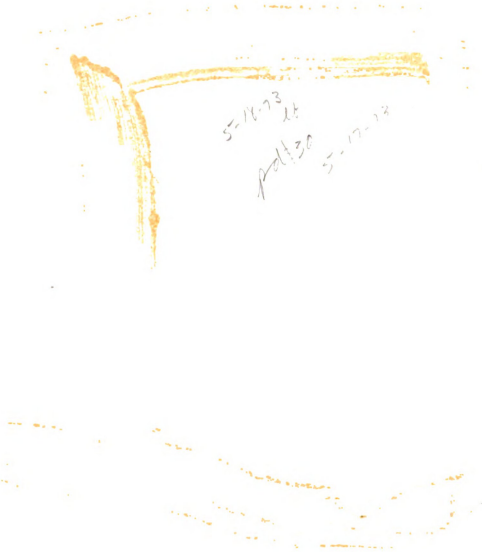

ABSTRACT

ANALYSIS OF ASYMMETRIC ROTOR
MOLECULAR SPECTRA
AND
DATA ACQUISITION AND TREATMENT
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The various Hamiltonians now available for calculating the vibration-rotation energy levels of asymmetric rotor molecules are compared and their application is outlined. The means of forming "reduced" Hamiltonians and the restrictions on their use are briefly described. A means of fitting several molecular isotopes simultaneously is described.

Computer programs were written to apply the results of the above work to infrared spectra. Ground state combination differences from the $2\nu_1$ band of $HD^{130}Te$, which is a prolate XYZ molecule were fit to the planar Hamiltonian and to the KFC Hamiltonian to second-order with T_6 restrained to be zero. The Watson Hamiltonian to second-order was used to fit upper and ground states of the $2\nu_1$ band of the molecular species $HD^{130}Te$, $HD^{128}Te$, $HD^{126}Te$, $HD^{125}Te$, and $HD^{124}Te$ simultaneously. The planar

Hamiltonian was used to fit the upper states of the Coriolis coupled bands ν_1 and ν_3 of H_2S. The rotational and second-order constants and the perturbation constants required for the above fits are listed.

Also described in this work are methods and principles involved in the acquisition of spectral data, baseline adjusting, smoothing, and deconvolution by means of a minicomputer. A means of deconvolution based on successive approximations has been further developed and programmed on a minicomputer. The need for variable relaxation, normalization, and a point simultaneous method for the deconvolution process is explained. These methods of treating data were applied to several HDS and D_2S vibration-rotation bands. The results for the Q-branch of the $\nu_1+\nu_3$ band of HDS are shown.

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By

Paul Daniel Willson

A THESIS

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TO MY DAD

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I am very grateful to my wife and children who have daily loved and cared for me during this time. I am also grateful for the many people who have been praying for me and the completion of this work.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

In the last ten years a number of new developments have occurred in the theory for molecular asymmetric-top vibration-rotation Hamiltonians. This work includes a comparison of various Hamiltonians now available, especially in their application to the analysis of the vibration-rotation spectra obtained in our laboratory of nonlinear triatomic molecules.

During this same period the field of digital electronics has grown rapidly and is changing the tools available to the experimentalist. With the addition of a minicomputer to our laboratory, many means of data processing formerly prohibited could now be done. Therefore, much of this work has been devoted to the development of ways of digitally processing the raw spectral data, preparing it for measurement,viz. the application of digital methods to baseline adjusting, digital smoothing and deconvolution of high-resolution infrared spectra of molecules.

CHAPTER I

THE VIBRATION-ROTATION HAMILTONIAN

FOR AN ASYMMETRIC MOLECULE

In this study, we will be considering asymmetric-top triatomic molecules. In the past ten years many theoretical advances have been made in the Hamiltonian for such molecules. Let us begin with the general form of the vibration-rotation Hamiltonian as given by Chung and Parker[1] in 1963.

Second-Order Planar Hamiltonian

To second order of approximation their result is

$$\begin{aligned} H = h_v &+ XP_x^2 + YP_y^2 + ZP_z^2 + \tfrac{1}{4}\tau_{xxxx}P_x^4 + \tfrac{1}{4}\tau_{yyyy}P_y^4 + \tfrac{1}{4}\tau_{zzzz}P_z^4 \\ &+ \tfrac{1}{4}\tau_{yyzz}(P_y^2P_z^2 + P_z^2P_y^2) + \tfrac{1}{4}\tau_{xxzz}(P_x^2P_z^2 + P_z^2P_x^2) \\ &+ \tfrac{1}{4}\tau_{xxyy}(P_x^2P_y^2 + P_y^2P_x^2) + \tfrac{1}{4}\tau_{yzyz}(P_yP_z + P_zP_y)^2 \\ &+ \tfrac{1}{4}\tau_{xzxz}(P_xP_z + P_zP_x)^2 + \tfrac{1}{4}\tau_{xyxy}(P_xP_y + P_yP_x)^2 \end{aligned} \qquad (I\text{-}1)$$

where P_x, P_y, and P_z are components of the total angular momentum; h_v is essentially a constant for a given vibrational state; X, Y, and Z are the inverse moments of inertia, e.g. $X = h/8\pi^2cI_x$, where I_x is the principal moment of

inertia about the x axis; and the taus are centrifugal distortion constants. The Hamiltonian angular momentum operators will be evaluated in $\psi(J,K)$ space, where $\psi(J,K)$ arethe rigid symmetric rotor wave functions,such that

$$< J,K \mid P^2 \mid J,K > = J(J+1)$$

$$< J,K \mid P_z \mid J,K > = K$$

where $P^2 = P_x^2 + P_y^2 + P_z^2$ and $P_aP_b - P_bP_a = -iP_c$, with a,b,c and x,y,z being cyclic. Reductions of the Hamiltonian due to angular momentum commutation rules are based on the above space.

It is convenient to attach to the molecule a rectangular coordinate system along the molecular principal axes, (a,b,c), such that the molecule lies in the ab plane. Then using A_e, B_e, and C_e as the equilibrium inverse moments of inertia, it follows that $C_e = A_eB_e/(A_e+B_e)$, which implies that C_e will be less than A_e or B_e. The choice of $A_e > B_e$ then yields the conventional ordering $A_e > B_e > C_e$.

The above conditions led to the planarity relations as given by Dowling,[2] and by Oka and Morino.[3] These are a consequence of the molecule being planar and lying in the ab plane and are independent of the space the Hamiltonian is evaluated in. The relationscan be expressed by

$$(I^e_{cc}/I^e_{\alpha\alpha})^2\tau_{\alpha\alpha cc} = (I^e_{aa}/I^e_{\alpha\alpha})^2\tau_{\alpha\alpha aa} + (I^e_{bb}/I^e_{\alpha\alpha})^2\tau_{\alpha\alpha bb}$$

and

$$\tau_{acac} = \tau_{bcbc} = 0 \qquad \text{(I-2)}$$

where I^e_{aa}, I^e_{bb}, and I^e_{cc} are the equilibrium moments of inertia along the a, b, and c axes respectively and α may take on the values a,b, and c.

There are six possible ways the molecular axes (a,b,c) may be related to the body-fixed axes (x,y,z) which are listed in Table I. The Hamiltonian (I-1) may be evaluated in $\psi(J,K)$ space using any of the six ways or representations. But for a near symmetric-top molecule, two of them will yield diagonal matrix elements of the Hamiltonian which are close to the eigenvalues of that matrix. Since these two ways will be the most likely to diagonalize with small round-off error, one of them should normally be used. Therefore for a near prolate asymmetric-top we choose the so-called I^r representation (although I^ℓ would do as well);

Table I. Molecular Axes Identifications

Body-Fixed Axes	Molecular Axes					
x	b	c	c	a	a	b
y	c	b	a	c	b	a
z	a	a	b	b	c	c
Type	I^r	I^ℓ	II^r	II^ℓ	III^r	III^ℓ

and for a near oblate asymmetric-top, we use the III^r representation as found in Table I.

After choosing the representation,one may apply the planarity conditions as well as the commutation relation

$$(P_aP_b + P_bP_a)^2 = 2(P_a^2P_b^2 + P_b^2P_a^2) + 5P_c^2 - 2P^2$$

so that the Hamiltonian (I-1) simplifies to the planar form

$$H = h_v + AP_a^2 + BP_b^2 + CP_c^2 + \tau_{aaaa}O_{aaaa}$$
$$+\tau_{bbbb}O_{bbbb} + \tau_{aabb}O_{aabb} + \tau_{abab}O_{abab} \qquad (I-3)$$

where

$$O_{aaaa} = \tfrac{1}{4}[P_a^4 + r^2P_c^4 + r(P_a^2P_c^2 + P_c^2P_a^2)]$$
$$O_{bbbb} = \tfrac{1}{4}[P_b^4 + s^2P_c^4 + s(P_b^2P_c^2 + P_c^2P_b^2)]$$
$$O_{aabb} = \tfrac{1}{4}[2rsP_c^4 + (P_a^2P_b^2 + P_b^2P_a^2) + s(P_a^2P_c^2 + P_c^2P_a^2)$$
$$+ r(P_b^2P_c^2 + P_c^2P_b^2)]$$
$$O_{abab} = \tfrac{1}{4}[2(P_a^2P_b^2 + P_b^2P_a^2) - 2P^2 + 5P_c^2] \qquad (I-4)$$

The constants retain the same a,b subscripts for both the oblate and the prolate case, but one must evaluate the angular momentum operators in the (x,y,z) coordinates using the I^r relations for the prolate case and the III^r relations for the oblate case as found in Table I.

The terms r and s in Eq.(I-4) are defined as

$$r = C_e^2/A_e^2$$
$$s = C_e^2/B_e^2$$

Since the equilibrium constants are not generally known, the ground state constants are often used, i.e.

$$r = B_0^2/(A_0 + B_0)^2$$

$$s = A_0^2/(A_0 + B_0)^2$$

Moncur[4] and Snyder[5] used the Hamiltonian as given by Eq.(I-3), but included an empirical fourth-order term, $H_K P_z^6$, when fitting their H_2Te and H_2S data respectively.

Fourth-Order Hamiltonian

Although all of the terms in the planar Hamiltonian are determinable from experimental data, not all of the terms in Eq.(I-1) are determinable. Since Chung and Parker's 1963 paper, many changes in the Hamiltonian have been made. Olson and Allen[6] produced an important simplification of the Hamiltonian for the orthorhombic point groups through wise use of angular momentum commutation relations. Chung and Parker extended their previous work by publishing a study[7] of the fourth-order centrifugal distortion effect. It was then shown by Kneizys, Freedman, and Clough[8] that the Hamiltonian for the orthorhombic point groups, could be given in much simplified form through extensive rearrangement, again based on angular momentum relations.

The form of the resulting Hamiltonian is, for a given vibrational state, a power series in the angular momentum

components which needs for its specification, to fourth-order of approximation, three coefficients, X, Y, and Z, of terms of the second-power in the body-fixed angular momentum components (these being the three effective rotational constants); six coefficients T_i of fourth-power angular momentum terms (these being the second-order centrifugal distortion constants τ_i, plus fourth-order, ρ_i, corrections to them); and ten coefficients of sixth-power angular momentum terms (these being the fourth-order centrifugal distortion coefficents Φ_i). Later Watson[11] showed that the Kneizys, Freedman, and Clough's Hamiltonian, Ref.(8), Eq.(3) or Eq.(6), could be used for asymmetric-top molecules of any point group whatsoever, and thus its use need not be restricted to molecules of the orthorhombic point group.

The Hamiltonian just described, but slightly modified by Yallabandi and Parker[10], [the operator associated with Φ_{10}, which Kneizys et.al. took as $(P_x^2P_y^2P_z^2 + P_z^2P_y^2P_x^2)$ was replaced by $(P_x^2P_z^2P_y^2 + P_y^2P_z^2P_x^2)$], which we shall refer to as the KFC Hamiltonian, takes the form

$$H = h_v + H_2 + H_4 + H_6 \qquad \text{(I-5)}$$

with

$$H_2 = XP_x^2 + YP_y^2 + ZP_z^2$$

$$H_4 = T_1P_x^4 + T_2P_y^4 + T_3P_z^4 + T_4(P_y^2P_z^2 + P_z^2P_y^2)$$
$$+ T_5(P_z^2P_x^2 + P_x^2P_z^2) + T_6(P_x^2P_y^2 + P_y^2P_x^2)$$

$$H_6 = \Phi_1P_x^6 + \Phi_2P_y^6 + \Phi_3P_z^6 + \Phi_4(P_x^2P_y^4 + P_y^4P_x^2)$$
$$+ \Phi_5(P_y^2P_x^4 + P_x^4P_y^2) + \Phi_6(P_y^2P_z^4 + P_z^4P_y^2)$$
$$+ \Phi_7(P_z^2P_y^4 + P_y^4P_z^2) + \Phi_8(P_z^2P_x^4 + P_x^4P_z^2)$$
$$+ \Phi_9(P_x^2P_z^4 + P_z^4P_x^2) + \Phi_{10}(P_x^2P_z^2P_y^2 + P_y^2P_z^2P_x^2)$$

This Hamiltonian, as stated by Kneizys et al., although developed in the III^r representation, can be generalized to any representation by the appropriate identification of the rotational constants with the x,y,z axes(see Table I).

The KFC Hamiltonian still contains experimentally indeterminable coefficients. But Watson[11,12] succeeded in showing how one can obtain from the KFC Hamiltonian a "reduced" Hamiltonian devoid of redundant or experimentally indeterminable coefficients. The reduction of the Hamiltonian can be carried out in an infinite number of ways, but not entirely without restrictive conditions. Watson's theory requires one constraint to be imposed on the coefficients T_i, thereby reducing them to five independent ones, and three constraints to be imposed on the coefficients Φ_i, therby reducing them to seven independent ones.

Mathematically the reductions are achieved by applying

a unitary transformation of the form

$$U = \exp(iS_3)\exp(iS_5)$$

with

$$S_3 = s_{111}(P_xP_zP_y + P_yP_zP_x)$$

and

$$S_5 = s_{311}(P_x^3P_zP_y + P_yP_zP_x^3) + s_{131}(P_xP_z^3P_y + P_yP_z^3P_x) + s_{113}(P_xP_zP_y^3 + P_y^3P_zP_x)$$

to the Hamiltonian given by Eq.(I-5). The constants s_{311}, s_{131}, and s_{113} are chosen such that the appropriate Φ terms are zero; and s_{111} is chosen such that the appropriate T term is zero.

From the unitary transformation a new set of constants, i.e. experimentally determinable coefficients, which have the same angular momentum dependence as the old set, but different theoretical interpretations in terms of molecular parameters, is obtained. The theoretical interpretations depend on the exact reduction used and will vary considerably. Henceforth, we will denote those coefficients following the transformation, which are experimentally determinable, by tildes, e.g. $\tilde{T}_1$.

The details of Watson's theory, as Ford, Yallabandi, and Parker[13] show, allows one to set either $\tilde{T}_4$, $\tilde{T}_5$, or $\tilde{T}_6$ equal to zero with the restrictive conditions stated in

Table II. Three Allowed Ways of Setting a $\tilde{T}_i$ Equal to Zero

Case	Constraint $\tilde{T}_i=0$, where i =	Condition
1	4	$\tilde{Y} \neq \tilde{Z}$
2	5	$\tilde{Z} \neq \tilde{X}$
3	6	$\tilde{X} \neq \tilde{Y}$

Table III. The 20 Allowed Ways of Setting Three Coefficients $\tilde{\Phi}_i$ Equal to Zero.

Case	Constraint $\Phi_i=\Phi_j=\Phi_k=0$ where i,j,k,=	Condition
1	4,5,10	$\tilde{X} \neq \tilde{Y}$
2	6,7,10	$\tilde{Y} \neq \tilde{Z}$
3	8,9,10	$\tilde{Z} \neq \tilde{X}$
4	4,6,10	$\tilde{X} \neq \tilde{Y} \neq \tilde{Z}$
5	5,7,10	$\tilde{X} \neq \tilde{Y} \neq \tilde{Z}$
6	6,8,10	$\tilde{Y} \neq \tilde{Z} \neq \tilde{X}$
7	7,9,10	$\tilde{Y} \neq \tilde{Z} \neq \tilde{X}$
8	4,8,10	$\tilde{Z} \neq \tilde{X} \neq \tilde{Y}$
9	5,9,10	$\tilde{Z} \neq \tilde{X} \neq \tilde{Y}$
10	4,9,10	$\tilde{X} \neq \tilde{Y} \neq \tilde{Z} \neq \tilde{X}$
11	5,6,10	$\tilde{X} \neq \tilde{Y} \neq \tilde{Z} \neq \tilde{X}$
12	7,8,10	$\tilde{X} \neq \tilde{Y} \neq \tilde{Z} \neq \tilde{X}$
13	5,6,7	$\tilde{X} \neq \tilde{Y} \neq \tilde{Z}$
14	4,5,6	$\tilde{X} \neq \tilde{Y} \neq \tilde{Z}$
15	6,7,8	$\tilde{Y} \neq \tilde{Z} \neq \tilde{X}$
16	7,8,9	$\tilde{Y} \neq \tilde{Z} \neq \tilde{X}$
17	4,5,9	$\tilde{Z} \neq \tilde{X} \neq \tilde{Y}$
18	4,8,9	$\tilde{Z} \neq \tilde{X} \neq \tilde{Y}$
19	4,6,8	$\tilde{X} \neq \tilde{Y} \neq \tilde{Z} \neq \tilde{X}$
20	5,7,9	$\tilde{X} \neq \tilde{Y} \neq \tilde{Z} \neq \tilde{X}$

Table II. The restrictive conditions for the values of the rotational constants, e.g. $\tilde{X} \neq \tilde{Y}$, might be thought to be of little consequence except for accidentally symmetric rotors. However, even if two rotational constants are different by an amount of the same order of magnitude as the centrifugal constants, Watson[11] indicates that the reduction breaks down, and another reduction should be used.

The restrictive conditions given in Tables II and III result from the expressions obtained for the "s" constants, i.e. the "s" terms are functions of the differences of two rotational constants to a negative power, so that when the constants are equal, the value of U becomes infinite, viz. Eq.(32), Ref.10.

The simplest way to obtain constraints on the coefficients $\tilde{\Phi}_i$, is to set three of them equal to zero. Ford et al.[13] have found that this can be done in 20 ways. Twelve of these take $\tilde{\Phi}_{10}$ equal to zero and thereby give rise to somewhat more symmetrical appearance of Hamiltonian than the remaining eight ways. In no case may $\tilde{\Phi}_1$, $\tilde{\Phi}_2$, or $\tilde{\Phi}_3$ be taken equal to zero. Table III lists the 20 ways of reduction described.

Watson has given another entirely different reduction of the KFC Hamiltonian, based on Eq.(6) of Ref.8. His reduced Hamiltonian, as written by Ford et al.[13], is given by

$$H = h_v + H_2 + H_4 + H_6 \qquad \text{(I-6)}$$

with

$$H_2 = \tilde{X}^* P_x^2 + \tilde{Y}^* P_y^2 + \tilde{Z}^* P_z^2$$

$$H_4 = \tilde{D}_1 P^4 + \tilde{D}_2 P^2 P_z^2 + \tilde{D}_3 P_z^4 + \tilde{D}_4 P^2 (P_x^2 - P_y^2)$$
$$+ \tilde{D}_5 [P_z^2 (P_x^2 - P_y^2) + (P_x^2 - P_y^2) P_z^2]$$

$$H_6 = \tilde{H}_1 P^6 + \tilde{H}_2 P^4 P_z^2 + \tilde{H}_3 P^2 P_z^4 + \tilde{H}_4 P_z^6 + \tilde{H}_5 P^4 (P_x^2 - P_y^2)$$
$$+ \tilde{H}_7 P^2 [P_z^2 (P_x^2 - P_y^2) + (P_x^2 - P_y^2) P_z^2]$$
$$+ \tilde{H}_8 [P_z^4 (P_x^2 - P_y^2) + (P_x^2 - P_y^2) P_z^4]$$

The constraints in terms of Φ and T are

$$\Phi_1 + \tfrac{1}{2}\Phi_2 = \Phi_5$$

$$\tfrac{1}{2}\Phi_1 + \Phi_2 = \Phi_4$$

$$\Phi_7 + \Phi_8 = \Phi_{10}$$

$$\tfrac{1}{4}(T_1 + T_2) - \tfrac{1}{2}T_6 + 2(\Phi_7 + \Phi_8) - (\Phi_1 + \Phi_2) = 0$$

with the restrictive condition that $\tilde{X}^* \neq \tilde{Y}^*$. The terms X^*, Y^*, and Z^* differ from the X, Y, and Z of Eq.(I-5) by fourth-order corrections[13].

It should be noted that we have used the notation X, Y, and Z for the rotational constants in each of the Hamiltonian expressions because each of the Hamiltonians can be used as written for any representation.

Yallabandi and Parker[10] specify that the reduced

Hamiltonians should be used directly for the analysis of pure rotation data. But for vibration-rotation bands, upper-vibrational state sets of coefficients and lower-vibrational state sets of coefficients should be used in H_2 and H_4, but only a single set of coefficients should be used in H_6. The variation in the sets of coefficients for H_4 is accounted for by the fourth-order vibrational correction terms contained therein. The variation in H_2 is accounted for by the standard expressions for the variation of the effective rotational constants with vibrational state.

Because H_4 includes fourth-order vibrational corrections, the so-called ρ_i's which generally can not be ignored, the planarity relations given by Eq.(I-2), which hold only for the pure second-order centrifugal distortion terms, will not apply to the reduced Hamiltonians. However, if the fourth-order corrections are ignored, the planarity conditions can be applied to the KFC Hamiltonian to obtain a planar Hamiltonian. When this is done, the resulting Hamiltonian is identical in form to the planar Hamiltonian, Eq.(I-4), except for the last term, O_{abab}. The last term of Eq.(I-4) includes the second-order centrifugal contributions to the rotational constants, whereas in the KFC Hamiltonian, these centrifugal contributions are still contained explicitly in the definition of X, Y, and Z

(see Moncur[4],page 8). It should be noted that the planar Hamiltonian fulfills the specifications for determinable coefficients as given by Watson[11].

Coriolis Coupling

Coriolis coupling between two or three excited vibrational states is frequently observed. This coupling perturbs the vibrational levels slightly, but even more perturbs the rotational states within the vibrational levels and hence affects the whole vibration-rotation Hamiltonian.

The effect of this perturbation on the planar Hamiltonian for oblate molecules is well described by Snyder[5] and by Moncur[4], and so only a cursory description will be given here. Snyder has found this coupling to be observable between the vibrational states (v_1,v_2,v_3) and $(v_1\pm1,v_2,v_3\mp1)$. He also found two terms need to be added to the existing planar Hamiltonian in the off-diagonal location to calculate the coupling.

The resulting Hamiltonian is given by

$$H = H_1 + H_2 + H_I \qquad (I-7)$$

where H_1 and H_2 are the vibration-rotation Hamiltonians already discussed for the vibrational states 1 and 2 and H_I is the interaction term which couples the states.

$$H_I = iG_z(q_1q_3 - q_3q_1)P_z + G_{xy}q_1q_3(P_xP_y + P_yP_x) \qquad (I\text{-}8)$$

Evaluation of H_I for the vibrational states yields

$$\langle v_1,v_2,v_3|H_I|v_1+1,v_2,v_3-1\rangle = [2iG_zP_z + G_{xy}(P_xP_y + P_yP_x)][(v_1+1)v_3]^{\frac{1}{2}}/2 \qquad (I\text{-}9)$$

and

$$\langle v_1,v_2,v_3|H_I|v_1-1,v_2,v_3+1\rangle = [-2iG_zP_z + G_{xy}(P_xP_y + P_yP_x)][v_1(v_3+1)]^{\frac{1}{2}}/2 \qquad (I\text{-}10)$$

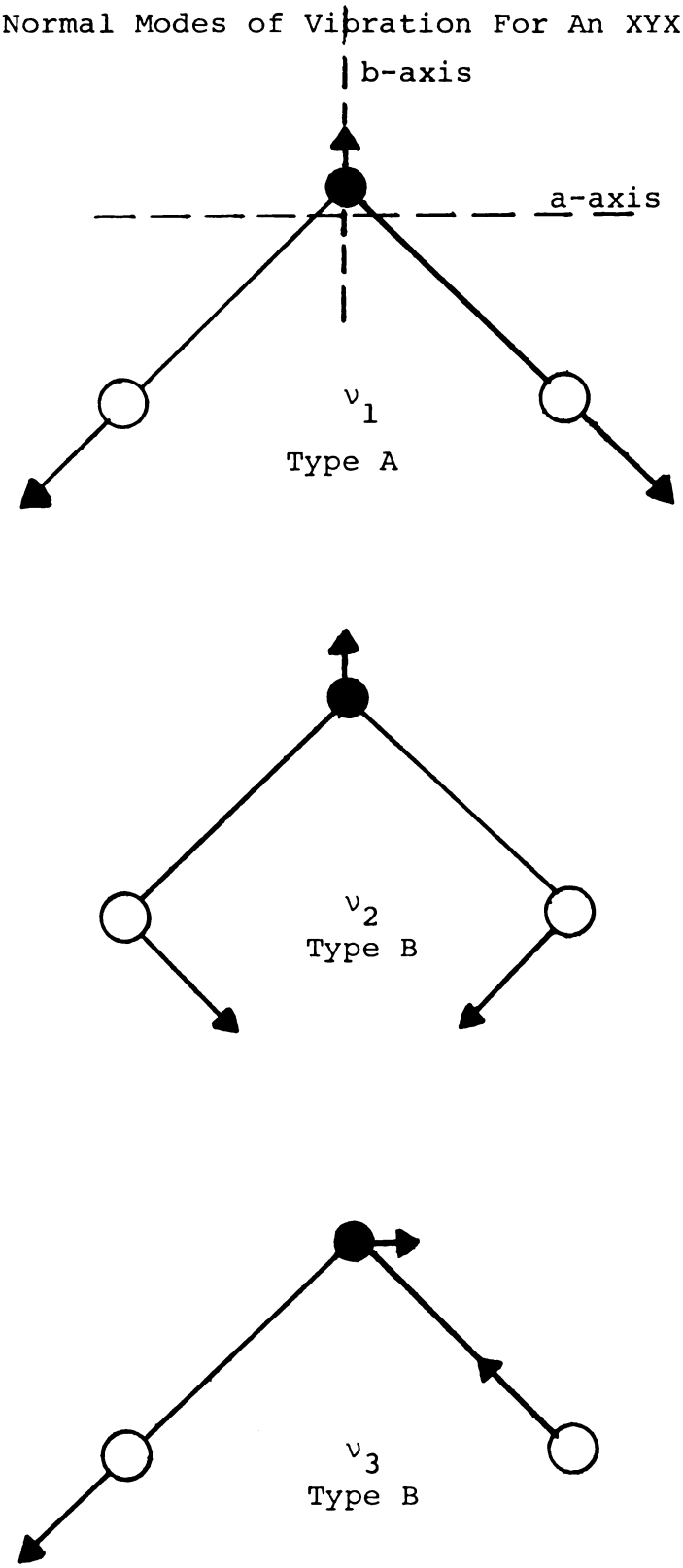
CHAPTER II

APPLYING THE HAMILTONIAN

The Hamiltonians described in Chapter I are used to calculate the energy levels for a given vibrational state of an asymmetric-top molecule. But in near infrared spectroscopy the energy levels themselves are not observed, but rather transitions between energy levels are observed. That is, the observed absorption lines are transitions from an energy level in the ground vibrational state to some energy level in an excited vibrational state. Most often, several absorption lines will have the same upper state energy level, or the same ground state energy level, so that the difference between two line frequencies is a difference between energy levels within one vibrational state. When the value of that difference involves only the energy levels of the ground state, it is commonly called a ground state combination difference, GSCD.

The absorption lines are clustered in bands with all of the transitions in the same band occurring between the same two vibrational states. Since there are three independent normal modes of vibration for a planar triatomic

Fig. I. Normal Modes of Vibration For An XYX Molecule.



asymmetric-top molecule, three vibrational quantum numbers, (v_1,v_2,v_3), are required to designate the state (see Figure I). The transitions originate from dipole moment changes which occur for a molecule lying in the ab plane along the a-axis for type A bands and along the b-axis for type B bands.

The Wang Transformation

A Hamiltonian, when evaluated in angular momentum space, i.e. $\psi(J,K)$ space, yields an independent matrix, E, for each J value. Because of the cross diagonal symmetry within each such matrix and because nonzero terms appear always in a checker board pattern, each matrix can be factored into four noninteracting sub-matrices, which are denoted by E^+, E^-, O^+, and O^-. The factoring is mathematically done by applying the Wang Transformation, W, i.e.

$$(E^+,E^-,O^+,O^-) = W^{-1}E\,W\ . \qquad \text{(II-1)}$$

where

$$W = W^{-1} = 2^{-\frac{1}{2}} \begin{Vmatrix} \cdots & & & & \cdots \\ & -1 & & 1 & \\ & & -1 \quad 1 & & \\ & & 2^{\frac{1}{2}} & & \\ & & 1 \quad 1 & & \\ & 1 & & 1 & \\ \cdots & & & & \cdots \end{Vmatrix}$$

This is equivalent to choosing a new basis $\psi(J,K,\gamma)$, given by

$$\psi(J,K,\gamma) = 2^{-\frac{1}{2}}[\ \psi(J,K) + (-1)^{\gamma}\psi(J,-K)]\ .$$

The ± notation in Eq.(II-1) refers to the sign of $(-1)^{\gamma}$ above, whereas the E or O refers to the evenness or oddness of K.

When Coriolis coupling is present the submatrix E^{+} (or O^{+}) of one excited vibrational state is coupled to the E^{-} (O^{-}) submatrix of another excited vibrational state. The resulting terms are shown in Figures II and III. When the coupling does not occur, each of the four submatrices, viz. E^{+},E^{-},O^{+}, and O^{-}, has the same terms shown, but they are independent of one another.

The elements of the submatrices correspond to the Hamiltonian evaluated in $\psi(J,K)$ space, e.g. for E_1^{+} ,

$$E_{26} = \langle J,2|H_1|J,6\rangle$$

It should be noted that all of the $E_{K,K'}$ terms are real and that in the figures use has been made of the relations

$E_{K,K}=E_{-K,-K}$; $E_{K,K+2}=E_{K+2,K}=E_{-K,-K-2}=E_{-K-2,-K}$; etc.

Also all of the $I_{K,K'}$ terms are pure imaginary, but the whole coupled submatrix is Hermitian.

Appendix I contains a list of the angular momentum operators evaluated in $\psi(J,K)$ space which are necessary to calculate the elements of the energy matrices.

Fig.II. Elements of the Submatrix $\begin{vmatrix} E_1^+ & I_{12}^e \\ I_{12}^{e\dagger} & E_2^- \end{vmatrix}$ for the Hamiltonian $H_1 + H_2 + H_I$.

$$\left[\begin{array}{ccccc|cccc}
E_{00} & 2^{\frac{1}{2}}E_{02} & 2^{\frac{1}{2}}E_{04} & 2^{\frac{1}{2}}E_{06} & 0 & -2^{\frac{1}{2}}I_{02} & 0 & 0 & 0 \\
2^{\frac{1}{2}}E_{02} & (E_{22}+E_{-22}) & (E_{24}+E_{-24}) & E_{26} & E_{28} & -I_{22} & -I_{24} & 0 & 0 \\
2^{\frac{1}{2}}E_{04} & (E_{24}+E_{-24}) & E_{44} & E_{46} & E_{48} & I_{24} & -I_{44} & -I_{46} & 0 \\
2^{\frac{1}{2}}E_{06} & E_{26} & E_{46} & E_{66} & E_{68} & 0 & I_{46} & -I_{66} & -I_{68} \\
0 & E_{28} & E_{48} & E_{68} & E_{88} & 0 & 0 & I_{68} & -I_{88} \\
\vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \vdots \\
\hline
2^{\frac{1}{2}}I_{02} & I_{22} & -I_{24} & 0 & 0 & (E_{22}-E_{-22}) & (E_{24}-E_{-24}) & E_{26} & E_{28} \\
0 & I_{24} & I_{44} & -I_{46} & 0 & (E_{24}-E_{-24}) & E_{44} & E_{46} & E_{48} \\
0 & 0 & I_{46} & I_{66} & -I_{68} & E_{26} & E_{46} & E_{66} & E_{68} \\
0 & 0 & 0 & I_{68} & I_{88} & E_{28} & E_{48} & E_{68} & E_{88} \\
\vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \ddots
\end{array}\right]$$

Fig.III. Elements of the Submatrix $\begin{vmatrix} O_1^+ & I_{12}^o \\ I_{12}^{o\dagger} & O_2^- \end{vmatrix}$ for the Hamiltonian $H_1 + H_2 + H_I$.

$$\left[\begin{array}{ccccc|ccccc}
(E_{11}+E_{-11}) & (E_{13}+E_{-13}) & (E_{15}+E_{-15}) & E_{17} & \cdots & -(I_{11}+I_{-11}) & -I_{13} & 0 & 0 & \cdots \\
(E_{13}+E_{-13}) & (E_{33}+E_{-33}) & E_{35} & E_{37} & \cdots & I_{13} & -I_{33} & -I_{35} & 0 & \cdots \\
(E_{15}+E_{-15}) & E_{35} & E_{55} & E_{57} & \cdots & 0 & I_{35} & -I_{55} & -I_{57} & \cdots \\
E_{17} & E_{37} & E_{57} & E_{77} & \cdots & 0 & 0 & I_{57} & -I_{77} & \cdots \\
\vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \vdots & \ddots \\
\hline
(I_{11}+I_{-11}) & -I_{13} & 0 & 0 & \cdots & (E_{11}-E_{-11}) & (E_{13}-E_{-13}) & (E_{15}-E_{-15}) & E_{17} & \cdots \\
I_{13} & I_{33} & -I_{35} & 0 & \cdots & (E_{13}-E_{-13}) & (E_{33}-E_{-33}) & E_{35} & E_{37} & \cdots \\
0 & I_{35} & I_{55} & -I_{57} & \cdots & (E_{15}-E_{-15}) & E_{35} & E_{55} & E_{57} & \cdots \\
0 & 0 & I_{57} & I_{77} & \cdots & E_{17} & E_{37} & E_{57} & E_{77} & \cdots \\
\vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \vdots & \ddots
\end{array}\right]$$

Identification of Levels

The eigenvalues of these submatrices constitute the energy levels of the Hamiltonian. They are found explicitly by applying the unitary transformation matrix, S, to the energy matrix, E, which diagonalizes it, i.e. $E' = S^{-1}E\,S$. In the transformed space K is not a good quantum number. But the energy levels may be identified uniquely by assigning three quantum numbers, (J,K_-,K_+), to each, where $K = K_-$ in the limit as the molecule approaches a prolate symmetric-top, and $K = K_+$ in the limit as the molecule approaches an oblate symmetric-top.

To evaluate the angular momentum operators, one must choose the arbitrary phase factor for P_x or for P_y. We have chosen this factor such that P_y has real and positive matrix elements, hence P_x has pure imaginary matrix elements, viz.

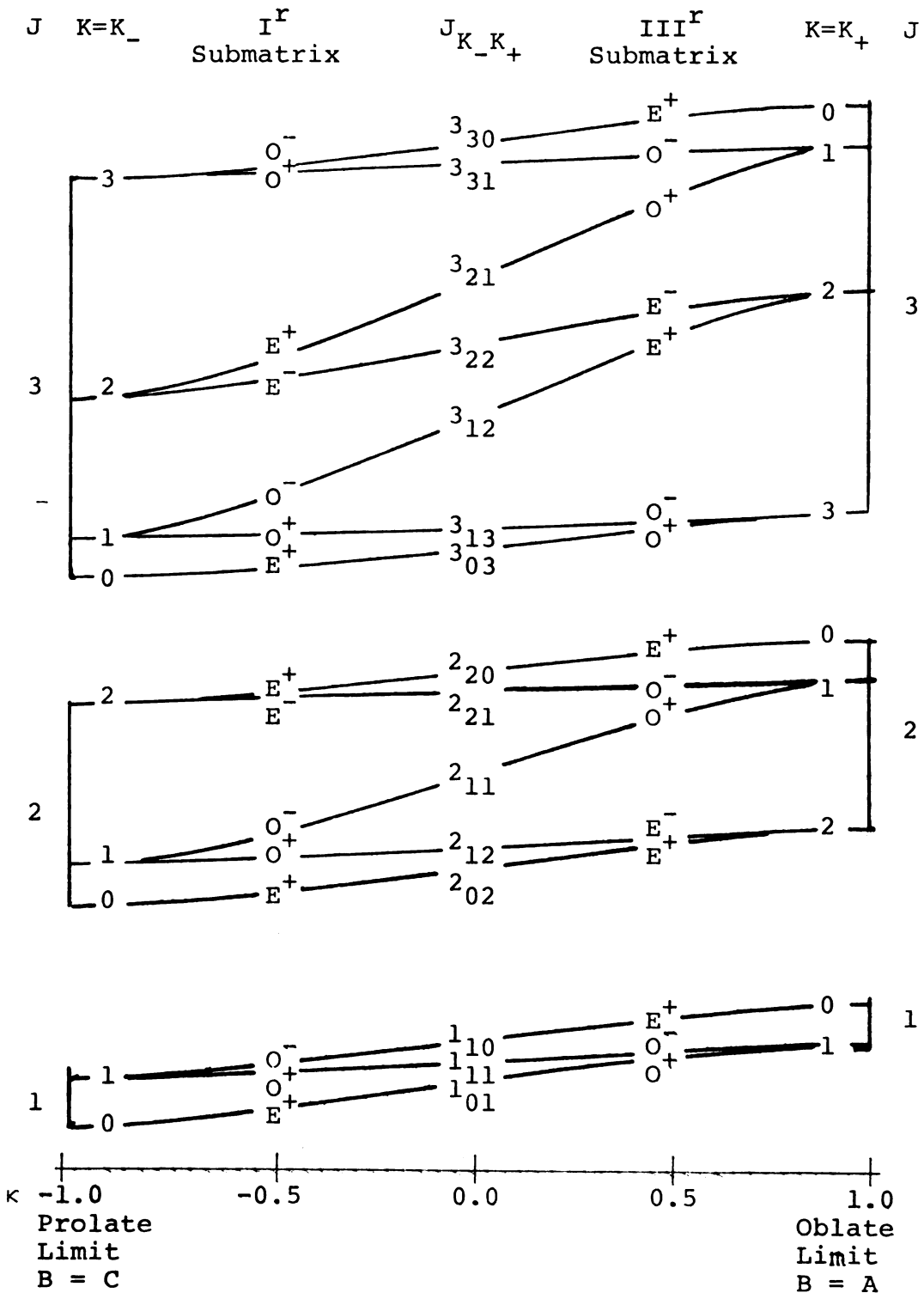
$$< J,K \mid P_x \mid J,K+1 > = (i/2)[J(J+1) - K(K+1)]^{\frac{1}{2}}. \quad \text{(II-2)}$$

For this phase convention all of the symmetry arguments concerning the assigning of energy levels as given by King, Hainer, and Cross[14] apply to this work. Therefore the evenness or oddness of the K_- and K_+ values within a submatrix must agree with those given in Table IV, which agrees with Table VII in Ref.14. The assigning of the levels within each submatrix must be such that

Table IV. Classification of the Submatrices E^+, E^-, O^+, and O^-.

Submatrix	even J		odd J		even J		odd J		Size of Submatrix	
	I^r representation				III^r representation					
	K_-	K_+	K_-	K_+	K_-	K_+	K_-	K_+	even J	odd J
E^+	e	e	e	o	e	e	o	e	J/2 + 1	(J+1)/2
E^-	e	o	e	e	o	e	e	e	J/2	(J-1)/2
O^+	o	e	o	o	o	o	e	o	J/2	(J+1)/2
O^-	o	o	o	e	e	o	o	o	J/2	(J+1)/2

Fig.IV. Energy Level Diagram



for increasing energy, the value of K_- increases and the value of K_+ decreases in an even fashion. Figure IV shows the assignments of energy levels for J equal to 1,2, and 3.

Evaluation of Coefficients

If we ignore the vibrational term, h_v, we can write each of the Hamiltonians in the form

$$H = \Sigma\ x^i \chi^i \ . \qquad \text{(II-3)}$$

where x^i are the coefficients and χ^i are the angular momentum operators. The equation for the energy matrix elements then becomes

$$E_{rs} = \Sigma\ x^i \chi^i_{rs} \qquad \text{(II-4)}$$

The ath eigenvalue of the energy matrix is given by

$$E_a = \Sigma\Sigma\ (s^{-1})_{ar} E_{rs} S_{sa} \qquad \text{(II-5)}$$

In terms of Eq.(II-4), this becomes

$$E_a = \Sigma\ x^i \langle \chi^i \rangle_a \qquad \text{(II-6)}$$

where

$$\langle \chi^i \rangle_a = \Sigma\Sigma\ (S^{-1})_{ar} \chi^i_{rs} S_{sa} \qquad \text{(II-7)}$$

i.e. $\langle \chi^i \rangle_a$ is the expectation value of the ith Hamiltonian angular momentum operator.

The coefficients , x^i, are determined by least squares fitting the frequencies of the observed lines to the

differences of the calculated energy levels, i.e. to $\nu_o - E_g + E_u$, where E_g is the ground state rotational energy†, E_u is the excited state rotational energy, and ν_o is the vibrational contribution, referred to as the band center, which comes from the h_v term in the Hamiltonian.

If Eq.(II-5) were linear in x^i, the method of least squares would directly yield the values of the coefficients. But since the unitary transformation matrix, S, is itself a function of the x^i, Eq.(II-5) is nonlinear in x^i and a longer procedure must be used.

Generally one begins with an estimate of the rotational constants, A, B, and C obtained either from past work on the molecule or by using combination differences as described by Moncur.[4] From these rotational constants the energy matrices are calculated using Eq.(II-4), and then diagonalized to obtain the energy levels and the angular momentum operator expectation values. Those expectation values, $\langle \chi^i \rangle$, and energies corresponding to the energy levels of the observed transitions are used to calculate the normal matrix for the least squares fit. The least squares fit yields the values δ^i, where

$$\Delta E_a = \Sigma \, \delta^i \langle \chi^i \rangle_a \qquad \text{(II-8)}$$

such that $E_a + \Delta E_a$ are on the average closer to the values which are necessary for fitting the observed lines. Then the new constants, $x^i + \delta^i$, are used to calculate new

†Actually the E's are term values, differing from energy by a factor of 1/hc.

energy levels and the whole procedure is repeated until convergence is reached.

Isotopic Substitution

When several atomic isotopes are present simultaneously in the molecules under study, the absorption bands of each isotope are observed overlapping one another. The small differences in the frequencies of the lines for different isotopes can partly be accounted for by making a linear change in the Hamiltonian coefficients with atomic mass.[15] That is, Eq.(II-3) would become

$$H = (x^i + \xi^i \Delta m)\chi^i \qquad \text{(II-9)}$$

where ξ^i is the mass dependent constant and Δm is the mass of the most abundant isotope less the mass of the isotope being fit.

The use of Eq.(II-9) requires many more operations than the simpler approximation

$$E_a = (x^i + \xi^i \Delta m)\langle\chi^i\rangle_a \qquad \text{(II-10)}$$

which we have used successfully. Eq.(II-10) differs from Eq.(II-9) in that $\langle\chi^i\rangle$ is a function of $(x^i + \xi^i \Delta m)$ in Eq.(II-9), but only of x^i in Eq.(II-10).

The band center, ν_o, is also fit to the observed data and a linear plus quadratic change in it with change in atomic mass, is sufficient to complete the compensation

for the differences in the frequencies of the lines for different isotopes. i.e. ν_o is replaced by $\nu_o + \xi^m \Delta m + \xi^{mm} (\Delta m)^2$.

Computer Programs

To apply the preceding material to experimental data, three computer programs were written. The programs are similar in nature and parallel one another in operation. ICDFIT was written to fit combination differences, ISPECFIT was written to fit single spectral bands, and SPECFIT2 was written to fit simultaneously two bands which are Coriolis coupled.

Because of the complexity of the programs, each major part was written as a subroutine. Due to the volume of data, which must be stored and sorted by the programs, core storage and superfluous calculations had to be economized. The programs were written for a batch computer, specifically the CDC 3600, where core storage is not shared with other users.

Appendix III is a listing of the Fortran source for ISPECFIT. The other programs were written very similarly to ISPECFIT, using some of the same subroutines. This program and the program ICDFIT incorporate Eq.(II-10), which allow the user to fit different isotopes simultaneously.

The main part of each program reads all of the control cards and the data cards, sequences the operations, sets up the data for the normal matrix, changes the Hamiltonian coefficients, and iterates the fitting procedure.

The subroutine PMAKE calculates the angular momentum operators for whichever Hamiltonian the user chooses. The planar Hamiltonian, Eq.(I-3), the KFC Hamiltonian, Eq.(I-5), and the Watson Hamiltonian, Eq.(I-7), are available in the programs and are selected by a control card. All nineteen angular momentum operators for the KFC Hamiltonian are included. Since only fifteen are determinable, the user must choose, using Tables II and III as a guide, those best for his molecule. Both the prolate and the oblate form of the planar Hamiltonian are included, hence, since the KFC Hamiltonian and the Watson Hamiltonian will calculate the energy levels for oblate or prolate molecules, any one of the Hamiltonians may be chosen to fit any type of planar molecule.

The subroutine CAPPA prints the Hamiltonian chosen, along with the current coefficients. It also calculates Ray's asymmetry parameter, κ, using the equation

$$\kappa = (2B-A-C)/(A-C) \qquad \text{(II-11)}$$

Note that

$$-1 \leq \kappa \leq 1$$

When κ is positive, the molecule is oblate, becoming an oblate symmetric-top for $\kappa = +1$. When κ is negative, the molecule is prolate, becoming a prolate symmetric-top for $\kappa = -1$. If is positive, the program chooses the III^r representation and identifies the (E^+, E^-,O^+,O^-) submatrices with the quantum numbers as listed in Table IV. If κ is negative, the program chooses the I^r representation and identifies the submatrices accordingly.

WANGT calculates the Wang transformed energy matrices. SYMDIG diagonalizes the resulting symmetrical energy matrices (HERMDIG in SPECFIT2 diagonalizes the Hermitian energy matrices required for Coriolis coupling). Diagonalization is done by the Jacobi method, which is outlined in detail in Appendix II. Both the eigenvalues and the eigenfunctions are calculated.

The expectation values of the angular momentum operators are calculated using Eq.(II-7) in the subroutine FORMEP. FORMEP also assigns the quatum numbers to the energy levels.

REGRESS is a stepwise multiple regression routine originally written by M. A. Efroymson.[16] It is used to determine the least squares "best" values for the coefficients, δ^i, as required to solve Eq.(II-8). The routine is different from most weighted least squares routines in that the variables are added to the solution

one at a time in the order in which they will make the greatest improvement in the "goodness of the fit". The routine also decides which variables are determinable and does not add the indeterminate variables to the fit.

The user weights his data according to the expected accuracy of his measurements, $\Delta\nu_i$, choosing $w_i \propto (\Delta\nu_i)^{-2}$. The program normalizes the weights so that the average weight, w_i, is equal to one. If for the ith line

$$\Delta_i^2 w_i \geq \text{XOUT } (\Sigma\ \Delta_i^2 w_i)/(N-m)$$

where Δ_i is the deviation between the observed line frequency and the calculated frequency, N is the total number of nonzero weighted lines and m is the number of independent variables in the fit, that line's weight will be set to zero during the next iteration. It has been observed that a good value for XOUT for our data is approximately 12.

CHAPTER III

REDUCTION OF SPECTRAL DATA

Spectral data "originate" in the form of a voltage signal from the detector circuit of the spectrometer, whose relative amplitude is a measure of the absorption of infrared radiation by the gas under consideration. The voltage signal, recorded as a function of frequency, traces out the spectrum, which for asymmetric-top molecules consists of hundreds or thousands of "lines", many of which overlap in a complicated fashion. In the past these absorption "lines" were recorded on paper strip charts along with Fabry-Perot equal frequency spaced fringes of visible light generated simultaneously in the spectrometer.[17] The line centers were measured from the paper by utilizing a fairly complicated optical display.[18] No pre-processing of the raw spectral data was done except that done by the amplifier through RC smoothing.

With the recent addition of a PDP-12, a Digital Equipment Corporation minicomputer, to our laboratory,

processing of the raw data before measuring line centers became possible. That is, the raw data, after RC smoothing, are digitized and recorded in digital form on magnetic tape under the control of computer software. Then under the control of the operator the computer is used to adjust the baseline and remove any anomalies in the data. The data are also smoothed digitally by the method of least squares. The above steps prepare the data for deconvolution, which enhances the spectral resolution, presently by as much as 2.5 over the original data. The method employed is a modification of one developed and used for resolution enhancements of a much lesser degree by Van Cittert[19] and Burger and Van Cittert.[20,21]

The spectral lines in the deconvoluted data can then be measured using a combination of the data manipulating "power" of the computer and the knowledge and judgment of the scientist. A computer program has been written to display simultaneously, the lines, along with a mirror reflection and their difference. Based on the symmetry of the above information the scientist chooses the line centers.

The remainder of this chapter will deal in more detail with the theory and application of these operations. The following chapter will deal with the method

of deconvolution.

If the spectra are to be deconvoluted, they must meet some basic criteria, i.e.

a) the signal to noise ratio should be greater than 200:1 after RC and digital smoothing,

b) the 100% absorption and 0% absorption levels must be fixed to known values,

c) the full width at half height, (FWHH), of single lines must each contain a sufficient number of data points, e.g. approximately 30 points for a resolution enhancement of 3.

If the data is not to be deconvoluted, less stringent restrictions can be set.

Acquisition of Data

Since the spectrum is obtained nearly linearly in time, it is simplest and sufficient to sample the data, via the analog-to-digital converter, linearly in time. The time between samples is chosen to yield the number of samples-per-FWHH required. However, were we able to do so, we would sample at exactly equal frequency intervals. We depend on the frequency of the spectrometer to be changing linearly in time over a range much greater than the FWHH of a single line.

The voltage signal to be sampled is zero offset and

electronically amplified such that its range is within that required by the analog-to-digital converter, i.e. -1 to +1 volt.

Before recording the spectrum, the operator should record the "zero" signal, i.e. 100% absorption, and again whenever a change in that zero is made. This information is required for adjusting the baseline.

Noise or Error in the Data

Noise or errors in either coordinate of a data point affects smoothing, deconvolution, etc. The sources of noise or error are different for the two coordinates. The method of driving the monochromator in our spectrometer is the greatest source of error in the abscissa of the data points, is only partly random in character, and tends to become worse at the slowest drive rate. Therefore, it ultimately determines what the longest observation time may be.

Noise in the ordinate of the data points is electronic in nature and mostly stems from the detector circuitry and the associated electronics. The latter noise is generally "white" in character and can be decreased by increasing the period of observation. Noise whose frequency is much higher than that of the signal can be averaged out, whereas noise whose frequency is

similar to that of the signal, cannot be distinguished from it.

A third source of noise is regular in character and comes from 60 Hertz power and 90 and 450 Hertz choppers found in and around the spectrometer. Noise of this character becomes a problem when the data is sampled at regular intervals, for it can then be folded into the data, becoming a false signal of frequency less than F/2 where F is the sampling frequency. This signal is commonly said to come from aliasing of Nyquist folding.[22]

Smoothing of Data

To average out the high frequency noise, we use a combination of RC filtering and digital smoothing. Averaging of repeated runs has not been possible because our monochromator is not driven sufficiently linearly and reproducibly.

Stewart[23] has given a good introduction to the effects of RC smoothing on individual lines, as well as references to other work on the subject. The principal effects include loss of height, increase in FWHH, drag of the peak, and asymmetry in the shape of the line. Edwards and Strome[24] have made a careful study of these effects for both Gaussian and Lorentzian single lines, as well as the effects on doublets. They conclude that the optimum

value of RC is near 0.1 FWHH of single lines, independent of whether or not the data is to be digitized and that if the data is to be digitized the optimum RC value is independent of the number of samples per FWHH.

Digital smoothing is easily done by convoluting a "smoothing function" with the data. The "smoothing function" chosen may drastically alter the result,e.g. one may obtain any derivative of the data by selecting the appropriate function (see Appendix IV). To maintain the symmetry of the original data and a point for point correspondence between the original data and the convolved result, the "smoothing function" must be symmetrical about a single point in it.

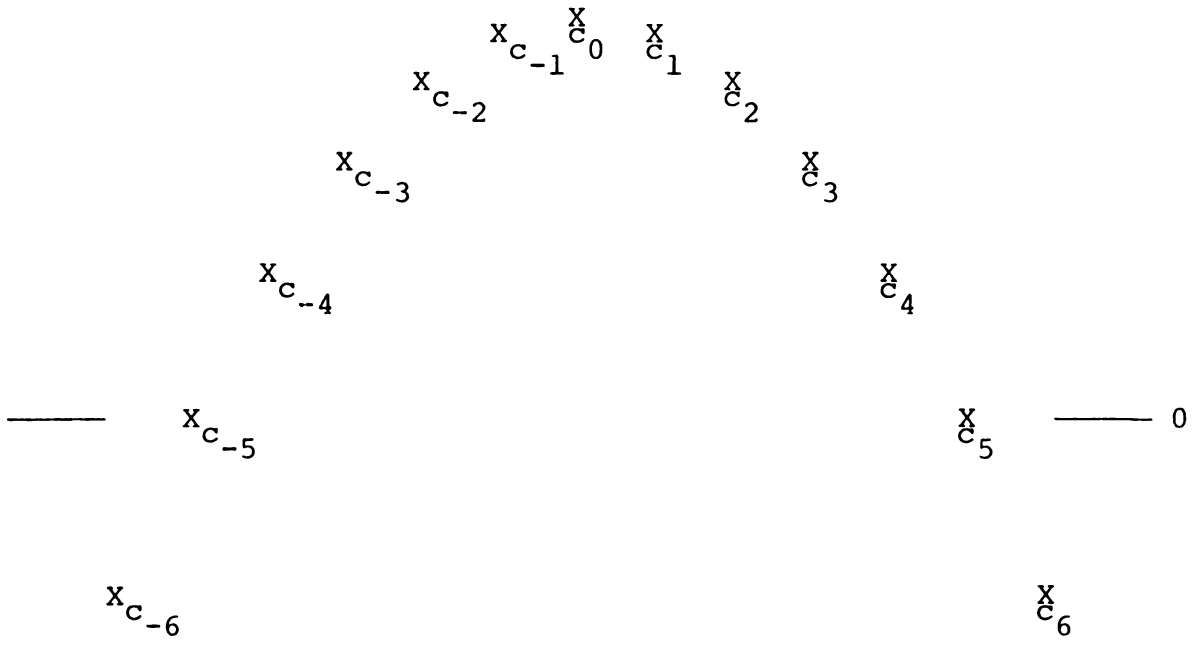
We have chosen to use a smoothing function which gives us the same result as obtained by fitting the data by the the method of least squares to a running cubic polynomial, i.e. for the ordinate of each data point,y, is substituted b_0, whose value is determined by fitting the equation

$$y = b_0 + b_1x + b_2x^2 + b_3x^3$$

to the spectral region immediately surronding that data point. This operation, as done by convolution, requires that the data should be linear in the abscissas over the range which the fitting is done(see Figure V).

In a study of the effects of digital least squares

Fig. V. Smoothing Function For a 13 Point Smooth.



$$c_{-i} = c_i$$

$$c_0 = 0.174825$$
$$c_1 = 0.167832$$
$$c_2 = 0.146853$$
$$c_3 = 0.111888$$
$$c_4 = 0.062937$$
$$c_5 = 0$$
$$c_6 = -0.076923$$

The numbers, c_i, (referred to as convolutes) are convoluted with the data to be smoothed; the result will be a least squares fit to a cubic polynomial about each point, provided the points are equally spaced in the values of the abscissas.

smoothing of calculated Gaussian and Lorentzian single lines, calculated doublets, and observed lines, we[25] have shown that the most important parameter is the smoothing range compared to the FWHH of the lines and that the optimum value of the smoothing range is about 0.7 FWHH. In addition we have shown that multiple smoothing by successive least squares fitting to a shorter range cubic polynomial is no longer a least squares fit to a cubic polynomial, and is less effective in improving the signal to noise ratio than a single least squares fit to a polynomial of the proper range.

To reduce the amplitude of aliased frequencies we have chosen to multiple sample, i.e. average 2^n rapidly but equally spaced samples into one digitzed data point, which is then stored on the magnetic tape.

The methods of smoothing just discussed will reduce high frequency noise. For low frequency noise, such as drift due to detector response, we use a method of adjusting the baseline.

Base Line Adjusting

Our data is absorption spectra and therefore the baseline corresponds to zero absorption or 100% transmission. This means two things. First of all the 100% absorption level must be known, since it can not be obtained directly from the data, and this level will remain unchanged throughout the experiment as long as

the amplifier "zero" or offset is not changed. Secondly, changes in the baseline, which occur due to changes in detector response, source intensity, and other sundry causes, affect the "gain" of the signal, and so, must be compensated for by changing the gain in the digitized data.

Once the data is in digital form "zero" and 100% absorption must be defined in terms of numbers. For convenience of calculation as well as need for precision, we have chosen "zero" to correspond to 0000_8 (0_{10}) and 100% absorption to correspond to 2000_8 (1024_{10}). Therefore absorption lines actually appear as peaks in the data and henceforth will be treated as peaks.

After the data is recorded, the difference between the 100% absorption octal value recorded at the beginning of the run and the octal number 2000_8 must be added to the data. And then the "gain" of the data must be changed in a continuous way so that the base line of the spectra is set to zero. The computer program which can do this operation is written so that a variable, t, whose value can be changed continuously by the operator by turning a knob while viewing the data, alters the data values by the formula

$$y' = 2000_8 - (2000_8 + t)(2000_8 - y).$$

In this fashion, slow changes in the baseline of the spectra are easily removed. Since at times it is often very difficult for a physicist to tell where the baseline of a spectrum is, it is impossible to have the computer automatically determine it.

In practice, first the zero level, then the gain should be corrected before smoothing digitally is done, so that any "staircasing" due to roundoff errors and other minor errors which creep in while correcting spurious data values will be smoothed out. After these operations have been completed accurately, the spectrum is ready for deconvolution.

Deconvolution

The radiation signal, as it passes through the spectrometer, is changed by the spectrometer. In effect one can represent the spectrometer with its slits and optical components by a function which is convolved with the spectrum. The electronic components in the system likewise alter the voltage from the detector and can be represented by a function convolved with the spectrum. The end result is that the true spectrum is observed convolved with numerous other functions representing the components of the system. The convolution of these "numerous other functions" together, quickly takes on a Gaussian character

and is called the instrument function.[26]

Originally our purpose in deconvolution of the spectrum was to remove this instrument function from the spectral data and thereby enhance the resolution of the data. More recently we and others[27] have found that one can actually enhance the resolution of the spectrum by using a function which is greater than just the instrument function and includes doppler broadening, etc.

Numerous methods of deconvolution have been proposed and used with moderate success. Resolution enhancement of a factor of approximately 1.4 is apparently obtainable by most of the methods. Since Jansson and the Florida State University group[28] obtain resolution enhancement of approximately 2, we have adopted and improved their method for our minicomputer and can now obtain a resolution enhancement of approximately 2.5. The method is described in detail in the next chapter.

Measuring Line Centers

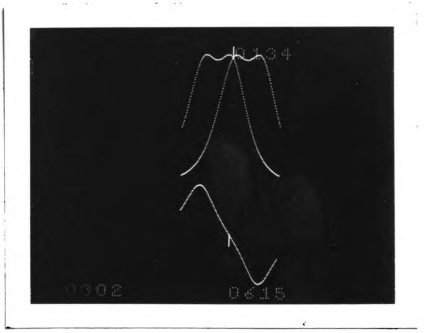
After the data is deconvoluted the centers of the spectral lines are measured and transformed into wavenumbers for fitting to a Hamiltonian. When the lines are well resolved, numerous methods of measuring the lines work. For partially resolved lines, it has generallly been found not possible to give the computer sufficient

criteria to automatically measure the line centers.

The program developed and written by Hurlock and Hanratty[29] to measure the lines, displays the spectral region under consideration and that same region reversed about the center of the screen. The operator decides where the line centers exist using the symmetry of the display as well as difference between the line and its reverse, which can also be displayed, as criteria. The measurement is made in terms of the nearest half separation of points (see Figure VI).

The Fabr y-Perot fringes are measured automatically by the computer program simply from using an a-priori-separation and minimizing the difference between the line and its reversal. If the fringes are properly calibrated, the program transforms the measurements of the infrared lines directly into wavenumbers.

Fig.VI. Measuring Line Centers by Line Reversal.



Upper Traces: The region of the spectrum selected by the operator and that same region reversed about the cursor.

Lower Trace: The difference between the region and that region reversed.

CHAPTER IV

DECONVOLUTION OF SPECTRA

As described in the previous chapter, the observed spectral lines consist of the "real" spectral lines convolved with a number of other functions. Calling W the "real" spectrum, S the observed spectrum, and A the convolution of these "other" functions, we can write

$$S(y) = \int_{-\infty}^{\infty} W(x)\ A(y-x)\ dx = \int W\ A \qquad \text{(IV-1)}$$

We desire to solve Eq.(IV-1) for W, that is to deconvolute S. Theoretically this can be done most easily by dividing the Fourier transform of S by the transform of A and transforming the result back. In general, the results of such an operation on experimental spectra have been unreliable.

In the recent years a number of people, Ref. 28, 30,31,32,33, and 34, have tried with success different methods of pseudo-deconvolution. In these methods the solution to Eq.(IV-1) is obtained indirectly by an iterative method without transforming the functions. Of these methods, the one used by Jansson, Hunt and Plyler[28] seemed to be most successful, yielding the

greatest improvement in resolution.

Van Cittert Method

Jansson et.al. adopted a method developed by van Cittert[19] which is based on the Fredholm solution to integral equations of the first kind. Jansson altered van Cittert's method by adding a variable over-relaxation parameter which,in effect, added boundary conditions to the solution, i.e. he constrained all ordinate data values to remain within a given range,viz. 0% to 100% absorption.

We have studied Jansson's method in detail, especially in relation to Gaussian shaped lines, and have found ways of improving and extending the method.

In van Cittert's method the first approximation of W in the solution of Eq.(IV-1) is $W_1 = S$. The second is

$$W_2 = W_1 + (S - \int A\, W_1)$$

The nth is

$$W_n = W_{n-1} + (S - \int A\, W_{n-1}) \qquad \text{(IV-2)}$$

which can be written as

$$W_n = nS - n(n-1)S_1/2! + \cdots + S_{n-1} \qquad \text{(IV-3)}$$

where

$$S_1 = \int A\, W_1$$

$$S_n = \int A\, S_{n-1} = \int S\, A_{n-1}$$

$$A_0 = A \; ; \quad A_n = \int A\, A_{n-1}$$

Eq.(IV-3) can also be written as

$$W_n = \int W\, X_n \qquad \text{(IV-4)}$$

where

$$X_n = nA - n(n-1)A_1/2! + n(n-1)(n-2)A_2/3! + \cdots + A_{n-1}$$

It is proved by Burger and van Cittert[21] that if

$$|1 - J_A| < 1 \qquad \text{(IV-5)}$$

then

$$W_n \to W \text{ as } n \to \infty$$

where J_A is the Fourier transform of A. This in turn implies that X_n behaves as a delta function as $n \to \infty$. The condition, Eq.(IV-5), is satisfied by Gaussian shaped lines as well as by our spectral lines. Hence, the method should theoretically work for deconvoluting our spectra.

In Figure VII we give an example of the function $A = \exp(-x^2) = X_1$ and its related functions X_2 and X_5. Note the negative lobes which appear in the latter functions. When using this method to deconvolute, similar lobes appear in the early iterations for the approximation of W, e.g. in W_5. When deconvoluting a Gaussian line, S, using a Gaussian function for A, we have found that if the half width of A, Δ_A, is less than approximately .7 Δ_S, the lobes do eventually disappear. But as the half width of A approaches that of S, then even in numerous iterations, the lobes do not disappear (see Figure VIII), thereby limiting the resolution enhancement

Fig.VII. The Functions X_1, X_2, and X_5 for $X_1 = A = \exp(-x^2)$.

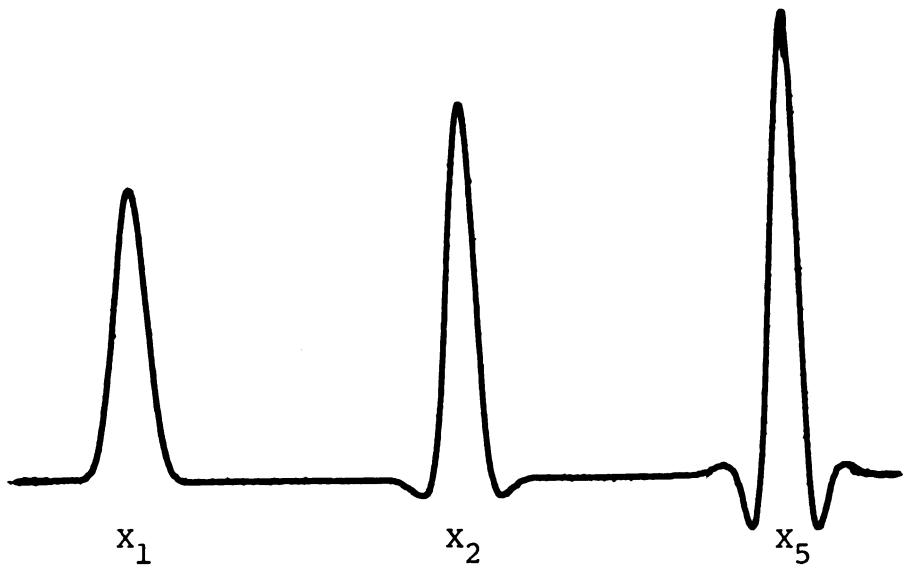
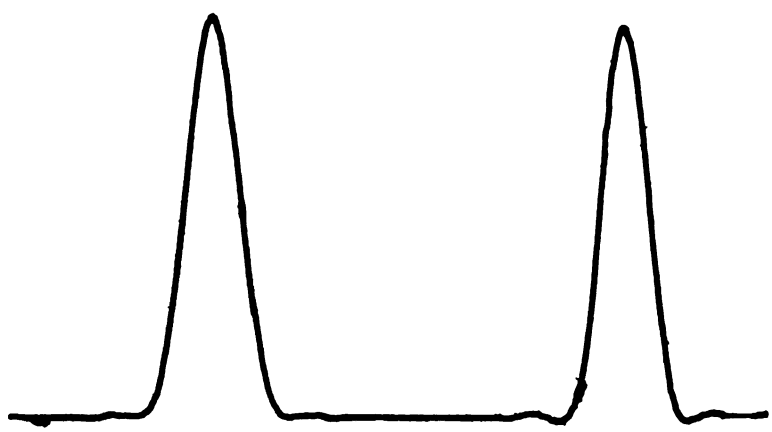


Fig.VIII. Results of Deconvolution by van Cittert's Method.



possible by this method.

Jansson[35] added to Eq.(IV-2) a variable over-relaxation factor, here denoted by α, so that Eq.(IV-2) becomes

$$W_n = W_{n-1} + \alpha(S - \int A\, W_{n-1}) \qquad \text{(IV-6)}$$

In numeric notation this becomes

$$W_i(n) = W_i(n-1) + \alpha(y_i)\left[S_i - \sum_{j=-m}^{j=m} A_{-j} W_{i+j}(n-1)\right] \qquad \text{(IV-7)}$$

where $y_i = W_i(n-1)$.

Jansson chose

$$\alpha(y_i) = b(1.0 - 2.0|y_i - 0.5|) \qquad \text{(IV-8)}$$

where "b" is a selected constant. The triangular shaped function, which is plotted in Figure IX, forced the data ordinate values to stay within the real experimental boundaries, i.e. $0 \leq y_i \leq 1$.

Adding the boundary conditions enabled Jansson et. al.[28] to obtain resolution enhancements near a factor of two without the negative lobes showing up. In fact, they increased the resolution of their data beyond the optical resolution limit of their spectrometer.[27] We also observed that we could enhance the resolution of our spectra beyond the limit for our spectrometer.[36] The next question is what is the maximum resolution enhancement possible in practice and can it be successfully obtained for real spectra?

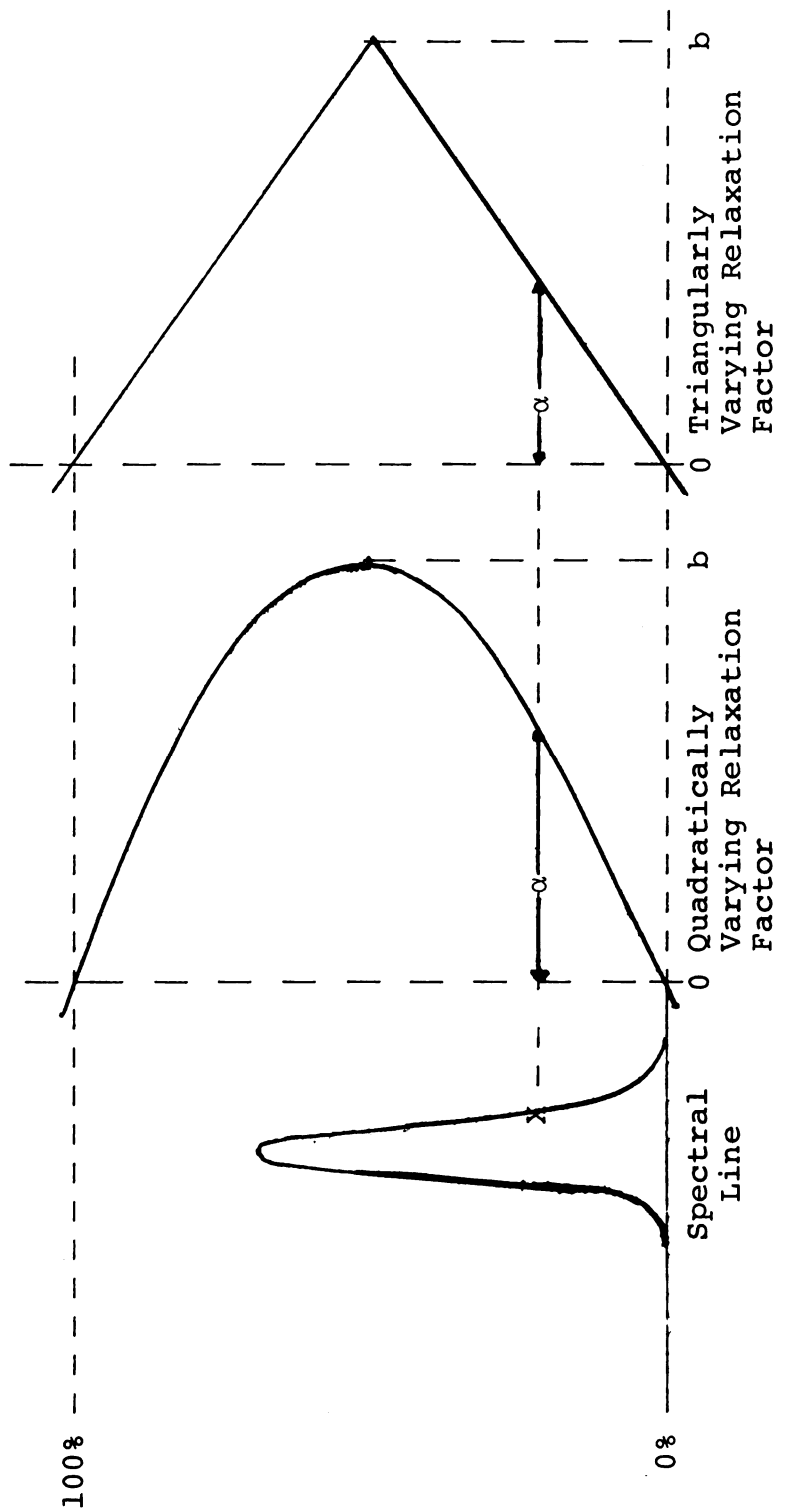


Fig.IX. Quadratic and Triangular Relaxation Functions.

Maximum Resolution Enhancement

It is quite easily shown that a Gaussian line convoluted with another Gaussian line is a Gaussian. The relationship between the line widths at half heights for Eq.(IV-1) when S, A, and W are Gaussian lines is easily found to be

$$\Delta_S/\Delta_W = [1 - (\Delta_A/\Delta_S)^2]^{-\frac{1}{2}} \qquad \text{(IV-9)}$$

where Δ_S, Δ_A, and Δ_W are the FWHH for S, A, and W respectively. We shall define the resolution enhancement to be Δ_S/Δ_W. From the plot of Eq.(IV-9) in Figure X, one can readily see that for large values of Δ_A/Δ_S, the maximum resolution enhancement will be limited by the precision of the ordinate values of the data. That is, when Δ_A/Δ_S is approximately 0.95 a 2% change in that value can make a 20% change in the resolution enhancement. It should be noted that the largest value Δ_A/Δ_S can be is one. If Δ_A/Δ_S should exceed one,then for lines in the spectrum which are singlets, i.e. separated from all other lines, the deconvolution process will diverge, and for lines which are very close to one another, i.e. so that there combined half width approaches the half width of A, the deconvolution process will yield a narrow single line. A 2% change in Δ_A/Δ_S is not unexpected in our data and in fact for a run which covers several 100 cm^{-1}, changes

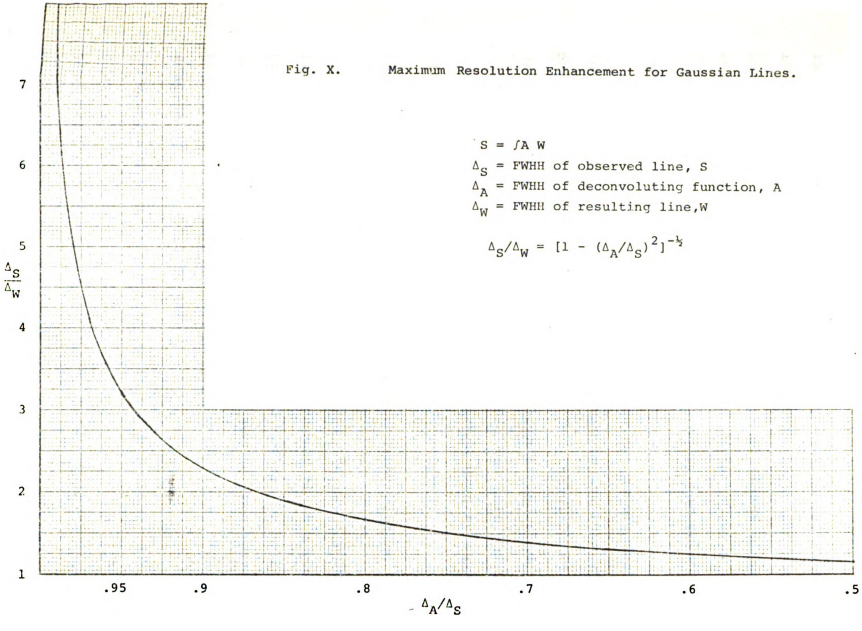


Fig. X. Maximum Resolution Enhancement for Gaussian Lines.

$S = \int A\ W$

Δ_S = FWHH of observed line, S

Δ_A = FWHH of deconvoluting function, A

Δ_W = FWHH of resulting line, W

$$\Delta_S/\Delta_W = [1 - (\Delta_A/\Delta_S)^2]^{-\frac{1}{2}}$$

in Δ_A/Δ_S by more than 10% can occur because the grating in our spectrometer is driven linearly in angle and not in frequency. Also variations in the half widths of the spectral lines of approximately 5% can be seen over a frequency range of 1 cm^{-1} which is caused by the driving train of the monochromator.

Even though our spectral lines are not purely Gaussian in shape, Eq.(IV-9) gives an upper limit to the resolution enhancement possible by the method of deconvolution we are using. In actual practice we have obtained resolution enhancements of approximately 2.5. This has been possible after making several changes in the method used by Jansson et.al. which we have adapted to our minicomputer.

Point Simultaneous vs. Point Successive Deconvolution

The summation in Eq.(IV-7) is over only data points from the previous iteration and is referred to as a point simultaneous method. Jansson chose to modify the method in order to obtain faster convergence and to save memory space required for the program in the computer, so that instead of Eq.(IV-7), he used

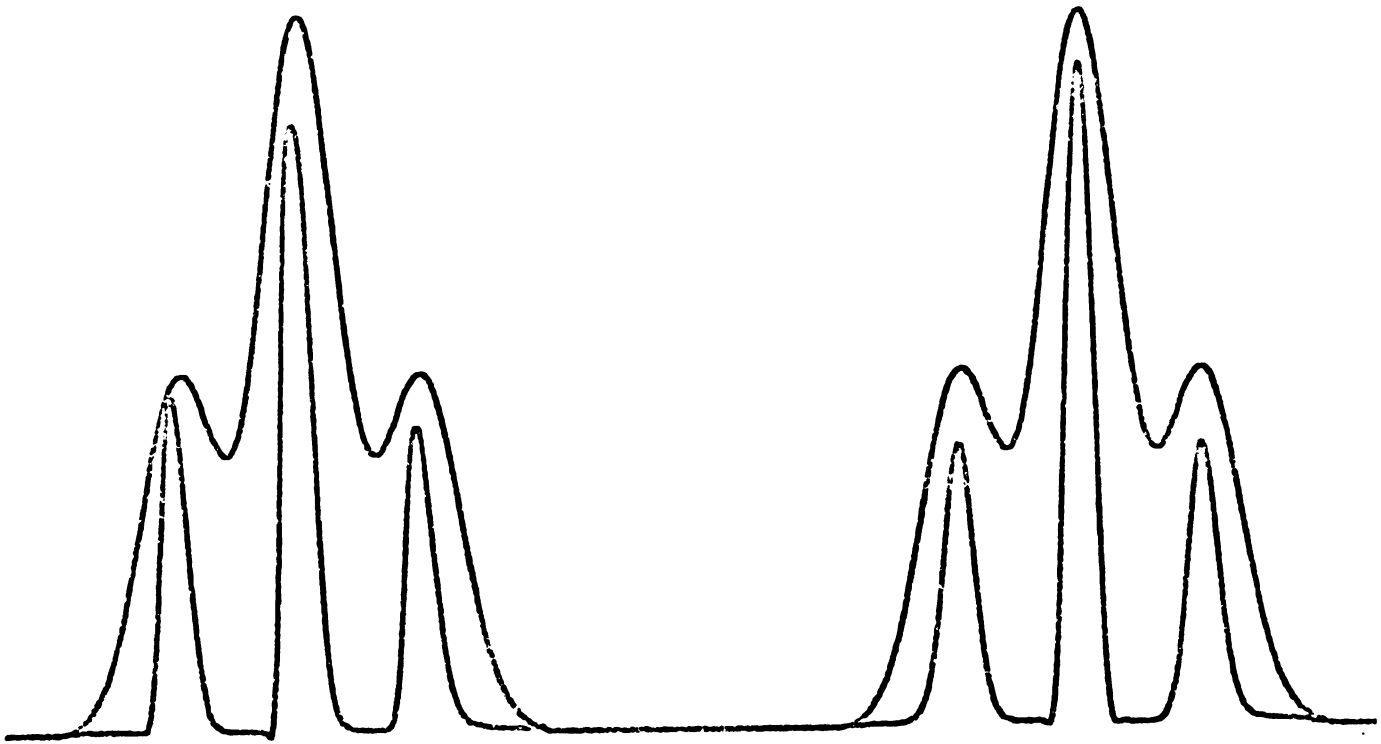
$$W_i(n) = W_i(n-1) + \alpha(y_i)\left[S_i - \sum_{j=-m}^{j=-1} A_{-j} W_{i+j}(n) - \sum_{j=0}^{j=m} A_{-j} W_{i+j}(n-1)\right] \quad \text{(IV-10)}$$

which is referred to as a point successive method.

The two methods as given by Eq.(IV-7) and (IV-10) behave quite differently. Because the point successive method involves an integral over results from both the last iteration and the present iteration,it tends to conserve the area from iteration to iteration under the curve W_n nearly independent of the value of b in Eq. (IV-8). As one approaches a peak the method changes the ordinates to increasing values, thereby increasing the area under the peak. That increased area is then added into the summation for the next data point, resulting in a proportionately smaller change in its value. Hence the centroid of the peak is moved to decreasing abscissa values.

The first few iterations move the peak centroid away from its true value; later iterations, as convergence is approached, move the peak centroid back towards its true location. For large values of b this peak centroid motion can be quite large. If the number of iterations is not sufficient for convergence, the true peak centroid may remain offset from that of deconvoluted result as shown in Figure XI. Figure XI shows a triplet which has been deconvoluted by a point successive method superimposed with the original triplet which is symmetrical. Also apparent in the figure is the change in symmetry

Fig.XI. Point Successive vs. Point Simultaneous Deconvolution of Triplets.



Original (X 3) and result of point successive deconvolution by Eq.(IV-10).

Original (X 3) and result of point simultaneous deconvolution by Eq.(IV-7).

as the area of the whole multiplet was shifted to the left.

The point simultaneous method conserves peak centroids throughout the many iterations, but does not conserve the area under the peaks. That is, for large values of b in Eq.(IV-8), the area under the curve W_n can be drastically different from that of the original curve, S, and the area may be set into wild oscillations in magnitude from one iteration to another. To prevent such oscillations from beginning, small values of b must be used, and as a result more iterations are required to obtain convergence. We have found additional ways of changing the method, such that the oscillations are reduced.

Quadratic Relaxation

The discontinuity in the triangular over-relaxation factor given by Eq.(IV-8) tended to increase the probability of oscillations. By changing the shape of this factor from triangular to quadratic, i.e. by using

$$\alpha(y_i) = 4b(y_i - y_i^2) \qquad \text{(IV-11)}$$

and thereby eliminating the discontinuity and flattening the "top" of α, larger values of b could be used, resulting in faster convergence. Figure IX,page 50, demonstrates the shape of this function.

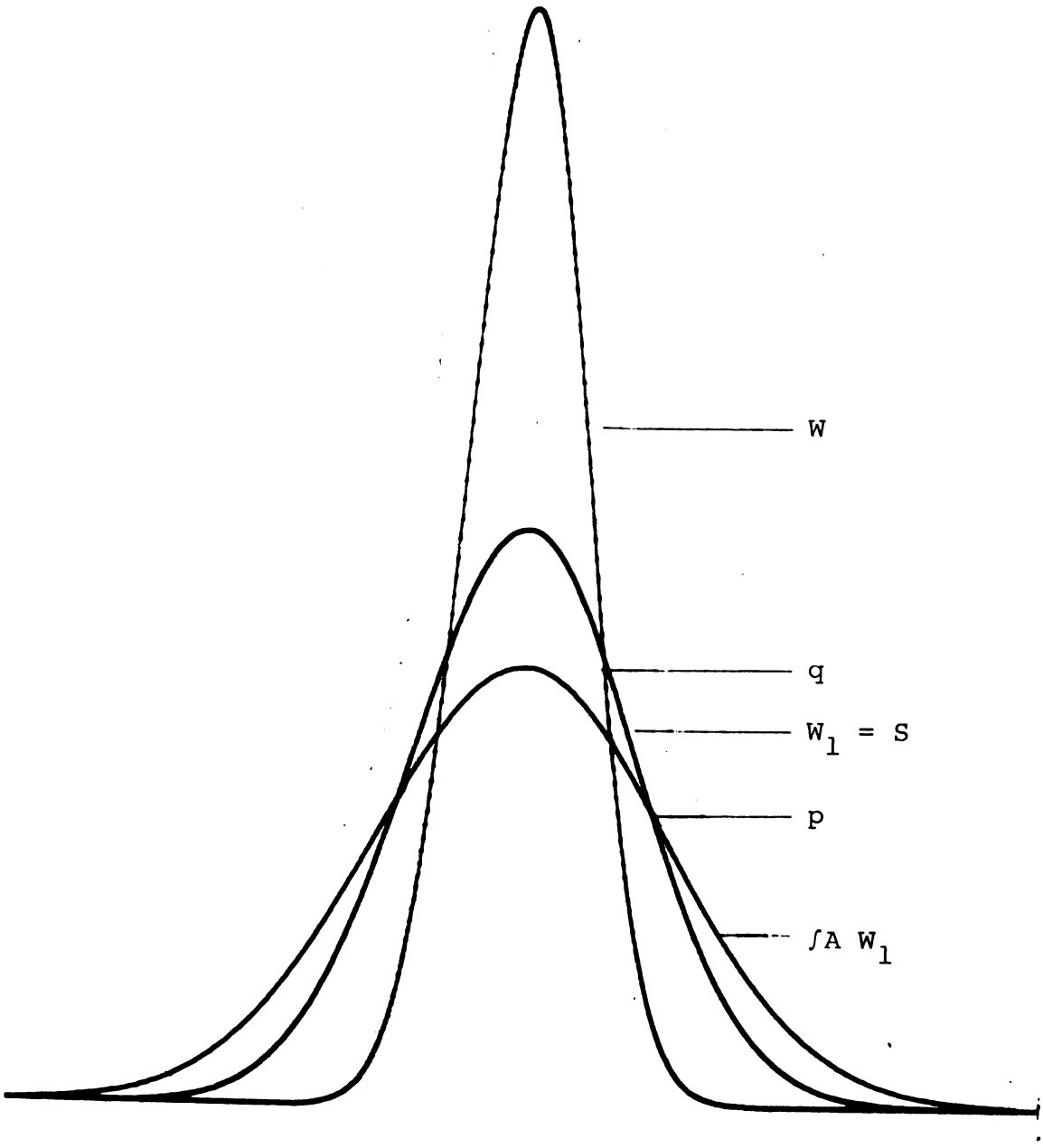
The value of α which is used to determine the value of the data point W_n from Eq.(IV-7),corresponding to the point marked x,on the Figure is as shown. The value of y in Eq.(IV-11) is the ordinate value at the point to be calculated taken from the result of the previous iteration. Hence the curve of the spectral line shown in the Figure must be that of the function W_{n-1} for the nth iteration.

Normalization

Let us now consider Eq.(IV-7) in more detail. From Figure XII, a plot of S, W, and $\int AW_1$,where A and S are Gaussian lines, one can readily see that on the first iteration the direction of change in the ordinate values, i.e. $(S - \int AW_1)$, will be wrong between the points p, where curves S and $\int AW_1$ cross,and q, where curves W and S cross. Eq.(IV-7) will then yield W_2 which passes through point p rather then point q. Since point p is farther out into the wing of the line than point q is,and because the value of α increases as one approaches the peak of the line, the area under W_2 will be greater than the area under S.

If one knows point q, then the curve $\int AW_1$ could be scaled before subtraction to pass through point q, and point q would become an invariant. Since point q should be in the result of deconvolution, the result of the first iteration should have a line shape closer to that

Fig.XII. A Plot of S, W, and $\int A\ W_1$ for Gaussian Lines.



The curve $W_2 = W_1 + (S - \int A\ W_1)$, which is not shown, will pass through point p, whereas, it is desirable for W_2 to pass through point q, since q is a point in the expected deconvoluted result, i.e. W.

of the desired result, i.e. W, and convergence should proceed at a faster rate. For Gaussian lines the necessary scaling factor can be calculated in terms of the resolution enhancement, for determining W_2. But for subsequent iterations the scaling factor is very difficult to determine. An alternative to using a scaling factor for the integral $\int AW_1$, which has a similar effect, is to scale W_2, or more generally, W_n, to the area of S. The scaling can be done by the computer at the time of calculating the next pass and is not difficult to do. In this way, i.e. using Eq.(IV-7) and scaling the results of each pass before making the next pass, the peak centroids and the area can be conserved.

Smoothing During the Time of Deconvolution

We have programmed the deconvolution process on a PDP-12 computer which has a twelve bit word length. The original data and the results of each iteration are stored as a fixed point number whose magnitude is generally between 0 and 1048_{10} (these values correspond to 0% absorption and 100% absorption respectively). Hence each data point is truncated before it is stored and truncation errors show up in the results. These errors appear as high frequency noise, which do not grow in magnitude unless large values of b are used. This "noise" does not

seem to remain "fixed" relative to the spectrum, but rather changes with each pass. However if the result of each pass is smoothed or even the result of every few passes is smoothed, then this high frequency "noise" is smoothed to lower frequency ripples close to the frequency of the deconvoluted lines. The ripples are enhanced in later iterations or passes and becomes a permanent part of the result. Therefore we do not smooth the results between passes except once or twice when close to convergence.

Conclusion

Our goal has been to obtain the maximum resolution enhancement with dependable results. To do this we need to use an "instrument function",A, whose half-width is a few percent smaller than the half-width of the observed lines, S. Since our spectrometer does not give us a symmetrical line, we prefer to use the narrowest smooth singlet which appears in the observed lines and has the characteristic line shape. This line can be made narrower by deconvoluting it with a narrow Gaussian function.

The spectrum is deconvoluted using point simultaneous, Eq.(IV-7), quadratic over-relaxation, Eq.(IV-11), method with normalization of the results between each iteration and smoothing of the results at completion of approximately

the sixth iteration and the twelfth iteration when convergence is nearly reached. Small values of b are used to keep the results from"blowing up", i.e. 3,1,1,1,6,1,1 etc. Resolution enhancements of approximately 2.5 have been obtained with reasonable results.

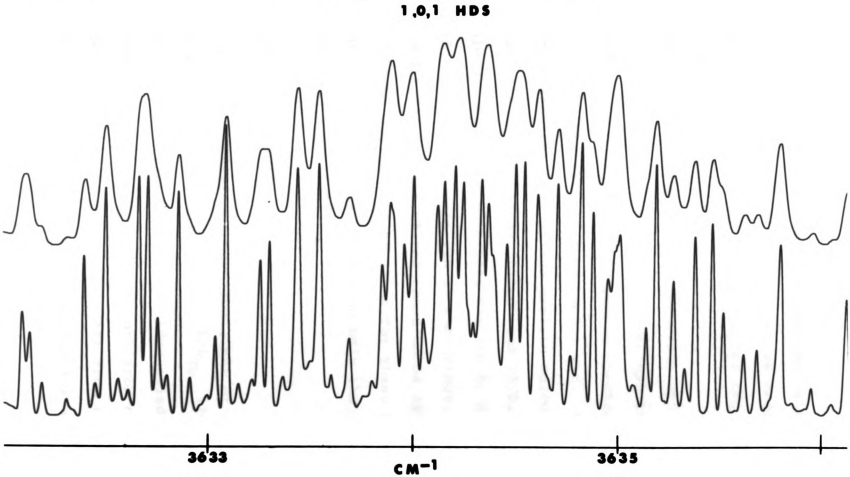
CHAPTER V

DATA ANALYSIS

The spectra of HDS and D_2S were recently run in the region from 3520 cm^{-1} to 3930 cm^{-1}, which includes the (1,0,1) and the (0,2,0) bands of HDS and the (2,0,0) and the (1,0,1) bands of D_2S, as well as some weaker bands which have not yet been identified. These spectra have been digitized and recorded on magnetic tape, digitally smoothed, baseline adjusted, and deconvoluted by the methods outlined in Chapters III and IV. The lines are now in various stages of measurement and analysis.

Figure XIII is a picture of the Q-branch of the (1,0,1) band of HDS mentioned above as it appears before and after deconvolution. It is typical of the resolution enhancement we obtain by deconvolution on the minicomputer. The line width of the original spectrum is approximately 0.05 cm^{-1} and that of the result after deconvolution is approximately 0.02 cm^{-1}. The maximum resolution for the grating in this region is 0.024 cm^{-1}; but the measured maximum resolution for the grating is only 70% of the theoretical resolution.[37] Hence the deconvolution has

Fig.XIII. The Q-Branch of the $\nu_1+\nu_3$ Band of HDS Deconvoluted.



narrowed the line width beyond that theoretically possible for the grating. This implies that we have also removed by deconvolution part of the Doppler and collision (pressure) broadening effects.

The computer programs ICDFIT, ISPECFIT, and SPECFIT2 have been used in the analysis of infrared spectra which were run before we could digitally record spectra. We include in this work three of those bands, viz. the (2,0,0) (Te-H stretch) band of the prolate molecule HDTe and the Coriolis coupled bands (1,0,0) and (0,0,1) of the oblate molecule H_2S. The HDTe band was run by N. K. Moncur and the H_2S bands were run by the author. The running conditions for all of the these bands are listed in Table V. The assignments of lines for these bands was done by Prof. T. H. Edwards and so only the results will be included here.[39,40]

The (2,0,0) Band of HDTe

The HDTe band contains absorption lines of the five different isotopes of Te, viz. ^{130}Te, ^{128}Te, ^{126}Te, ^{125}Te, and ^{124}Te. Over 900 transitions were identified and used to determine the molecular constants both from combination differences and from line fits. The data from each isotope was first fit separately and then the data for all of

Table V. Experimental Conditions.

	H_2S (37^o - 32.5^o) ν_1 and ν_3	HDTe (51^o - 46^o) $2\nu_1$
Grating	300 groves/mm 1st Order Single Pass	300 groves/mm 2nd Order Single Pass
Calibration	N_2O (1,2,0) HCl (1-0)	HCl (2-0) 3rd Order CO (2-0) 2nd Order
Detector	PbS-type P @77^oK	PbS-type O
Date of Run	#1 Chart IR-8/21/67 #2 ChartIIR-8/23/67	#1 Chart 2-3/18/73 #2 Chart 5
Source	Carbon Rod 2770^oK	300 watt Zr Arc
Pressures(torr)	#1 - 50,60 #2 - 54	3.5 mixture ≃.6 for HDTe
Path Length	6.4 m Multiple Traverse Cell	6.6 m White Cell
Chart Resolution	≃0.09 cm^{-1}	≃0.03 cm^{-1}
Calibration Fit	0.002	
Temp. of Gas	25^oC	-50^oC

the isotopes were fit simultaneously.

We have obtained a very good fit of the ground state combination differences for molecular isotope $HD^{130}Te$ for each of the three Hamiltonians given in Chapter I. The prolate form of the planar Hamiltonian, Eq.(I-3) was used; the KFC Hamiltonian, Eq.(I-5), with $T_6 = 0$ and $H_6 = 0$ was used; and the Watson Hamiltonian, Eq.(I-6), through second order was used. Each of them fit the data to approximately 0.004 cm^{-1}, but the planar Hamiltonian converged to the fit in the second iteration through the fitting process (see Chapter II, p.26), while the other Hamiltonians required more iterations. The constants obtained from the planar fit and the KFC fit are listed in Table VI.

The transitions and the ground state combination differences for all of the isotopes were fit simultaneously by the method described on pp.27-28 to the Watson Hamiltonian to second order constants. We found that the isotopes could be simultaneously fit by allowing a quadratic dependence of ν_0 on mass , a linear dependence of the rotational constants on mass, and treating the coefficients of the fourth-power angular momentum terms to be independent of mass. The coefficients of the sixth-power angular momentum terms were not found statistically significant. A very good fit of the 917 identified transitions was

Table VI. Ground State Constants of $HD^{130}Te$.

Planar Hamiltonian			cm^{-1}	KFC Hamiltonian $\tilde{T}_6 = 0$			cm^{-1}
A	6.1689_6	±	0.0002*	$\tilde{Z}$	6.1695_2	±	0.0003
B	3.1106_1	±	0.0003	$\tilde{X}$	3.1107_2	±	0.0003
C	2.0421_7	±	0.0002	$\tilde{Y}$	2.0416_8	±	0.0002
τ_{aaaa}	-0.00090_2	±	0.00001	$\tilde{T}_1$	-0.000058_5	±	0.000005
τ_{bbbb}	-0.00022_7	±	0.00002	$\tilde{T}_2$	-0.0000131_7	±	0.0000005
τ_{aabb}	0.00002_9	±	0.00004	$\tilde{T}_3$	-0.000224_8	±	0.000003
τ_{abab}	-0.00112_4	±	0.00003	$\tilde{T}_4$	-0.00010_1	±	0.00001
				$\tilde{T}_5$	-0.000496_4	±	0.000009

$\kappa = -0.482$

Total # of Points Fit =249

Standard Deviation of Fits=0.004 cm^{-1}

*95% Simultaneous Confidence Interval equals four times the standard errors of the coefficients.

Table VII. Molecular Constants for $2\nu_1$ of HDTe.

All isotopes were fit simultaneously relative to $HD^{130}Te$.

Watson Hamiltonian	Ground State	cm^{-1}	Upper State	cm^{-1}
$\tilde{Z}^*$	6.1693_{55}	± 0.0005	5.8386_{94}	± 0.0003
$\tilde{X}^*$	3.1108_{44}	± 0.00024	3.1104_{97}	± 0.00045
$\tilde{Y}^*$	2.0413_{69}	± 0.00034	2.0059_{28}	± 0.00024
$\tilde{D}_1$	-0.000034_{78}	± 0.0000024	-0.000034_{38}	± 0.000002
$\tilde{D}_2$	-0.000495_1	± 0.000009	-0.000498_4	± 0.000008
$\tilde{D}_3$	0.000305_5	± 0.000008	0.000310_4	± 0.000006
$\tilde{D}_4$	-0.000021_{85}	± 0.0000025	-0.000021_{78}	± 0.000002
$\tilde{D}_5$	-0.00030_{81}	± 0.00001	-0.00030_{34}	± 0.00001
ξ^z	0.00043_3	± 0.00008	0.00039_9	± 0.00006
ξ^x	0.0003_{47}	± 0.00014	0.0003_{33}	± 0.00014
ξ^y	0.00020_1	± 0.00007	0.00019_6	± 0.00007
ν_o	4063.971_0	± 0.0026		
ξ^m	0.110_0	± 0.002		
ξ^{mm}	0.0009	± 0.0004		

Total # Lines Fit = 917

Standard Deviation of Fit = 0.0035 cm^{-1}

obtained, viz. $\simeq 0.0035 cm^{-1}$. The assigned transitions are listed in Appendix V and the constants obtained for the fit are listed in Table VII. The mass dependence, Δm, as required for Eq.(II-10) is given by

Δm = 130 - atomic weight of the Te isotope..

The constant ξ^X is the variation in $\tilde{X}^*$, whereas ξ^m is the linear mass dependence of the band center.

The (1,0,0) and (0,0,1) Bands of H_2S

In contrast to the HDTe spectra, only lines due to $H_2{}^{32}S$ were analyzed in the Coriolis coupled (1,0,0)-(0,0,1) bands.† Since H_2S is an oblate molecule, the III^r representation was used. The planar Hamiltonian was evaluated in this representation and used to fit the coupled states. Attempts were made to fit the ground state combination differences to the Watson Hamiltonian and to the KFC Hamiltonian with $T_6 = 0$, but they were not successful, apparently implying that the condition given in Table II, i.e. $X \neq Y$, is not met to the order of magnitude necessary (see comment on p.9), Hence the reason for using the planar Hamiltonian. Table VIII lists the constants obtained for the two bands and Appendix VI lists the assigned transitions. The ground state constants given by Snyder[5] were used in fitting the transitions.

†See Figure XIV.

Table VIII. Molecular Constants for ν_1 and ν_3 of H_2S.

Planar Hamiltonian	ν_1	cm^{-1}	ν_3	cm^{-1}
ν_o	2614.413_{61}	± 0.006 *	2628.54_{73}	± 0.06
A	10.204_{08}	± 0.005	10.145_{79}	± 0.009
B	8.888_{82}	± 0.005	8.926_{47}	± 0.004
C	4.661_{61}	± 0.002	4.670_{21}	± 0.003
τ_{aaaa}	-0.0079_{28}	± 0.0001	-0.0063_{86}	± 0.0007
τ_{bbbb}	-0.00476	± 0.00007	-0.0043_{93}	± 0.0004
τ_{aabb}	0.00457_{8}	± 0.00007	0.005_{308}	± 0.001
τ_{abab}	-0.00140_{5}	± 0.00006	-0.0023_{8}	± 0.0006
H_K	$-5.5X10^{-8}$	± $0.4X10^{-8}$	$-1.5X10^{-7}$	± $0.6X10^{-7}$
# Lines	194		60	

Coriolis Constants:

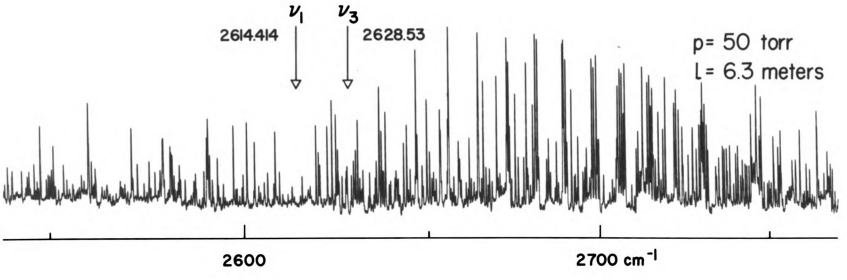
G_z	0.05 ± 0.04	cm^{-1}
G_{xy}	-0.269_{6} ± 0.003	cm^{-1}

Total # Lines Fit= 254

Standard Deviation of Fit= 0.006 cm^{-1}

*95% Simultaneous Confidence Interval equals six times the standard errors of the coefficients.

Fig.XIV. Survey Spectra of ν_1 and ν_3 of H_2S



CHAPTER VI

CONCLUSION

This work described the vibration-rotation Hamiltonians recently developed for the asymmetric-top molecule and outlines how they can be used in fitting observed molecular infrared spectra for molecules of any symmetry whatsoever. Computer programs were written which put this theory into practice for observed data. The programs were then used to successfully fit three different Hamiltonians to the ground state energy level differences of the prolate XYZ molecule, HDTe. The Watson Hamiltonian was used to fit simultaneously all five of the molecular isotopes which were observed in the (2,0,0) band of HDTe. The planar Hamiltonian was used to fit the Coriolis coupled (1,0,0) - (0,0,1) bands of the oblate XYX molecule, H_2S.

With the number of Hamiltonians now available to the infrared spectroscopist the "best" Hamiltonian for different molecules may have to be found. We have not found advantages in using the "reduced"Hamiltonians,as compared with using the planar Hamiltonian, for triatomic molecular spectra. In fact the planar Hamiltonian has the

advantage of not having the restrictive conditions on the rotational constants and also fits the observed data as well, if not better than do the "reduced" Hamiltonians and uses fewer constants to make the fit. Using several Hamiltonians to fit the same data may be helpful in finding lines which are incorrectly assigned.

This work also outlined in detail a process of digitally smoothing and deconvoluting spectra, which was programmed on a PDP-12 minicomputer. A number of interesting improvements were made in the method of deconvolution among which are "quadratic over-relaxation," desirability of point simultaneous deconvolution, and normalization in deconvolution. Infrared bands of HDS and D_2S were processed by the minicomputer using the programs developed, and enhanced the resolution of the spectra of those bands by as much as 2.5 over that of the original data.

All of the computer programs for the minicomputer were written in assembly level language so that the full power of the computer could be utilized. The programs are capable of processing large volumes of points in a reasonable length of time, e.g. approximately 45 minutes per pass for 225,000 points in the deconvolution process. The data can be monitored continuously by the operator during all operations. He can take full control over

the value of every data point in every step of an operation, or he can allow the program to automatically control the operation.

These programs should facilitate the finding of new methods and the best procedure in the deconvolution process. Currently ten to thirteen iterations are necessary for convergence in deconvolution; with the right procedure this number of iterations may be reduced. The minicomputer facility,if properly used, could be developed into an even more useful tool.

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APPENDICES

APPENDIX I

NONVANISHING ANGULAR MOMENTUM MATRIX ELEMENTS

Listed below are the nonvanishing matrix elements for the angular momentum operators of the various Hamiltonians evaluated in the symmetric top basis $\psi(J,K)$.

$$\langle K|P_x|K\pm1\rangle = \pm i/2\ [f-K(K\pm1)]^{\frac{1}{2}}$$

$$\langle K|P_y|K\pm1\rangle = 1/2\ [f-K(K\pm1)]^{\frac{1}{2}}$$

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

$$j = f-K^2$$

$$g_{\pm} = [(J\mp K-1)(J\mp K)(J\pm K+1)(J\pm K+2)]^{\frac{1}{2}}$$

$$m_{\pm} = [(J\mp K-2)(J\pm K+3)(J\mp K-3)(J\pm K+4)]^{\frac{1}{2}} g_{\pm}$$

The diagonal terms, $\langle K|\chi^i|K\rangle$ where χ^i is equal to:

$$P_z = K$$

$$P_y^2 = P_x^2 = \tfrac{1}{2}j$$

$$P^2 = f$$

$$P_z^2 = K^2$$

$$(P_y^2P_z^4 + P_z^4P_y^2) = (P_x^2P_z^4 + P_z^4P_x^2) = jK^4$$

$$P_y^4 = P_x^4 = (3j^2-2j+3K^2)/8$$

$$P^4 = f^2$$

$$P_z^4 = K^4$$

$$P^2P_z^2 = fK^2$$

$$(P_x^2P_z^2 + P_z^2P_x^2) = (P_y^2P_z^2 + P_z^2P_y^2) = jK^2$$

$$(P_x^2P_y^2 + P_y^2P_x^2) = (j^2+2j-3K^2)/4$$

$$P^2(P_x^2 - P_y^2) = 0$$

$$P_y^6 = P_x^6 = (5j^3-10j^2+25jK^2+8j-20K^2)/16$$

$$P^6 = f^3$$

$$P_z^6 = K^6$$

$$P^4P_z^2 = f^2K^2$$

$$P^2P_z^4 = fK^4$$

$$(P_z^2P_y^4 + P_y^4P_z^2) = (P_z^2P_x^4 + P_x^4P_z^2) = K^2(3j^2-2j+3K^2)/4$$

$$(P_x^2P_y^4 + P_y^4P_x^2) = (P_y^2P_x^4 + P_x^4P_y^2) = (j^3+6j^2-19jK^2-8j+20K^2)/8$$

$$(P_x^2P_z^2P_y^2 + P_y^2P_z^2P_x^2) = \tfrac{1}{2}j^2K^2-[(K+2)^2g_+^2 + (K-2)^2g_-^2]/8$$

The off-diagonal terms, $\langle K|\chi^i|K\pm2\rangle$ where χ^i is equal to:

$$P_y^2 = -P_x^2 = \tfrac{1}{4}g_\pm$$

$$(P_xP_y + P_yP_x) = \pm i/2\ g_\pm$$

$$P_y^4 = -P_x^4 = \tfrac{1}{4}(j-2\mp 2K)g_\pm$$

$$(P_y^2P_z^2 + P_z^2P_y^2) = -(P_x^2P_z^2 + P_z^2P_x^2) = \tfrac{1}{2}(K^2\pm 2K+2)g_\pm$$

$$P^2(P_x^2 - P_y^2) = -\tfrac{1}{2}fg_\pm$$

$$[P_z^2(P_x^2 - P_y^2) + (P_x^2 - P_y^2)P_z^2] = -(K^2\pm 2K+2)g_\pm$$

$$P_y^6 = -P_x^6 = [15j^2\mp 60jK-70j+105K(K\pm 1) \pm 125K+136]g_\pm/64$$

$$(P_x^2P_y^4 + P_y^4P_x^2) = -(P_y^2P_x^4 + P_x^4P_y^2) = (j^2\mp 4jK+6j-41K^2\mp 102K-72)g_\pm/32$$

$$(P_y^2P_z^4 + P_z^4P_y^2) = -(P_x^2P_z^4 + P_z^4P_x^2) = \tfrac{1}{4}[K^4+(K\pm 2)^4]g_\pm$$

$$(P_z^2P_y^4 + P_y^4P_z^2) = -(P_z^2P_x^4 + P_x^4P_z^2) = \tfrac{1}{2}(K^2\pm 2K+2)[f-(K^2\pm 2K+2)]g_\pm$$

$$P^4(P_x^2 - P_y^2) = -\tfrac{1}{2}f^2g_\pm$$

$$P^2[P_z^2(P_x^2 - P_y^2) + (P_x^2 - P_y^2)P_z^2] = -(K^2\pm 2K+2)fg_\pm$$

$$[P_z^4(P_x^2 - P_y^2) + (P_x^2 - P_y^2)P_z^4] = -[K^4+(K\pm 2)^4]g_\pm/2$$

The off-diagonal terms, $\langle K|\chi^i|K\pm 4\rangle$ where χ^i is equal to:

$$P_y^4 = P_x^4 = m_\pm/16$$

$$(P_x^2P_y^2 + P_y^2P_x^2) = -m_\pm/8$$

$$P_y^6 = P_x^6 = (3j \mp 12K-20)m_\pm/32$$

$$(P_z^2P_y^4 + P_y^4P_z^2) = (P_z^2P_x^4 + P_x^4P_z^2) = (K^2\pm 4K+8)m_\pm/8$$

$$(P_x^2P_z^2P_y^2 + P_y^2P_z^2P_x^2) = -(K\pm 2)^2m_\pm/8$$

$$(P_x^2P_y^4 + P_y^4P_x^2) = (P_y^2P_x^4 + P_x^4P_y^2) = (-j+4K+4)m_\pm/16$$

The off-diagonal terms, $\langle K|\chi^i|K\pm6\rangle$ where χ^i is equal to:

$$P_y^6 = -P_x^6 = [(J\mp K-5)(J\mp K-4)(J\pm K+5)(J\pm K+6)]^{\frac{1}{2}} m_\pm/64$$

$$(P_x^2P_y^4 + P_y^4P_x^2) = -(P_y^2P_x^4 + P_x^4P_y^2) = -[(J\mp K\pm5)(J\mp K-4)(J\pm K+5)(J\pm K+6)]^{\frac{1}{2}} m_\pm/32$$

APPENDIX II

JACOBI METHOD OF DIAGONALIZATION

Consider a Hermitian matrix A, which we desire to diagonalize

$$A = \begin{vmatrix} a_{11} & a_{12} & a_{13} & \cdots & a_{1N} \\ a_{21} & a_{22} & \cdots & & \\ a_{31} & \cdots & & & \\ \vdots & & & & \\ a_{N1} & & & & \end{vmatrix}$$

If for $i \neq j$, there exists an $|a_{ij}|$ much greater than any other off diagonal element, we may neglect all but a_{ij} and diagonalize the two by two matrix

$$\begin{vmatrix} a_{ii} & a_{ij} \\ a_{ji} & a_{jj} \end{vmatrix} \equiv \begin{vmatrix} c_1 & b \\ b^* & c_2 \end{vmatrix}$$

The eigenvalues of a Hermitian matrix are given by

$$\text{Determinate } (a_{mn} - \lambda_r \gamma_{mn}) = 0 \qquad \text{(A-II-1)}$$

The eigenvectors are given by

$$\sum_{\ell} (a_{n\ell} - \lambda_r \gamma_{n\ell}) s_{\ell r} = 0$$

where $\begin{vmatrix} s_{1r} \\ s_{2r} \\ \vdots \\ s_{Nr} \end{vmatrix}$ is the eigenvector.

It then follows that the unitary transformation matrix is

$$S = \begin{vmatrix} s_{11} & s_{12} & s_{13} & \cdots & s_{1N} \\ s_{21} & s_{22} & \cdots & & \\ s_{31} & \cdots & & & \\ \vdots & & & & \\ s_{N1} & & & & \end{vmatrix}$$

which diagonalizes A, i.e. $S^{\dagger} A\, S = D$ where D is the matrix of eignvalues, which we will denote by λ. For our two by two submatrix Eq.(A-II-1) becomes

$$(c_1 - \lambda)(c_2 - \lambda) - bb^* = 0$$

which has the solutions

$$\lambda_{\pm} = (c_1+c_2)/2 \pm [(c_1-c_2)^2/4 + bb^*]^{\frac{1}{2}} \qquad \text{(A-II-2)}$$

If U is the unitary transformation matrix which diagonalizes the small submatrix

$$U = \begin{vmatrix} \alpha_+ & \alpha_- \\ \beta_+ & \beta_- \end{vmatrix}$$

then we get the four equations which follow from diagonalization

$$(c_1 - \lambda_\pm)\alpha_\pm + b\beta_\pm = 0$$

$$(c_2 - \lambda_\pm)\beta_\pm + b^*\alpha_\pm = 0 \qquad \text{(A-II-3)}$$

From normalization, i.e. $U^\dagger U = 1$, we get

$$\alpha_+^2 + \beta_+^2 = 1$$

$$\alpha_-^2 + \alpha_-^2 = 1$$

$$\alpha_+\alpha_- + \beta_+^*\beta_- = 0 \qquad \text{(A-II-4)}$$

These equations may be solved for α_+, α_-, β_+, and β_- except for an arbitrary phase factor. We will choose that factor so that α_+ and β_- are real.

Let us define

$$R = (c_1-\lambda_+) = (c_1-c_2)/2 - [(c_1-c_2)^2/4 + bb^*]^{\frac{1}{2}} \qquad \text{(A-II-5)}$$

then it follows that

$$(c_2-\lambda_-) = -R$$

and from Eqs.(A-II-4) and (A-II-5) we get

$$\beta_+ = -R\alpha_+/b$$

$$\alpha_- = R\beta_-/b^* \qquad \text{(A-II-6)}$$

Using Eq.(A-II-6) and Eq.(A-II-4) we get

$$\alpha_+ = \beta_- = (1 + R^2/bb^*)^{-\frac{1}{2}}$$

$$\beta_+ = -\alpha_-^* = -(1 + R^2/bb^*)^{-\frac{1}{2}}R/b \qquad \text{(A-II-7)}$$

In summary:

$$U^{\dagger} \begin{vmatrix} c_1 & b \\ b^* & c_2 \end{vmatrix} U = \begin{vmatrix} \lambda_+ & 0 \\ 0 & \lambda_- \end{vmatrix} = \begin{vmatrix} \alpha & -\beta \\ \beta^* & \alpha \end{vmatrix} \begin{vmatrix} c_1 & b \\ b^* & c_2 \end{vmatrix} \begin{vmatrix} \alpha & \beta \\ -\beta^* & \alpha \end{vmatrix}$$

where

$$\lambda_+ = c_1 - R$$

$$\lambda_- = c_2 + R$$

$$\alpha = (1 + R^2/bb^*)^{-\frac{1}{2}}$$

$$\beta = \alpha R/b$$

$$R = (c_1-c_2)/2 - [(c_1-c_2)^2/4 + bb^*]^{\frac{1}{2}}$$

If the condition a_{ij} is much greater than any other off diagonal element does not hold, one may use the above method iteratively to find a series of transformations, each of which will cause the largest remaining off diagonal element to go to zero. The iteration can be carried until the precision desired is obtained. This is the Jacobi method of diagonalization.

Each submatrix in the diagonalization affects other off diagonal elements as well as the elements in the submatrix. Let us now derive that effect.

Consider the 4 x 4 matrix

$$A = \begin{vmatrix} a_{11} & a_{12} & a_{13} & a_{14} \\ a_{21} & a_{22} & a_{23} & a_{24} \\ a_{31} & a_{32} & a_{33} & a_{34} \\ a_{41} & a_{42} & a_{43} & a_{44} \end{vmatrix}$$

Let us choose a rotation involving the a_{24} term. Then

$$S_1 = \begin{vmatrix} 1 & 0 & 0 & 0 \\ 0 & \alpha & 0 & \beta \\ 0 & 0 & 1 & 0 \\ 0 & -\beta^* & 0 & \alpha \end{vmatrix} ; \quad S_1^{-1} = S_1^\dagger = \begin{vmatrix} 1 & 0 & 0 & 0 \\ 0 & \alpha & 0 & -\beta \\ 0 & 0 & 1 & 0 \\ 0 & \beta^* & 0 & \alpha \end{vmatrix}$$

so that

$$A' = S_1^\dagger A S_1 = \begin{vmatrix} a_{11} & (\alpha a_{12} - \beta^* a_{14}) & a_{13} & (\beta a_{12} + \alpha a_{14}) \\ (\alpha a_{21} - \beta a_{41}) & (a_{22} - R) & (\alpha a_{23} - \beta a_{43}) & 0 \\ a_{31} & (\alpha a_{32} - \beta^* a_{34}) & a_{33} & (\beta a_{32} + \alpha a_{34}) \\ (\beta^* a_{21} + \alpha a_{41}) & 0 & (\beta a_{23} + \alpha a_{43}) & (a_{44} + R) \end{vmatrix}$$

Initially the transformation matrix is the identity matrix.

So that initially

$$A = S_0^\dagger A S_0 \ ,$$

then

$$A' = S_1^\dagger S_0^\dagger A S_0 S_1 \ ,$$

and iterating

$$A'' = S_2^\dagger A' S_2 = S_2^\dagger S_1^\dagger S_0^\dagger A S_0 S_1 S_2$$

so that finally

$$A_T = S^{\dagger} A\, S$$

where

$$S = S_0 S_1 S_2 \cdots S_N \ .$$

We see, therefore, for the case at hand, if

$$S_0 = \begin{vmatrix} s_{11} & s_{12} & s_{13} & s_{14} \\ s_{21} & s_{22} & s_{23} & s_{24} \\ s_{31} & s_{32} & s_{33} & s_{34} \\ s_{41} & s_{42} & s_{43} & s_{44} \end{vmatrix} \ ,$$

then

$$S = S_0 S_1 = \begin{vmatrix} s_{11} & (\alpha s_{12} - \beta^* s_{14}) & s_{13} & (\beta s_{12} + \alpha s_{14}) \\ s_{21} & (\alpha s_{22} - \beta^* s_{24}) & s_{23} & (\beta s_{22} + \alpha s_{24}) \\ s_{31} & (\alpha s_{32} - \beta^* s_{34}) & s_{33} & (\beta s_{32} + \alpha s_{34}) \\ s_{41} & (\alpha s_{42} - \beta^* s_{44}) & s_{43} & (\beta s_{42} + \alpha s_{44}) \end{vmatrix}$$

Generalizing from the example we get the relations for a rotation involving the $a_{\ell k}$ term ($\ell < k$).

$$s'_{ij} = \begin{cases} (\alpha s_{i\ell} - \beta\, s_{ik}) & \text{if } j = \ell \\ (\beta s_{i\ell} + \alpha s_{ik}) & \text{if } j = k \\ s_{ij} & \text{if } j \neq \ell, k \end{cases}$$

$$a'_{ij} = \begin{cases} 0 & \text{if } i = \ell,k;\ j = \ell,k \\ (a_{\ell\ell}-R) & \text{if } i = j = \ell \\ (a_{kk}+R) & \text{if } i = j = k \\ (\alpha a_{i\ell}-\beta^* a_{ik}) & \text{if } j = \ell;\ i \neq \ell,k \\ (\beta a_{i\ell}+\alpha a_{ik}) & \text{if } j = k;\ i \neq \ell,k \\ a'^*_{ji} & \text{if } i = \ell,k;\ j \neq \ell,k \\ a_{ij} & \text{if } i \neq \ell,k;\ j \neq \ell,k \end{cases}$$

If computerized, the diagonalization cannot be improved once λ_+ and λ_- do not change, that is when

$$R \leq c_2 \cdot 2^N$$

where $c_1 > c_2$ and N is the number of bits which store the mantissa of c_2 in the computer. Eq.(A-II-5) can be written as

$$R = [(c_1-c_2)/2][1 - (1 + 4bb^*/(c_1-c_2)^2)^{\frac{1}{2}}]$$

Since $R \to 0$ as $bb^* \to 0$, for small R

$$R \simeq -bb^*/(c_1-c_2)$$

Therefore, the most natural place to stop diagonalization is when

$$bb^* < c_2(c_1-c_2) \cdot 2^{-N}$$

for all b's.

The necessary calculations are

		mode
1)	BAB = bb^*	real
2)	CDF = $(c_1-c_2)/2$	real
3)	R = CDF - $[(CDF)^2 + BAB]^{\frac{1}{2}}$	real
4)	ALFA = $(1 + R^2/BAB)^{-\frac{1}{2}}$	real
5)	BETA = (R)(ALFA)/b	complex
6)	c_1-R	real
7)	c_2+R	real
8)	ALFA * S(I,L)-S(I,K) * CONJG(BETA)	complex
9)	BETA * S(I,L)+S(I,K) * ALFA	complex
10)	BETA * A(I,L)+A(I,K) * ALFA	complex
11)	ALFA * A(I,L)-A(I,K) * CONJG(BETA)	complex

APPENDIX III

LISTING OF PROGRAM ISPECFIT

```
      PROGRAM ISPECFIT                                                  I>0
      COMMON/BLKP/P(19,4,25),PI(2,25),NP(3),PH(4,25)
      COMMON/BLKAP/AP(15,50 )
      COMMON /PMAK/HAM,VIBZ,VIBXY,MSPM,LPS
      COMMON /BL5/NODATA,OBSNO,AVEWHT,NOVAR,LNOUT,SIGDIF ,NFIT,
     1XOUT,IFCOEN,IFSTEP,IFPRED,SIGMAY1,DELSIG
      DIMENSION IHEAD(10)
      COMMON A(25,25),S(25,25),AS(600),JIN(2,2500),INDEX,NVAR(24,2),IBN
      COMMON/BLK1/PAR(19,4),V (3),NPAR(24,4)
      EQUIVALENCE (NPAR(1),NPAR1),(NPAR(49),NPAR2)
      EQUIVALENCE (PAR(1),PAR1),(PAR(20),PGD1),(PAR(39),PAR2),(PAR(58),
     1PGD2)
      DIMENSION DATA(36),CONST(30)
      COMMON/BL3/WT(1 00),DELPAR(35)
      TYPE INTEGER HAM
C CONSTANTS WHICH ARE DEPENDENT ON THE MAXIMUM ARRAY  IN COMMON BLKP
      NODATA=0
      NMAX=25
      JMIN=0 $ JMAX=49
C  35 PARAMETERS MAY BE VARIED
      ENDFILE 50
      ENDFILE 51
      ENDFILE 52
      DO 4 I=1,76
    4 PAR(I)=0.
  115 CONTINUE
      SIGMA=0.
      NFIT=1
C MSPM MUST BE GE 1 TO WRITE OUT MATRIX ELEMENTS IN PMAKE,ITS VALUE IS THE (
C  NUMBER PMAKE WRITES THE MATRIX ELEMENTS ONTO
      MSPM=0
      REWIND 50
      REWIND 51
      REWIND 52
C
      READ(5,500,IFHEAD,IFHAM,IFPA1,IFPD1,IFPA2,IFPD2,IFNOVAR,IFDATA,IPRT,
     1IFPAV,IFPRED,IFCOEN,IFSTEP,IFUEL
  500 FORMAT (16I2)
C IFHEAD=1  READ HEADING CARD
C IFHAM=0 READ HAMILTONIAN CARD
C IFPA1=0  READ THREE GROUND STATE PARAMETER CARDS
C IFPD1=0  READ THREE ISOTOPE GRD STATE PAR) CARDS
C IFPA2=0  READ THREE UPPER  STATE PARAMETER CARDS
C IFPD2=0  READ THREE ISOTOPE UPR STATE PAR) CARDS
C IFNOVAR=0 READ VARIABLE CARD
C IFDATA=1  READ FREQUENCY CARDS UNTIL END DATA IS FOUND
C IPRT=1    PRINT THE ENERGY MATRICES
C IFPAV=0,1,2,3  SEE COMMENTS IN FORMEPG
C IFPRED=1  PRINT PREDICTED FREQUENCIES FROM REGRESSION ANALYSIS
C IFCOEN=1 DO NOT PRINT CORRELATION COEFFECIENTS IN REGRESSION
C IFSTEP=1  DO NOT PRINT EACH STEP IN REGRESSION
C IFUEL=0  SET UPPER STATE H,S=TO LOWER STAE H,S
      IF (IFHEAD.NE.0) GO TO 6.8
C
      READ(5,525, (IHEAD(N),N=1,10)
525   FORMAT(10A8)
```

```
608   CONTINUE
      IF (IFHAM.NE. ) GO TO 610
C
      READ(5,530,HAM,NFITS,LNOUT,PARFRAC,SIGDIF,XOUT,BDLN,ISO
  530 FORMAT (3I5,4E5.0,I5)
610   CONTINUE
      IF (HAM.LT.1) HAM=1
      IF (NFITS.EQ. ) NFITS=5
      IF (LNOUT.EQ. ) LNOUT=2
      IF (PARFRAC.EQ. ) PARFRAC=1.0
      IF (SIGDIF.EQ.0) SIGDIF=.02
      IF (XOUT.EQ.0) XOUT=12.
      IF (BDLN.EQ.0) BDLN=10.
      IF (ISO.EQ. ) ISO=130                                          H
      IF (IFPA1.NE. )GO TO 600
C
      READ(5,505, ( PAR(I,1),I=1,19)
600   CONTINUE
      IF (IFPD1.NE. )GO TO 601
C
      READ(5,505, ( PAR(I,2),I=1,19)
  505 FORMAT (3E15. /6E10.0/1 E8. )
  601 CONTINUE
      IF (IFPA2.NE. )GO TO 602
C
      READ(5,506,(PAR(I,3),I=1,3),V (1) (PAR(I,3),I=4,19)
  506 FORMAT (4E15. /6E10.0/1 E8. )
 602  CONTINUE
      IF (IFPD2.NE. )GO TO 603
C
      READ(5,507 ,(PAR(I,4),I=1,3),V0(2),V0(3),(PAR(I,4),I=4,19)
  507 FORMAT (5E15. /6E10.0/1 E8. )
  603 CONTINUE
      NVAR(20,1)=NVAR(20,2)=NVAR(21,1)=NVAR(21,2)=
      DO 12 I=1,19
      DO 12 J=2,4,2
      IJ=J/2
      NVAR(I,IJ)=
      IF (PAR(I,J)) NVAR(I,IJ)=1
   12 CONTINUE
      IF (IFNOVAR.NE. ) GOTO 606
C INDICATES PARAMETERS TO VARY
      READ(5,515,((NPAR(I,J),I=1,24),J=1,4)
  515 FORMAT (24I2)
606   CONTINUE
      NGS=0
      NOVAR=1
      DO 16 J=1,4
      DO 16 I=1,24
      IF(IFUEL.EQ.1)GO TO 14
      IF((I.LT.10).OR.(I.GT.19))GO TO 14
      IJ=(J+1)/2
      IF(IJ.EQ.1)GO TO 22
      K=J-2
      NPAR(I,J)=NPAR(I,K)
      IF(NPAR(I,J).NE.0)NVAR(I,IJ)=1
```

```
      GO TO 16
   22 K=J+2
      NPAR(I,J)=NPAR(I,K)+NPAR(I,J)
   14 IF(NOVAR.GT.35)NPAR(I,J)=0
      IF(NPAR(I,J).EQ.0)GO TO 16
      NPAR(I,J)=NOVAR $ NOVAR=NOVAR+1
      IJ=(J+1)/2 $ NVAR(I,IJ)=1
      IF (IJ.EQ.1)NGS=1
   16 CONTINUE
      IF ( NVAR(20,1).OR.NVAR(21,1)) 10,8
   10 NVAR(1,1)=NVAR(2,1)=1
      NGS=1
    8 IF (NVAR(20,2).OR.NVAR(21,2)) 7,6
    7 NVAR(1,2)=NVAR(2,2)=1
    6 CONTINUE
      LPS1=LPS2=0
      N1=N2=3
      DO 15 I=1,19
      IF (NVAR(I,1).EQ.0)GO TO 13
      N1=N1+1 $ NVAR(I,1)=N1
      LPS1=I
   13 IF (NVAR(I,2).EQ.0) GO TO 15
      N2=N2+1 $ NVAR(I,2)=N2
      LPS2=I
   15 CONTINUE
      IF(IFDATA.NE.1) GO TO 64
      JMIN=49 $ JMAX=0
      DO 3 I=1,50
    3 JIN(I)=0
      DO 502 M=1,1000
C
C READ AND PACK IN THE OBSERVED TRANSITIONS
C STORAGE HAS BEEN SET UP FOR 1000 DATA POINTS
      READ(5,510)JU,KNU,KPU,JL,KNL,KPL,OBSFRE,W,ISTOP,ID,LAST
  510 FORMAT (2X,5(I2,1X),I2,F2.0,F6.0,1X,I3,A5,A8)
      IF (JU.GT.JMAX) JMAX=JU
      IF (JL.GT.JMAX) JMAX=JL
      IF (JU.LT.JMIN) JMIN=JU
      IF (JL.LT.JMIN) JMIN=JL
      IF(LAST.EQ.8HEND DATA)GO TO 503
      INDL=JL*JL+JL+KNL+1-KPL
      INDU=JU*JU+JU+KNU+1-KPU
      JIN(1,INDL)=JIN(2,INDU)=1
      WT(M)=W
      WRITE (51) JU,KNU,KPU,JL,KNL,KPL,OBSFRE,W,ISTOP,ID,INDU,INDL
  502 CONTINUE
  503 CONTINUE
      NODATA=M-1
      IF (JMAX.GT.49) JMAX=49
C
  604 CONTINUE
      DELSIG=SIGDIF+1.0
    1 CONTINUE
      LPS=LPS1
      IF (IFJEL) GO TO 17
      DO 20 I=10,19
```

```
      PAR(I,4)=PAR(I,2)
      PAR(I,3) = PAR(I,1)
   20 CONTINUE
   17 CONTINUE
      REWIND 51
      REWIND 50
      REWIND 52
      JBAND=8H  GROUND
      CAPP=CAPPA(PAR1,JBAND,HAM,IHEAD,NPAR1 ,PGD1,ISO)
      IF (SIGDIF.GE.DELSIG) GO TO 2
      IF(NFIT.GT.NFITS) GO TO 2
      J=JMIN
      IF (J.LT.0) J=J
C FORM THE GROUND STATE ENERGY LEVELS
      INDEX=0 $ IBN=1
   18 CONTINUE
      IF (J.GT.JMAX) GO TO 50
      N=0
      JAGAIN=0
      JEO=1
      NP(3)=J/2+1
      NP(1)=J
      ISAV=INDEX
      CALL FORMEP1 (-1,NMAX,JEO,PAR1,P,NP,CAPP)
      IF (ISAV.EQ.INDEX) GO TO 28
      INDEX=ISAV $ IER=IPRT
C CALCULATE OPERATOR MATRIX ELEMENTS IN J,K SPACE
      CALL PMAKE (J,JEO,NMAX,PAR1,P,PI,NP)
C WANG TRANSFORM IT
      CALL WANGT (A,N,JEO,JAGAIN,NMAX,PAR1,PH,P,NP)
C DIAGONALIZE THE GROUND STATE HAMILTONIAN
      CALL SYMDIG (N,IER)
C FORM THE EXPECTATION VALUES OF THE P OPERATORE
      CALL FORMEP1 (IFPAV,NMAX,JEO,PAR1,P,NP,CAPP)
      JAGAIN=1
   28 JEO=2
      NP(3)=J/2
      ISAV=INDEX
      CALL FORMEP1 (-1,NMAX,JEO,PAR1,P,NP,CAPP)
      IF (ISAV.EQ.INDEX) GO TO 29
      INDEX=ISAV $ IER=IPRT
      IF (JAGAIN.EQ.0) CALL PMAKE (J,JEO,NMAX,PAR1,P,PI,NP)
      N=0
      CALL WANGT (A,N,JEO,JAGAIN,NMAX,PAR1,PH,P,NP)
      CALL SYMDIG (N,IER)
      CALL FORMEP1 (IFPAV,NMAX,JEO,PAR1,P,NP,CAPP)
   29 JEO=3
      NP(3)=(J+1)/2
      N=0
      JAGAIN=0
      ISAV=INDEX
      CALL FORMEP1 (-1,NMAX,JEO,PAR1,P,NP,CAPP)
      IF (ISAV.EQ.INDEX) GO TO 36
      INDEX=ISAV $ IER=IPRT
      CALL PMAKE (J,JEO,NMAX,PAR1,P,PI,NP)
      CALL WANGT (A,N,JEO,JAGAIN,NMAX,PAR1,PH,P,NP)
```

```
      JAGAIN=1
      CALL SYMDIG (N,IER)
      CALL IFORMEP1 (IFPAV,NMAX,JEO,PAR1,P,NP,CAPP)
   36 JEO=4
      ISAV=INDEX
      CALL IFORMEP1 (-1,NMAX,JEO,PAR1,P,NP,CAPP)
      IF (ISAV.EQ.INDEX) GO TO 38
      INDEX=ISAV $ IER=IPRT
      IF (JAGAIN.EQ.0) CALL PMAKE (J,JEO,NMAX,PAR1,P,PI,NP)
      N=0
      CALL WANGT (A,N,JEO,JAGAIN,NMAX PAR1,PH,P,NP)
      CALL SYMDIG(N,IER)
      CALL IFORMEP1 (IFPAV,NMAX,JEO,PAR1,P,NP,CAPP)
   38 J=J+1
      GO TO 18
C GROUND STATE ENERGIES ARE DONE  AND STORED IN AG
   50 CONTINUE
C
      INDEX=INDEX
    2 CONTINUE
      LPS=LPS2
      INDEX=INDE
      JBAND=3H   UPPER
      IBN=2
C CALCULATE THE UPPER STATE ENERGIES
      CAPP=CAPPA(PAR2,JBAND,HAM,IHEAD,NPAR2 ,PGD2,ISO)
      IF (NPAR(22,4).OR.V (1))PRINT 107,VO(1),NPAR(22,4)
      IF (NPAR(23,4).OR.V (2))PRINT 108,VO(2),NPAR(23,4)
      IF (NPAR(24,4).OR.V (3))PRINT 109,VO(3),NPAR(24,4)
      IF (SIGDIF.GE.DELSIG) GO TO 100
      IF (NFIT.GT.NFITS) GO TO 10
      IF (NFIT.EQ.NFITS) IFCOEN=1
      IF (NFIT.EQ.NFITS) IFPRED=0
      J=JMIN
      IF (J.LT.0) J=1
   33 CONTINUE
      N=0
      JAGAIN=0
      JEO=1 $ NP(1)=J $ NP(3)=J/2+1
      ISAV=INDEX
      CALL IFORMEP1 (-1,NMAX,JEO,PAR2,P,NP,CAPP)
      IF (ISAV.EQ.INDEX) GO TO 40
      INDEX=ISAV $ IER=IPRT
      CALL PMAKE (J,JEO,NMAX,PAR1,P,PI,NP)
      CALL WANGT (A,N,JEO,JAGAIN,NMAX,PAR2,PH,P,NP)
      CALL SYMDIG(N,IER)
      CALL IFORMEP1 (IFPAV,NMAX,JEO,PAR2,P,NP,CAPP)
      JAGAIN=1
   40 JEO=2
      NP(3)=J/2
      ISAV=INDEX
      CALL IFORMEP1 (-1,NMAX,JEO,PAR2,P,NP,CAPP)
      IF (ISAV.EQ.INDEX) GO TO 78
      INDEX=ISAV $ IER=IPRT
      IF (JAGAIN.EQ.0) CALL PMAKE (J,JEO,NMAX,PAR1,P,PI,NP)
      N=0
```

```
      CALL WAVGT (A,N,JEO,JAGAIN,NMAX PAR2,PH,P,NP)
      CALL SYMDIG(N,IER)
      CALL FORMEP1 (IFPAV,NMAX,JEO,PAR2,P,NP,CAPP)
   78 JEO=3
      NP(3)=(J+1)/2
      N=0
      JAGAIN=0
      ISAV=INDEX
      CALL FORMEP1 (-1,NMAX,JEO,PAR2,P,NP,CAPP)
      IF (ISAV.EQ.INDEX) GO TO 42
      INDEX=ISAV $ IER=IPRT
      CALL PMAKE (J,JEO,NMAX,PAR1,P,PI,NP)
      CALL WAVGT (A,N,JEO,JAGAIN,NMAX PAR2,PH,P,NP)
      CALL SYMDIG(N,IER)
      CALL FORMEP1 (IFPAV,NMAX,JEO,PAR2,P,NP,CAPP)
      JAGAIN=1
   42 JEO=4
      ISAV=INDEX
      CALL FORMEP1 (-1,NMAX,JEO,PAR2,P,NP,CAPP)
      IF (ISAV.EQ.INDEX) GO TO 44
      INDEX=ISAV $ IER=IPRT
      IF (JAGAIN.EQ.0) CALL PMAKE (J,JEO,NMAX,PAR1,P,PI,NP)
      N=0
      CALL WAVGT (A,N,JEO,JAGAIN,NMAX,PAR2,PH,P,NP)
      CALL SYMDIG(N,IER)
      CALL FORMEP1 (IFPAV,NMAX,JEO,PAR2,P,NP,CAPP)
   44 J=J+1
      IF (J.GT.JMAX )GO TO 90
      GO TO 33
C ALL UPPER STAES ARE CALCULATED ONCE
   90 CONTINUE
 1001 FORMAT (*0NUMBER OF LEVELS CALCULATED = *I6)
      PRINT 1001,INDEX
      REWIND 5
      SUMWHT=0.0
      OBSNO = 0
      I=0
      NT=0
C FIND THE G.S.C.D. AND PLACE THEM ON TAPE
   60 I=I+1
      READ (51) JU,KNU,KPJ,JL,KNL,KPL,OBSFRE,WT2,ISTOP,ID,INDU,INDL
      IF (EOF,5)67,61
   61 CONTINUE
      ISTP=ISO-ISTCP
C CALCULATE TRANSITION  FREQUENCIES AND COMPARE THEM TO OBSERVED FREQUENC
      IL=JIN(1,INDL) $ IU=JIN(2,INDU)
      FREQ=AS(IU)-AS(IL)+V0(1)+V0(2)*ISTP+V0(3)*ISTP*ISTP
      DO 62 IJ=1,2
      IUL=IL
      IF (IJ.EQ.2) IUL=IU
      DO 62 II=1,19
      N=NVAR(II,IJ) $ IF (N.EQ.0) GO TO 62
      CONST(N)=AP(N,IUL)
      I2=IJ*2
      FREQ=FREQ+ISTP*PAR(II,I2)*CONST(N)
   62 CONTINUE
```

```
      DATA(NOVAR)=OBSFRE -FREQ
      IF (WT(I)) 985,985,982
  982 DIFFE=ABS (DATA(NOVAR))
      IF (DIFFE,LE.BDLN) GO TO 986
  984 NT=NT+1
      IF (NT.GT.1) GO TO 983
      PRINT 228
  983 PRINT 230,JU,KNU,KPJ,JL,KNL,KPL,OBSFRE,FREQ,DATA(NOVAR),WT2,I
      WT(I)=0.0
  985 OBSNO=OBSNO-1.
  986 NUM=0
      SUMWHT =SUMWHT +WT(I)
      DO 64 IJ=1,4
      ISF=1
      IF ((IJ.EQ.2).OR.(IJ.EQ.4)) ISF=ISTP
      DO 64 II=1,19
      N=NPAR(II,IJ) $ IF (N.EQ.0) GO TO 64
      IN= (IJ+1)/2 $ NN=NVAR(II,IN) $ DATA(N)=CONST(NN)*ISF
   64 CONTINUE
      DO 66 IN=1,3,2
      I1=(IN+1)/2 $ I1=NVAR(1,I1) $ I2=I1+1
      N=NPAR(20,IN) $ IF (N.EQ.0) GO TO 65
      DATA(N)=(CONST(I1)+ CONST(I2))/2.
   65 N=NPAR(21,IN) $ IF (N.EQ.0)GO TO 66
      DATA(N)=(CONST(I1)- CONST(I2))/2.
   66 CONTINUE
      ISF=1.0
      DO 69 IJ=22,24
      N=NPAR(IJ,4) $ IF (N.EQ.0)GO TO 69
      DATA(N) = ISF
   69 ISF=ISF*ISTP
      WRITE (50) JU,KNU,KPU,JL,KNL,KPL,OBSFRE ,FREQ,
     1 (DATA(L),L=1,NOVAR),I,WT2,ISTOP,ID
      GO TO 60
C FIT THE DATA
   67 CONTINUE
      OBSNO = NODATA +OBSNO
      AVEWHT=SUMWHT/OBSNO
      REWIND 50
      REWIND 51
      DO 108 I=1,35
  108 DELPAR(I)=0.
      CALL REGRESS
      NFIT = NFIT+1
      DO 70 I=1,4
      DO 70 K=1,19
      N=NPAR(K,I) $ IF (N.EQ.0) GO TO 70
      PAR(K,I) = PAR(K,I)+DELPAR(N)*PARFRAC
   70 CONTINUE
      DO 76 I=1,3,2
      N=NPAR(20,I) $ IF (N.EQ.0) GO TO 74
      PAR(1,I) = PAR(1,I) + DELPAR(N)*PARFRAC/2.0
      PAR(2,I) = PAR(2,I) + DELPAR(N)*PARFRAC/2.0
   74 N=NPAR(21,I) $ IF (N.EQ.0) GO TO 76
      PAR(1,I) = PAR(1,I) + DELPAR(N)*PARFRAC/2.0
      PAR(2,I) = PAR(2,I) - DELPAR(N)*PARFRAC/2.0
```

```
 76 CONTINUE
    DO 80 I=22,24
    N=NPAR(I,4) $ IF (N.EQ.0) GO TO 80
    K=I-21
    VO(K)=VO(K) + DELPAR(N)*PARFRAC
 80 CONTINUE
    SIG = ABS((SIGMA-SIGMAY1)/SIGMAY1)
    SIGMA=SIGMAY1
    IF (NGS.EQ.0) GO TO 2
    GO TO 1
100 CONTINUE
    GO TO 115
197 FORMAT (/3X* VO = *F10.3,6X,I2,20X*BAND CENTER*)
198 FORMAT(***29X,E12.5,I3)
199 FORMAT (2X*DOVO = * 20X,E12.5,I3)
226 FORMAT(*1    UPPER*5X*LOWER*7X*CALC CD*3X*OBSERVED CD*8X*WEIGHT*)
228 FORMAT        (//* THE WEIGHTS OF THE FOLLOWING LINES WILL NOW BE S
   1ET TO ZERO*/*  UPPER J K- K* LOWER  J K- K* *7X*OBSERVED FREQUENCY
   1* 8X*CALC FREQUENCY*7X*DIFFERENCE*12X*WEIGHT*)
230 FORMAT (2(6X,3I3),7X,E16.9 ,9X,E16.9 ,7X,E10.3,4X,F10.2,I10    )
    END
```

```
      SUBROUTINE PMAKE (J,JEO,NMAX,PAR,P,PI,NP)
      COMMON /PMAK/HAM,VIBZ,VIBXY,MSPM,LPS
C  THIS PROGRAM CALCULATES THE MATRIX ELEMENTS OF THE OPERATORS IN J,K SPAC
C THE DIMENSION OF P MUST BE 19*4*(JMAX/2+1)
      DIMENSION P(19,4,NMAX),PI(2,NMAX),NP(3)
      DIMENSION PAR(3)
       TYPE INTEGER HAM
C  ZERO THE P MATRIX
      M=1
      MM=NMAX*19*4
      DO 6 I=M,MM
    6 P(I)=0.0
      MM=2*NMAX
      DO 8 I=1,MM
    8 PI(I)=0.0
      N=0
      IF(J.EQ.0)GO TO 380
C  THE K EVEN ELEMENTS ARE CALCULTED AND STORED SEPATRATE FROM THE ODD
      GO TO (2,2,4,4) JEO
C  K IS EVEN
2     KEO=(J/2)*2
      GO TO 5
C  K IS ODD
4     KEO=((J+1)/2)*2-1
5     PPF=J*(J+1)
      K = KEO +2
      NK=KEO/2+2
      N=NK-1
      GO TO (359,100,260) HAM
C KENT MONCURS HAMILTONIAN
  359 CONTINUE
      IF (PAR(1).LT.PAR(3)) GO TO 37
C  OBLATE PLANAR FORM
      R = PAR(2)/(PAR(1)+PAR(2)    )
      R=R*R
      S = PAR(1)/(PAR(1)+PAR(2))
      S=S*S
  360 NK = NK-1
      K=K-2
      PK=K*K
      KN = 1-K
      IF (KN.LT.1) KN=1
      IF (KN.GT.4) KN =4
      GO TO (362,364,366,380) KN
  362 PPK = PPF-PK
C CALCULATE THE DIAGONAL TERMS
      IF (NK.LE.0) GO TO 380
      P(1,1,NK) = .5*PPK
      P(2,1,NK) = .5*PPK
      P(3,1,NK) = PK
      P(4,1,NK) = .25*(PPK*(.375*PPK-.25)+.375*PK+R*PK*(PPK+R*PK))
      P(5,1,NK) = .25*(PPK*(.375*PPK-.25)+.375*PK+S*PK*(PPK+S*PK))
      P(6,1,NK)=.25*((R+S)*PK*PPK+2.*R*S*PK*PK+.25*PPK*(PPK+2.)-.75*PK)
      P(7,1,NK) = .25*(5.*PK-2.*PPF+.5*PPK*(PPK+2.)-1.5*PK)
      P(10,1,NK) = PPF*PPF*PPF
       P( 11,1,NK)  =  PPF*PPF*PK
```

```
      P(12,1,NK)  = PPF*PK*PK
      P(13,1,NK)  =  PK*PK*PK
      PI(  1,NK)=K*VIBZ
      IF (KED.EQ. ) GO TO 380
      IF (KED-K) 365,360
  364 PPK=PPF-PK
  365 G = (J-K-1)*(J-K)*(J+K+1)*(J+K+2)
      PPG =-SQRT(G)
C CALCULATE THE K,K+2 TERMS
      NK=NK+1
      IF (NK.LE.0) GO TO 38
      P(1,2,NK) = .25*PPG
      P(2,2,NK) = -.25*PPG
      P(4,2,NK) = . 625*PPG*(PPK-2.-2*K+2.*R*(PK+2.+2*K))
      P(5,2,NK) =-. 625*PPG*(PPK-2.-2*K+2.*S*(PK+2.+2*K))
      P(6,2,NK) = .125*PPG*(S-R)*(PK+2.+2*K)
      PPG=-PPG
      PI(  2,NK)= .5*VIBXY*SQRT((PPF-PK-K)*(PPF-PK-3*K-2))
      NK=NK-1
      IF (KED.EQ.1) GO TO 380
      IF (KED-K-2) 368,36
  366 PPK=PPF-PK
      G = (J-K-1)*(J-K)*(J+K+1)*(J+K+2)
      PPG = SQRT(G)
  368 PM = (J-K-3)*(J-K-2)*(J+K+3)*(J+K+4)
      PPM = PPG*SQRT(PM)
C CALCULATE THE K,K+4 TERMS
      NK=NK+2
      IF (NK.LE.0) GO TO 380
      P(4,3,NK) = . 15625*PPM
      P(5,3,NK) = . 15625*PPM
      P(6,3,NK) = -.3125*PPM
      P(7,3,NK) =-. 625*PPM
      NK=NK-2
      IF (K.GT.-1) GO TO 36
      GO TO 38
C  PROLATE SPHEROIDAL FORM
  370 R = PAR(1)/(PAR(1)+PAR(3))
      R=R*R
      S = PAR(3)/(PAR(1)+PAR(3))
      S = S*S
  371 NK=NK-1
      K=K-2
      PK=K*K
      KN=1-K
      IF (KN.LT.1) KN=1
      IF (KN.GT.4) KN=4
      GO TO(372,374,376,380) KN
  372 PPK=PPF-PK
C CALCULATE THE DIAGONAL TERMS
      IF (NK.LE.0) GO TO 380
      P(1,1,NK) = .5*PPK
      P(2,1,NK) = .5*PPK
      P(3,1,NK) = PK
      P(4,1,NK)=.25*(PK*PK+R*R*.125*(3.*PPK*PPK-2.*PPK+3.*PK)+R*PPK*PK)
      P(5,1,NK)= .25*((S*S+1.)*.125*(3.*PPK*PPK-2.*PPK+3.*PK)*S*.25*(PPK
```

```
     1*PP(K-2,*PPK-3,*PK))
      P(6,1,VK) = .25*( R*S*.25 *(3*PPK*PPK-2*PPK*3*PK) *PPK*PK*S*PPK*PK
     1*R*.25 *(PPK*PPK-2*PPK-3*PK))
      P(7,1,VK) = .25*(2*PK*PPK-2.*PPF*2.5*PPK)
      P(10,1,VK) = PPF*PPF*PPF
       P(11,1,NK) = PPF*PPF*PK
       P(12,1,NK) = PPF*PK*PK
       P(13,1,NK) = PK*PK*PK
      PI(1,NK) = K*VIBZ
      IF (KEO.EQ. ) GO TO 380
      IF (KEO-K) 375,371
  374 PPK=PPF-PK
  375 G = (J-K-1)*(J-K)*(J+K+1)*(J+K+2)
      PPG=SQRT(G)
C CALCULATE THE K,K+2 TERMS
      NK=VK+1
      IF (NK.LE.0) GO TO 380
      P(1,2,VK) = -.25*PPG
      P(2,2,VK) =  .25*PPG
      P(4,2,VK) = .25*R*PPG*(R*.25*(PPK-2.*K-2.)+.5*(PK+2*K+2))
      P(5,2,VK) = .25*((S*S-1.)*.25*(PPK-2*K-2))*PPG
      P(6,2,VK) = .125*(R*S*(PPK-2.-2 *K)*(S-1.)*(PK+2.*K+2.))*PPG
      P(7,2,VK) = .25*PPG*(.625-(PK+2 *K+2.))
      PI(2,NK) = .5*VIBXY*SQRT((PPF-PK-K)*(PPF-PK-3.*K-2.))
      NK=VK-1
      IF (KEO.EQ.1) GO TO 380
      IF (KEO-K-2) 378,371
  376 PPK=PPF-PK
      G= (J-K-1)*(J-K)*(J+K+1)*(J+K+2)
      PPG=SQRT(G)
  378 PM = (J-K-3)*(J-K-2)*(J+K+3)*(J+K+4)
      PPM = PPG*SQRT(PM)
C CALCULATE THE K,K+4 TERMS
      NK=VK+2
      IF (NK.LE.0) GO TO 380
      P(4,3,VK) = .25*R*R*.0625*PPK
      P(5,3,VK) = .3125*PPM*(.5-S+.5*S*S)
      P(6,3,VK)= .03125*R*PPM*(S-1.)
      NK=VK-2
      IF (K.GT.-1) GO TO 371
      GO TO 380
C WATSONS HAMILTONIAN
  260 NK=VK-1
      K=K-2
      PK=K*K
      KN=1+K
      IF (KN.LT.1) KN=1
      IF (KN.GT.3) KN =3
      GO TO (262,264,270) KN
  262  PPK=PPF-PK
C CALCULATE THE DIAGONAL TERMS
      P(1,1,VK)=0.5*PPK
      P(2,1,VK)=0.5*PPK
       P(3,1,VK) = PK
       P(4,1,VK) = PPF*PPF
       P(5,1,VK) = PPF*PK
```

```
      P(5,1,NK)  = PK*PK
      P(10,1,NK) = PPF*PPF*PPF
      P(11,1,NK) = PPF*PPF*PK
      P(12,1,NK) = PPF*PK*PK
      P(13,1,NK) = PK*PK*PK
      PI(  1,NK)=K*VIBZ
      IF ( KEO . EQ. )  GO TO 38
      IF (KEO-K) 266,260
  264 PPK=PPF-PK
  266 G=(J-K-1)*(J-K)*(J+K+1)*(J+K+2)
      PPG=SQRT(G)
      NK=NK+1
      P(1,2,NK)  =-.25*PPG
      P(2,2,NK)  =  .25*PPG
      P(7,2,NK)=PPF*PPG*(-.5)
      P(3,2,NK)  =-PPG* (PK+2*K+2)
      P(4,2,NK)  =-PPG*.5* PPF*PPF
      P(15,2,NK)=PPG*PPF*(PK+2*K+2)*(-1.)
      P(16,2,NK)= .5*PPG*(PK*PK*(K+2.)*(K+2.)*(K+2.)*(K+2.))*(-1.)
      PI(  2,NK)= .5*VIBXY*SQRT((PPF-PK-K)*(PPF-PK-3*K-2))
      NK=NK-1
      IF(K.GT.0) GO TO 26
   270 GO TO 38
C KFC HAMILTONIAN
    10 NK=NK-1
      LP=LPS-8
      K=K-2
      PK=K*K
      KN =I-K
      IF (KN.LT.1) KN=1
      IF (KN.GT.5) KN=5
      GO TO (12,14,18,22,380) KN
    12 PPK=PPF-PK
      GO TO (40,41) LP
    41 CONTINUE
      P(10,1,NK) = .5*PPK*PK-.125*(2*PPF*PPF*(PK+4)-PPF*(2*PK*PK+26*PK
     1+8)*PK*PK*PK+24*PK*PK+28*PK)
      PDUM       =.25*PK*(3*PPK*PPK-2*PPK+3*PK)
      P(16,1,NK) =P(17,1,NK)=PDUM
      PDUM=PPK*PK*PK
      P(15,1,NK) =P(18,1,NK)=PDUM
      PDUM       = .125*(PPK*(PPK*(PPK+6.)-8.-19.*PK)+21.*PK)
      P(13,1,NK) =P(14,1,NK)=PDUM
      P(12,1,NK)= PK*PK*PK
        PDUM     =   (PPK*(25*PK+8-10*PPK+5*PPK*PPK)-21*PK )*.0625
      P(10,1,NK) =P(11,1,NK)=PDUM
    40 CONTINUE
      P(9,1,NK) = .25*(PPK*PPK+2.*PPK-3.*PK)
      P(8,1,NK)=PPK*PK
      P(7,1,NK)=PPK*PK
      P(6,1,NK)=PK*PK
      PDUM   =  .25*(1.5*PPK*PPK-PPK+1.5*PK)
      P(4,1,NK) = P(5,1,NK) = PDUM
      P(3,1,NK)=PK
      P(2,1,NK)=.5*PPK
      P(1,1,NK)=.5*PPK
```

```
      PI(  1,NK)=K*VIBZ
      IF (KEJ.EQ. ) GO TO 38J
      IF (KEJ - K) 16,10
   14 PPK=PPF-PK
   16 G = (J-K-1)*(J-K)*(J+K+1)*(J+K+2)
      PPG = SQRT(G)
      NK=NK+1
      GO TO (50,51) LP
   51 CONTINJE
      PDUMI       =  (PK*2.*(PK*4*K+12)+32*K+16)*.25*PPG
      P(13,2,NK) =-PDUM
      P(15,2,NK) = PDUM
      PDUMI       = .5*PPG*(PK+2*K+2)*(PPK-2*K-2)
      P(17,2,NK) =-PDUM
      P(16,2,NK) = PDUM
      PDUMI      = .3125*PPG*(PPK*         (PPK-4*K+6)-41*PK-102*K-72)
      P(14,2,NK) =-PDUM
      P(13,2,NK) = PDUM
      PDUMI       = PPG*(15*PPK*PPK-60*PPK*K-70*PPK+105*K*(K+1)+125*(K+1)
     1*11)*.015625
      P(11,2,NK) = PDUM
      P(10,2,NK) = -PDUM
   50 CONTINJE
      PDUMI     =.5*PPG*(PK+2*K+2)
      P(8,2,NK) = -PDUM
      P(7,2,NK) = PDUM
      PDUMI     =.5*PPG*(.25*(2*PPK+4*K+4))
      P(5,2,NK) = PDUM
      P(4,2,NK) = -PDUM
      PDUMI= .25*PPG
      P(2,2,NK) = PDUM
      P(1,2,NK) =-PDUM
      PI(  2,NK)= .5*VIBXY*SQRT((PPF-PK-K)*(PPF-PK-3*K-2))
      NK=NK-1
      IF (KEJ.EQ.1) GO TO 380
      IF (KEJ -K -2) 20,1
   18 PPK=PPF-PK
      G = (J-K-1)*(J-K)*(J+K+1)*(J+K+2)
      PPG = SQRT(G)
   20 PM = (J-K-3)*(J-K-2)*(J+K+3)*(J+K+4)
      PPM = PPG*SQRT(PM)
      NK=NK+2
      GO TO (60,61) LP
   61 CONTINJE
      P(12,3,NK) = -.125*(PK+4*K+4)*PPM
      PDUMI      =PPM*(PK+4*K+8)*.125
      P(17,3,NK) = P(16,3,NK) =PDUM
      PDUMI      =PPM*(4-PPK+K+4)*0.0625
      P(14,3,NK) = P(13,3,NK) = PDUM
      PDUMI      =PPM*(3*PPK-12*K-20)*.03125
      P(11,3,NK) = P(10,3,NK) = PDUM
      P(9,3,NK) = -.0625*PPM
   60 CONTINJE
      P(5,3,NK)=. 625*PPM
      P(4,3,NK)=. 625*PPM
      NK=NK-2
```

```
      IF (KEJ.EQ.2) GO TO 380
      IF (KEJ -K-4 ) 24,1
   22 PPK=PPF-PK
      G = (J-K-1)*(J-K)*(J+K+1)*(J+K+2)
      PPG = SQRT(G)
      PM = (J-K-3)*(J-K-2)*(J+K+3)*(J+K+4)
      PPM = PPG*SQRT(PM)
   24 PN = (J-K-5)*(J-K-4)*(J+K+5)*(J+K+6)
      GO TO (70,71) LP
   71 CONTINJE
      PPN = PPM*SQRT(PN)
      NK=NK+3
      P(10,4,NK) = -.5*PPN*.03125
      P(11,4,NK) = -P(10,4,NK)
       P(14,4,NK)  = .03125*PPN
       P(13,4,NK)  = -P(14,4,NK)
      NK=NK-3
   70 CONTINJE
      IF (K.GT.-2) GO TO 10
C WAIT FOR LAST TAPE OPERATION TO COMPLETE
  380 CONTINJE
      NP(1)=J $ NP(2)=JEO $ NP(3)=N
   26 CONTINJE
      IF (MSPM.LT.1) RETURN
      IF (UNIT,MSPM) 26,3
   30 BUFFER OUT (MSPM,1) (P(1,1,1),NP(3))
      RETURN
      END
```

```
      SUBROUTINE REGRESS
      COMMON/BLKAP/VECTOR(37,37),DATA(36),AVE(36),SIGMA(36),COEN(36),
     1SIGMCO(36),INDEX(36),AP(15,600)
      COMMON /BL5/NODATA,OBSNO,AVEWHT,NOVAR,LNOUT,SIGDIF ,NOPROB,
     1XOUT,IFCOEN,IFSTEP,IFPRED,SIGMAY,DELSIG
      COMMON/BL3/WT(100),DELPAR(35)
      EQUIVALENCE(VECTOR,AP)
      TYPE DOUBLE VECTOR, AVE, SIGMA, COEN, SIGMCO, SIGY
      TYPE DOUBLE DEVD,VARDEV,SWHT
      REWIND 50
      TOL =.0001 $  EFIN=EFOUT=.000000 01
      IFAVE=0
      IFCNST=0
      CNST=0.
      IFRAW=IFRESD=0
C  IFCNST=0  DO NOT HAVE CONST TERM IN EQUATION
C  ISTEP=0  DO NOT PRINT EACH STEP
C  IFRAW=0  DO NOT PRINT RAW SUMS AND SQUARES
C  IFAVE=0  DO NOT PRINT AVERAGES
C  IFRESD=0  DO NOT PRINT RESIDUAL SUMS AND SQUARES
C  IFCOEN=0  DO NOT PRINT PARTIAL COEFFICIENTS
C  IFPRED=1  DO NOT CALC PREDICTED DEVIATIONS OR SET WEIGHT TO ZERO
      NOIN = 0                                                          MPR
      VAR = 0.0
      K    = 0                                                          MPR
      FLEVEL = 0.
      NOENT = 0
      NOMIN = 0
      NOMAX = 0                                                         MPR
      ASSIGN 1000 TO NEXT
  565 NOVMI = NOVAR - 1                                                 MPR
  566 NOVPL = NOVAR + 1                                                 MPR
  110 DO 120 I=1,NOVPL
  130 DO 120 J=1,NOVPL
  120 VECTOR(I,J) = 0.0                                                 MPR
      N=0
  510 N=N+1
      READ (50)  JJ1,LL1,KK1,J,LL,KK,OBSFREQ,FREQ,(DATA(L),L=1,NOVAR
     1 ), NRJNWT2
      IF (EOF,50) 1,2
2     CONTINUE
      WHT=WT(N)
      IF (WHT.EQ. ) GO TO 510
      WHT=WHT/AVEWHT
  530 DO 540 I = 1, NOVAR                                               MPR
  550 VECTOR (I,NOVAR + 1) = VECTOR (I, NOVAR + 1) + DATA (I) * WHT     MPR
  560 DO 540 J = I, NOVAR                                               MPR
  540 VECTOR (I, J) = VECTOR (I, J) + DATA (I) * DATA (J) * WHT         MPR
      VECTOR(NOVPL,NOVPL)=VECTOR(NOVPL,NOVPL)+WHT
      GO TO 510
1     CONTINUE
      REWIND 50
  568 PRINT 90, NOPROB, NODATA,NOVAR, VECTOR(NOVPL,NOVPL), EFIN, EFOUT  MPR
  570 IF (IFRAW) 90,650,580
C     COMPLETED SUMS OF SQUARES AND CROSS PRODUCTS.  THESE ARE IN       MPR
C    1STORAGE IN LOCATION, VECTOR (I, J).
```

```
580   PRINT 15
 590   PRINT                20,(I,VECTOR(I,NOVPL),I=1,NOVMI)
 600   PRINT               25, VECTOR(NOVAR,NOVPL)
 610   PRINT                30
 620   PRINT                35, ((I,J,VECTOR(I,J),J=1,NOVMI),I=1,NOVMI)
 630   PRINT                40, (I,VECTOR(I,NOVAR),I=1,NOVMI)
 640   PRINT                45, VECTOR(NOVAR,NOVAR)
C      CALCULATION OF RESIDUAL SUMS OF SQUARES AND CROSS PRODUCTS                M
 650   IF(IFCNST) 90 ,735,651
 651   IF(VECTOR(NOVPL,NOVPL)) 652,652,655                                       M
 652   PRINT 654                                                                 M
       GO TO 915
 655   DO 660 I = 1, NOVAR                                                       M
 670   DO 660 J = I, NOVAR                                                       M
 660   VECTOR (I,J) = VECTOR (I,J) - (VECTOR(I,NOVPL) * VECTOR (J,NOVPL)         M
     * / VECTOR (NOVPL, NOVPL))                                                 M
 680   DO 690  I = 1, NOVAR                                                      M
 690   AVE(I)  = VECTOR(I,NOVPL) / VECTOR(NOVPL,NOVPL)                           M
 700   IF (IFAVE) 90 ,735,710
 710   PRINT                50
 720   PRINT                20, (I,AVE(I),I=1,NOVMI)
 730   PRINT                25, AVE(NOVAR)
 735   IF (IFRESD) 90,780,740
 740   PRINT                55
 750   PRINT                35,((I,J,VECTOR(I,J),J=1,NOVMI),I=1,NOVMI)
 760   PRINT                40, (I,VECTOR(I,NOVAR),I=1,NOVMI)
 770   PRINT                45, VECTOR(NOVAR,NOVAR)
 780   NOSTEP = -1                                                               M
 781   ASSIGN  132  TO NUMBER
 782   DEFRI   = VECTOR(NOVPL,NOVPL)
 790   DO 800  I = 1,NOVAR                                                       M
 791   IF(VECTOR(I,I)) 792,794,810                                               M
 792   PRINT  793, I                                                             M
       GO TO 915
 794   PRINT                795, I
 796   SIGMA(I) =     1.0                                                        M
 797   GO TO 800                                                                 M
 810   SIGMA(I) =DSQRT  (VECTOR (I,I))
 800   VECTOR(I,I) = 1.0                                                         M
 820   DO 850  I = 1,NOVMI                                                       M
 840   IP1 = I + 1                                                               M
 841   DO 850 J = IP1, NOVAR                                                     M
 850   VECTOR(I,J) = VECTOR(I,J) /( SIGMA(I)* SIGMA(J))                          M
 830   VECTOR(J,I) = VECTOR(I,J)                                                 M
 860   IF (IFCOEN) 90,951 ,870
 870   PRINT                60
 874   NOVM2  = NOVMI  - 1                                                       M
 875   DO 885  I = 1, NOVM2                                                      M
 880   IP1 =  I + 1                                                              M
 885   PRINT                35,(I,J,VECTOR(I,J),J=IP1,NOVMI)
 890   PRINT                40,(I,VECTOR(I,NOVAR),I=1,NOVMI)
 951   CONTINUE
       GO TO NEXT,(1 00,1581)
1000   NOSTEP = NOSTEP + 1                                                       M
1001   IF (VECTOR(NOVAR,NOVAR))1002,10 2,1015
1002   NSTPM1 = NOSTEP - 1                                                       M
```

```
      PRINT 1004, NSTPM1
      GO TO 915
 1015 DEFR=DEFR-1.0
      IF(NOENT.NE.0) DEFR=DEFR+2.0
 1016 IF (DEFR ) 1 17,1017, 1010
 1017 PRINT 1019 ,NOSTEP
      GO TO 915
 1010 SIGY =  SIGMA(NOVAR) *DSQRT  (VECTOR(NOVAR,NOVAR)/ DEFR)
 1020 VMIN = 0.0
 1030 VMAX = 0.0
 1035 NOIN = 0
 1040 DO 1050  I = 1,NOVMI
 1041 IF (VECTOR (I,I)) 1 42,1050,106
 1042 PRINT 1044, I, NOSTEP
      GO TO 915
 1060 IF(VECTOR(I,I) - TOL)   1050,1080,1080
 1080 VAR = VECTOR(I,NOVAR) * VECTOR(NOVAR,I) / VECTOR(I,I)
 1090 IF(VAR)1100,1 50,1110
 1100 NOIN = NOIN + 1
 1120 INDEX(NOIN) = I
 1130 COEN(NOIN)  = VECTOR(I,NOVAR) * SIGMA(NOVAR) / SIGMA (I)
 1140 SIGMCO(NOIN) = (SIGY / SIGMA(I)) *DSQRT (VECTOR(I,I))
 1150 IF (VMIN) 116 ,1170,904
  904 CONTINUE
      PRINT 906
      GO TO 915
 1160 IF(VAR - VMIN)1 50,1050,1170
 1170 VMIN = VAR
 1180 NOMIN = I
 1190 GO TO 1050
 1110 IF (VAR - VMAX)1050,105 ,1210
 1210 VMAX = VAR
 1220 NOMAX = I
 1050 CONTINUE
 1230 IF (NOIN) 9 3,1240,1245
  903 CONTINUE
      PRINT  907
      GO TO 915
 1240 PRINT                  65,SIGY
      SIGMAY=SIGY
 1260 GO TO 1350
 1245 IF( IFCNST) 9 0,1246,1250
 1246 CNST = 0.0
 1247 GO TO 1300
 1250 CNST = AVE(NCVAR)
 1270 DO 1280 I = 1,NOIN
 1290 J = INDEX(I)
 1280 CNST = CNST - (COEN(I) * AVE(J))
 1300 IF (IFSTEP) 9 0,132 ,1310
 1310 IF (NOENT) 1311,1311,1313
 1311 PRINT                  91,NOSTEP,K
 1312 GO TO 1314
 1313 PRINT                  92,NOSTEP,K
 1314 PRINT                  70,FLEVEL,SIGY,CNST,
     1(INDEX(J),COEN(J),SIGMCO(J),J=1,NOIN)
 1315 GO TO NUMBER, (1320,1580)
```

```
1320 FLEVEL = VMIN * DEFR / VECTOR (NOVAR,NOVAR)                        MPR
1330 IF(EFOUT + FLEVEL) 1350, 1350, 134                                 MPR
1340 K =  NOMIN                                                         MPR
1345 NOENT = 0                                                          MPR
     GO  TO  1391                                                       MPR
1350 FLEVEL = VMAX * DEFR / (VECTOR(NOVAR,NOVAR)-  VMAX)                MPR
1360 IF (EFIN - FLEVEL) 1370,1360,1380                                  MPR
1361 IF (EFIN) 138 ,1380,137                                            MPR
1370 K = NOMAX                                                          MPR
1390 NOENT =  K                                                         MPR
1391 IF(KO 1392,1392,140                                                MPR
1392 CONTINUE
1393 PRINT 1395, NOSTEP                                                 MPR
     GO TO 915
1400 DO 1410   I = 1,NOVAR                                              MPR
1420 IF (I-K) 1430,1410,1430                                            MPR
1430 DO 1440   J = 1, NOVAR                                             MPR
1450 IF (J-K) 1460,1440,1460                                            MPR
1460 VECTOR(I,J) = VECTOR(I,J) - (VECTOR(I,K) * VECTOR (K,J) / VECTOR   MPR
    -(K,K)                                                              MPR
1440 CONTINUE                                                           MPR
1410 CONTINUE                                                           MPR
1470 DO 1480  I = 1, NOVAR                                              MPR
1490 IF (I-K) 15 0,1480,1500                                            MPR
1500 VECTOR (I,K)  =  -  VECTOR (I,K) / VECTOR (K,K)                    MPR
1480 CONTINUE                                                           MPR
1510 DO 1520 J = 1, NOVAR                                               MPR
1530 IF (J-K) 1540,1520,1540                                            MPR
1540 VECTOR(K,J) =   VECTOR (K,J) / VECTOR (K,K)                        MPR
1520 CONTINUE                                                           MPR
1550 VECTOR(K,K) =  1.0 / VECTOR(K,K)                                   MPR
1560 GO TO 1000                                                         MPR
1380 PRINT 75, NOSTEP                                                   MPR
1381 IF (IFSTEP) 9 0,157 ,1580
1570 ASSIGN  158   TO NUMBER                                            MPR
1571 GO TO  1310                                                        MPR
1580 PRINT                1586,(L,VECTOR(L,L),L=1,NOVMI)
     DELSIG=ABS(SIGMAY-SIGY)/SIGMAY
     DO 949 I=1,NCIN
     K = INDEX(I)
     DELPAR(K)=COEN(I)
 949 CONTINUE
     IF (DELSIG.GT.SIGDIF) GO TO 158
     IFPRED=0
     IF (IFCOEN.NE.0) GO TO 1581
     IFCOEN=1
     ASSIGN 1581 TO NEXT
     GO TO 355
1581 IF( IFPRED)  90 ,1582,910                                          MPR
1582 CONTINUE
1583 PRINT                  85
     SWHT=SWDATA=0.
     IO=0
     VARDEV=0.
     SIGY=SIGY*SIGY*XOUT
     N=0
```

```
 1590 N=N+1
 1600 READ(5,50)   J1, LL1,KK1, J, LL, KK, OBSFREQ, FREQ,
     1 (DATA(L),L=1,NOVAR), NRUN,WT2,ISTOP,ID
      IF (EOF,50) 3,4
4     CONTINUE
 1610 YPRED = CNST                                                    MPR
 1620 DO 1630  I = 1,NOIN                                             MPR
 1640 K = INDEX(I)                                                    MPR
 1630 YPRED=  YPRED +  COEN(I) * DATA(K)                              MPR
 1650 DEV  =  DATA(NOVAR) -  YPRED                                    MPR
      FREQPRD=FREQ+YPRED
      IF (WT2  .GE.10 .0) GO TO 1658
      PRINT 1670, J1,LL1,KK1,J,LL,KK,FREQPRD,OBSFREQ,FREQ,DATA(NOVAR),
     1DEV,WT2,ISTOP,ID,NRUN
      DEV=WT2*DEV*DEV
      DEVD=DEV/AVEWHT
      IF (WT(NRUN)  .EQ.0.) GO TO 911
      SWHT=SWHT+WT2
      SNDATA = SNDATA+1
      VARDEV=VARDEV+DEV
      IF (IO.GT.LNCUT) GO TO 1660
      IF(DEVD-SIGY) 1660,912,912
 912  WT(NRUN)=0.
      IO=(IO+1)
      PRINT 1656
      GO TO 1660
 911  IF (WT2.NE. ) GO TO 913
      PRINT 1654
      GO TO 1660
 913  PRINT 1657
      IF (DEVD.LE.SIGY)WT(NRUN)=WT2
      IF (WT(NRUN).EQ.0.0) PRINT 1656
 1660 CONTINUE
      GO TO 1590
 1658 PRINT 1659, J1,LL1,KK1,J,LL,KK,FREQPRD,OBSFREQ,FREQ,DATA(NOVAR),
     1DEV,WT2,ISTOP,ID,NRUN
      GO TO 1590
3     CONTINUE
      REWIND 50
C        STANDARD DEVIATION FROM RESIDUALS
      VARDEV = (VARDEV*SNDATA)/(SWHT*(SNDATA-NOIN-1.))
      STDDEV= DSQRT(VARDEV)
 1785 PRINT 1790, STDDEV
      RETURN
 910  PRINT 1800
      RETURN
C     END...                                                         MPR
 900  PRINT 905
 915  CONTINUE
      RETURN
C...ABORT....
    5 FORMAT (3F1 .5,315,1H 912,5X,F6.4)
   10 FORMAT (6(F12.5))                                              MPR
   15 FORMAT (1H 49H                                  SUM  OF  VARIABLES//)MPR
   20 FORMAT (1H 11H     SUM X( I2,3H) = F12.4,8H  SUM X( I2,3H) =F12.4,MPR
     18H  SUM X( I2,3H) =F12.4,8H  SUM X(I2,3H) =F12.4 )             MPR
```

```
  25 FORMAT (17H      SUM   Y   =F12 4)                                    MPI
  30 FORMAT(1H0 70H                              RAW  SUM  OF  SQUARES  AMPI
    1ND  CROSS PRODUCTS// )                                               MPI
  35 FORMAT (1H 7H     X(I2,7H) VS X(I2,3H) = F15.6,                      MPI
    1         6H    X(I2,7H) VS X(I2,3H) = F15.6,                        MPI
    2         6H    X(I2,7H) VS X(I2,3H) = F15.6  )                      MPI
  40 FORMAT (1H 7H     X(I2,12H) VS   Y   =F15.6,
    1         6H    X(I2,12H) VS   Y   =F15.6,                           MPI
    2         6H    X(I2,12H) VS   Y   =F15.6  )                         MPI
  45 FORMAT (1H 21H     Y     VS   Y   =F15.6)                            MPI
  50 FORMAT (1H063H                                  AVERAGE  VALUE  OFMPI
    *  VARIABLES// )                                                      MPI
  55 FORMAT(1H077H                               RESIDUAL  SUMS  OF  SQUAMPI
    *RES  AND  CROSS PRODUCTS//)                                          MPI
  60 FORMAT(1H069H                                   PARTIAL  CORRELATIMPI
    *ON  COEFFICIENTS//)                                                  MPI
  65 FORMAT (25H   STANDARD ERROR OF Y = E12.5)
  70 FORMAT (11H   F LEVEL  E12.5/25H   STANDARD ERROR OF Y = E12.5/12H
    1   CONSTANT E12.5/56H              VARIABLE   COEFFICIENT   STD ERRMPI
    2OR OF COEF //  (16H               X-I3,E16.9,3X,E16.9))
  75 FORMAT (10H COMPLETED I5,20H STEPS OF REGRESSION)                    MPI
  80 FORMAT (8H       F6.2,2H  F12.5,3H   F12.5,2H  F12.5)                MPI
  85 FORMAT(//4X,5HUPPER,6X,5HLOWER,8X*PREDICTED* 7X *OBSERVED* 5X *CAL
    1CULATED* 4X*OBS-CALC*3X*DEVIATION*5X*WEIGHT*2X*ATOM ID*2X*NRUN*)
  90 FORMAT (22H1STEPWISE  REGRESSION //12H PROBLEM NO I10 //13H NO OF MPI
    1DATA = I5 //18H NO OF VARIABLES = I10 //30H WEIGHTED DEGREES OF FRMPI
    2EEDOM = F12.2 //28H F LEVEL TO ENTER VARIABLE = F12.9 //29H F LEVEMPI
    3L TO REMOVE VARIABLE = F13.9 /// )
  91 FORMAT (9H0STEP NO.I5 /19H   VARIABLE REMOVED I8)                    MPI
  92 FORMAT (9H0STEP NO.I5 /2H   VARIABLE ENTERING I8)                    MPI
  93 FORMAT (5H RUN  F6. ,3H   F10.5,3H   F10.5,3H   F10.5,3H   F10.5,   MPI
    13H   F10.5/(14H              F10 .5,3H   F10.5,3H   F10.5,3H   F10.MPI
    25,3H   F10.5))                                                      MPI
 654 FORMAT (31H  ZERO NUMBER OF DATA, SO LONG,)                          MPI
 793 FORMAT (31H ERROR RESIDUAL SQUARE VARIABLE I4,31H IS NEGATIVE,PROBMPI
    1LEM TERMINATED )                                                    MPI
 795 FORMAT (1H013H VARIABLE I5,13H IS CONSTANT )                        MPI
 905 FORMAT (42H ERROR IN CONTROL CARD, PROBLEM TERMINATED)              MPI
 906 FORMAT (25H ERROR, NUMIN PLUS, SOLONG)                              MPI
 907 FORMAT (26H  ERROR, NOIN MINUS, SOLONG )                            MPI
 918 FORMAT (////* THE WEIGHTS OF THEFOLLOWING LINES WILL NOW BE SET TO
    1ZERO*/(20I5//) )
1004 FORMAT (1H037HY SQUARE NON-POSITIVE,TERMINATE STEP  I 5)             MPI
1019 FORMAT (1H029H NO MORE DEGREES FREEDOM STEP I 5 )                    MPI
1044 FORMAT (1H010H SQUARE X-I5,17H NEGATIVE, SOLONG I5,6H STEPS)         MPI
1395 FORMAT (12H  K= . STEP I6, 7H SOLONG)                                MPI
1586 FORMAT (24H      DIAGONAL  ELEMENTS //21H   VAR.NO.     VALUE//     MPI
    1(1H  I 7, F16.6))                                                   MPI
1654 FORMAT (***1H1X,2H*-)
1656 FORMAT (***1H2X,1H*)
1657 FORMAT (***1H1X,1H*)
1659 FORMAT (2(2X,3I3),3F15.7,2F12.7,F11.2,2X,I4,A5,I5)
1670 FORMAT (2(2X,3I3),3F15.3,2F12.4,F11.2,2X,I4,A5,I5)
1790 FORMAT (* STD. DEV. CALCULATED FROM  LOW WEIGHTED LINES = *E12.5)
1800 FORMAT (*0SINCE THE PREDICTED FREQUENCIES ARE NOT CALCULATED,NO
    1WEIGHTS WILL BE ALTERED THIS  ITERATION,*)
```

```
END
```

```
      FUNCTION CAPPA (PAR,JBAND,HAM ,IHEAD,NPAR,PGDEL,ISO)
      DIMENSION X(21),D(11,19)
      DIMENSION PAR(19) ,IHEAD(10) ,PGDEL(19),NPAR(24,2)
      TYPE INTEGER HAM,D,X
      DATA ((X(I),I=1,19)=8HUA = X =,8H B = Y =,8H C = Z =,8HO   T1 =,
     18H    T2 =,8H    T3 =,8H    T4 =,8H    T5 =,8H    T6 =,8HO   H1 =,
     28H    H2 =,8H    H3 =,8H    H4 =,8H    H5 =,8H    H6 =,8H    H7 =,
     38H    H8 =,8H    H9 =,8H   H10 =,8HO(X+Y)/2 ,8H (X-Y)/2  )
      DO 10 I=1,11
      DO 10 J=1,19
   10 D(I,J)=8H
      D(1,1)=8HPX2      $ D(1,2)=8HPY2      $ D(1,3)=8HPZ2
      D(4,1)=8HPLANAR
C FINDS CAPPA AND PRINTS OUT THE STATE CONSTANTS
      IF (PAR(1).GE.PAR(2))GO TO 428
      PRINT 221
      AP=PAR(2) $ PAR(2)=PAR(1) $ PAR(1)=AP
  428 CONTINUE
      AP=PAR(1)
      B=PAR(2)
      C=PAR(3)
      X(1)=8HOA = X =  $X(2)=8H B = Y = $ X(3)=8H C = Z =
      D(5,1)=8HOBLATE
  420 IF (B.GT.C) GO TO 426
      C=B $ B=AP $ AP=PAR(3)
      X(1)=8HOB = X = $ X(2)=8H C = Y =  $ X(3)=8H A = Z =
      D(5,1)=8HPROLATE
      IF (B.LE.AP) GO TO 426
      PRINT 221
      PAR(3)=PAR(1) $PAR(1)=AP
      B=AP $ AP=PAR(3)
  426 CAPPA=(2.*B-AP-C)/(AP-C)
      IF (JBAND.NE.8H  GROUND) GO TO 20
      PRINT 217
      PRINT 218,(IHEAD(N),N=1,8)
   20 GO TO (21,22,23) HAM
   21 PRINT 121
  121 FORMAT (*0PLANAR-7 PARAMETER HAMILTONIAN,MONCUR-THESIS  *)
      D(3,1)=8H
      GO TO 40
   22 PRINT 122
  122 FORMAT (*0KFC-FORM,YALLABANDI AND PARKER,J.C.P.,49,410(1968)*)
      D(3,1)=8HKFC-NON
      GO TO 40
   23 PRINT 123
  123 FORMAT (*0  H-FORM,YALLABANDI AND PARKER,J.C.P.,49,410(1968)*)
      D(3,1)=8H  H-NON
   40 PRINT 250,JBAND,ISO
  250 FORMAT (1X,A8* STATE*10X
     1           *VARI (*I3*-ISOTOPE VARI-*/* CONSTANT VALUE*9X*ABLE  MA
     1SS)EFFECT ABLE OPERATOR*)
      GO TO (41,42,43) HAM
   41 IF (CAPPA.LT. ) GO TO 51
C PLANAR OBLATE
      D(1,4)=8H(1/4)*(P $ D(2,4)=8HX4 + R2* $ D(3,4)=8HPZ4 + R*
      D(4,4)=8H(PX2*PZ2 $ D(5,4)=8H + PZ2*P $ D(6,4)=8HX2))
```

```
      D(1,5)=8H(1/4)*(P $ D(2,5)=8HY4 + S2* $ D(3,5)=8HPZ4 + S*
      D(4,5)=8H(PY2*PZ2 $ D(5,5)=8H + PZ2*P $ D(6,5)=8HY2))
      D(1,6)=8H(1/4)*(2 $ D(2,6)=8H*R*S*PZ4 $ D(3,6)=8H + (PX2*
      D(4,6)=8HPY2 + PY $ D(5,6)=8H2*PX2) + $ D(6,6)= 8HS*(PX2*
      D(7,6)=8HPZ2 + PZ $ D(8,6)=8H2*PX2) + $ D(9,6)=8HR*(PY2*P
      D(10,6)=8HZ2+PZ2*P $ D(11,6)=4HY2))
      D(1,7)=8H(1/4)*(2 $ D(2,7)=8H*(PX2*PY $ D(3,7)=8H2 + PY2*
      D(4,7)=8HPX2) - 2 $ D(5,7)=8H*P2 + 5* $ D(6,7)=8HPZ2)
      D(1,10)=8HP6 $ D(1,11)=8HP4*PZ2 $ D(1,12)=8HP2*PZ4
      D(1,13)=8HPZ6
      GO TO 50
   51 CONTINUE
C PLANAR PRO-ATE
      D(1,4)=8H(1/4)*(P $ D(2,4)=8HZ4 + R2* $ D(3,4)=8HPY4 + R*
      D(4,4)=8H(PZ2*PY2 $ D(5,4)=8H + PY2*P $ D(6,4)=8HZ2))
      D(1,5)=8H(1/4)*(P $ D(2,5)=8HX4 + S2* $ D(3,5)=8HPY4 + S*
      D(4,5)=8H(PX2*PY2 $ D(5,5)=8H + PY2*P $ D(6,5)=8HX2))
      D(1,6)=8H(1/4)*(2 $ D(2,6)=8H*R*S*PY4 $ D(3,6)=8H + (PZ2*
      D(4,6)=8HPX2 + PX $ D(5,6)=8H2*PZ2) + $ D(6,6)= 8HS*(PZ2*
      D(7,6)=8HPY2 + PY $ D(8,6)=8H2*PZ2) + $ D(9,6)=8HR*(PX2*P
      D(10,6)=8HY2+PY2*P $ D(11,6)=4HX2))
      D(1,7)=8H(1/4)*(2 $ D(2,7)=8H*(PZ2*PX $ D(3,7)=8H2 + PX2*
      D(4,7)=8HPZ2) - 2 $ D(5,7)=8H*P2 + 5* $ D(6,7)=8HPY2)
      D(1,10)=8HP6 $ D(1,11)=8HP4*PZ2 $ D(1,12)=8HP2*PZ4
      D(1,13)=8HPZ6
      GO TO 50
   42 CONTINUE
C PHI-FORM
      D(1,4)=8HPX4
      D(1,5)=8HPY4 $ D(1,6)=8HPZ4
      D(1,7)=8H(PY2*PZ2 $ D(2,7)=8H + PZ2*P $ D(3,7)=8HY2)
      D(1,8)=8H(PX2*PZ2 $ D(2,8)=8H + PZ2*P $ D(3,8)=8HX2)
      D(1,9)=8H(PX2*PY2 $ D(2,9)=8H + PY2*P $ D(3,9)=8HX2)
      D(1,10)=8HPX6 $ D(1,11)=8HPY6 $ D(1,12)=8HPZ6
      D(1,13)=8H(PX2*PY4 $ D(2,13)=8H + PY4*P $ D(3,13)=8HX2)
      D(1,14)=8H(PY2*PX4 $ D(2,14)=8H + PX4*P $ D(3,14)=8HY2)
      D(1,15)=8H(PY2*PZ4 $ D(2,15)=8H + PZ4*P $ D(3,15)=8HY2)
      D(1,16)=8H(PZ2*PY4 $ D(2,16)=8H + PY4*P $ D(3,16)=8HZ2)
      D(1,17)=8H(PZ2*PX4 $ D(2,17)=8H + PX4*P $ D(3,17)=8HZ2)
      D(1,17)=8H(PZ2*PX4 $ D(2,17)=8H + PX4*P $ D(3,17)=8HZ2)
      D(1,18)=8H(PX2*PZ4 $ D(2,18)=8H + PZ4*P $ D(3,18)=8HX2)
      D(1,19)=8H(PX2*PZ2 $ D(2,19)=8H*PY2 + P $ D(3,19)=8HY2*PZ2*P
      D(4,19)=8HX2)
      GO TO 50
   43 CONTINUE
C H-FORM
      D(1,4)=8HP4 $ D(1,5)=8HP2*PZ2 $ D(1,6)=8HPZ4
      D(1,7)=8HP2*(PX2- $ D(2,7)=8HPY2)
      D(1,8)=8H(PZ2*(PX $ D(2,8)=8H2-PY2) + $ D(3,8)=8H (PX2-PY
      D(4,8)=8H2)*PZ2)
      D(1,10)=8HP6 $ D(1,11)=8HP4*PZ2 $ D(1,12)=8HP2*PZ4
      D(1,13)=8HPZ6 $ D(1,14)=8HP4*(PX2- $ D(2,14)=8HPY2)
      D(1,15)=8HP2*(PZ2* $ D(2,15)=8H(PX2-PY2 $ D(3,15)=8H) + (PX2
      D(4,15)=8H-PY2)*PZ $ D(5,15)=8H2)
      D(1,16)=8HPZ4*(PX2 $ D(2,16)=8H-PY2) + $ D(3,16)=8H(PX2-PY2
      D(4,16)=8H)*PZ2
```

```
   60 CONTINUE
      DO 54 N=1,19
      IF (NPAR(N,1).OR.NPAR(N,2).OR.PAR(N) .OR.PGDEL(N)) 62,64
   62 CONTINUE
      PRINT 214,((X(N),PAR(N),NPAR(N,1),(D(J,N),J=1,11)))
  214 FORMAT ( ( A8,1X,E15.8,I3,2X,15X,3X,10A8,A4) )
      IF (NPAR(N,2).OR.PGDEL(N)) PRINT 216,PGDEL(N),NPAR(2,N)
  216 FORMAT (***29X,E12.5,I3)
   64 CONTINUE
      IF (NPAR(20,1).EQ.0) GO TO 66
      PRINT 212,X(20),NPAR(20,1)
   66 IF (NPAR(21,1).EQ.0) GO TO 68
      PRINT 212,X(21),NPAR(21,1)
   68 CONTINUE
  212 FORMAT ( A8,16X,I3)
      PRINT 220,CAPPA
  220 FORMAT(//* KAPPA = *F14.7)
      RETURN
  217 FORMAT(*1*)
  218 FORMAT (10A8)
  221 FORMAT (6H*******ONLY TYPES I-R AND III-R WORK PROPERLY IN THIS PROGR
     1OGRAM ---- THEREFORE THE VALUES X AND Y OR X AND Z WILL BE EXCHANG
     2ED*)
      END
```

```
      SUBROUTINE FORMEP1 (IFPAV,NMAX,JEO,PAR,P,NP,CAPP)
      COMMON A(25,25),S(25,25),AS(600),JIN(2,2500),INDEX,NVAR(24,2),IBN
      COMMON/BLKAP/AP(15,500)
      DIMENSION P(19,4,NMAX),PAR(19),AVEP(19),NP(3)
C
C* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C     THIS ROUTINE  SORTS THE EIGENVALUES AND DETERMINES THE QUANTUM NUMBER
C  FOR EACH STATE   THE DIAGONAL ENERGIES FROM A ARE STORED IN AG AT LOCATI
C JIN(J*J+J+(N+1-KP)
C               THE AVERAGE VALUES ARE CALCULATED BY USING THE TRANSFORMATIO
C               MATIX AND APPLYING IT TO THE UNDIAGONALIZED OPERATOR VALUES
C
C OPTIONS ARE
C   IFPAV =0,1 THE DIAGONAL AND AVERAGE ENERGIES ARE PRINTED ONLY IF  THE
C               EXPECTATION VALUE OF THE ENERGY IS DIFFERENT FROM THE  DIAGO
C               ENERGY BY MORE THAN E-9.
C   IFPAV=2,>4 THE DIAGONAL AND AVERAGE ENERGIES ARE PRINTED
C   IFPAV > 3  THE NORMALIZED EXPECTATION VALUES OF EACH OPERATOR IS PRINTE
C* * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C
      EXPECT=1.0E-9
      RT2=1.414213562
      NT =0
      MT=1
      J=NP(1)
      NL=NP(3)
      IF (NL.GT.0) GO TO 10
      IF ((J.NE.0).OR.(JEO.NE.1)) RETURN
      IND=JIN(IBN,1)
      IF (IND.EQ. ) RETURN
      INDEX=INDEX+1
      DO 40 I=1,15
   40 AP(I,INDEX)=0.0
      AS(INDEX)=0.
      JIN(IBN,1)=INDEX
      RETURN
C  INITIALIZE QUANTUM NUMBER IDENTIFICATION
   10 CONTINUE
      IF (CAPP.LT.0) GO TO 28
      GO TO(21,22,23,24) JEO
C FOR 3-R NOTATION USE,OBLATE
   21 K2=-2 $ K1=J+2
      GO TO 30
   22 K2=1 $ K1=J+1
      GO TO 30
   23 K2=-1 $ K1=J+2
      GO TO 30
   24 K2=-1 $ K1=J+1
      GO TO 30
C FOR 1-R NOTATION USE ,PROLATE
   28 GO TO (121,122,123,124) JEO
  121 K1=(J/2)*2+2 $ K2=((J+1)/2)*2-J-2
      GO TO 30
  122 K1=(J/2)*2+2 $ K2=((J-1)/2)*2-J+1
      GO TO 30
  123 K1=((J+1)/2)*2+1 $ K2=(J/2)*2-J-1
```

```
      GO TO 30
  124 K1=((J+1)/2)*2+1 $ K2=(J/2)*2-J
   30 CONTINUE
      KP=K2 $ KN=K1
      DO 55 NN=1,NL
C DERIVE THE QUATUM NUMBERS FOR THE STATE
      KP=KP+2 $ KN=KN-2
      IND=J*J+J+KN+1-KP
      ITAR=JIN(IBN,IND)
      IF (ITAR.EQ.J) GO TO 65
      INDEX=INDEX+1
      IF (IPRAV.EQ.-1) RETURN
      IF (INDEX.GT.60 ) GO TO 242
      JIN(IBN,IND)=INDEX
      DO 50 NZ=1,19
   50 AVEP(NZ)=0.
C FORM THE EXPECTATION VALUES OF THE P OPERATORS IN H SPACE
C THE AVERAGE OF P(N,N)=SUM OVER I,J OF S*(I,N)*P(I,L)*S(L,N)
      VSQSUM=0.0
      DO 60 I=1,NL
      SINNS(I,NN)
      DO 59 L=I,NL
      MD=L-I+1
      IF (MD.GT.4) GO TO 60
      VSQ=SINN*S(L,NN)
C FORM THE SQUARE OF THE DIAGONAL ELEMENTS
      IF (MD.EQ.1) VSQSUM=VSQSUM+VSQ
      IF (MD.NE.1) VSQ=VSQ*2.0
      M=L
      IF (JEO.EQ.2) M=M+1
      IF ((JEO.EQ.1).AND.(MD.EQ.M).AND.(MD.GT.1)) VSQ=RT2*VSQ
      DO 32 LI=1,19
      AVEP(LI)=AVEP(LI)+VSQ*P(LI,MD,M)
      IF (M.GT.4) GO TO 32
C THE FOLLOWING TRANSFORMS THE MATRIX ELEMENTS BY THE WANG TRANSFORM
      GO TO  (94,98,102,104) JEO
   94 EO=1.
   96 IF((MD.EQ.1).AND.(M.EQ.2))AVEP(LI)=AVEP(LI)+EO*VSQ*P(LI,3,2)
      IF((MD.EQ.2).AND. (M.EQ.3))AVEP(LI)=AVEP(LI)+EO*VSQ*P(LI,4,3)
      GO TO 32
   98 EO=-1
      GO TO 96
  102 EO=-1
  106 MDL=MD+1
      IF((MD.LT.4).AND.(M.EQ.MD))AVEP(LI)=AVEP(LI)+EO*VSQ*P(LI,MDL,M)
      IF((MD.EQ.1).AND.(M.EQ.2))AVEP(LI)=AVEP(LI)+EO*VSQ*P(LI,4,2)
      GO TO 32
  104 EO=1.
      GO TO 106
   32 CONTINUE
   59 CONTINUE
   60 CONTINUE
C CHECK FOR INCORRECT EXPECTATION VALUES
      AVEEI=0.
      DO 58 LI=1,19
      AVEE=AVEE+PAR(LI)*AVEP(LI)
```

```
   62 CONTINUE
      AA=A(NN,NN)
      DIFF=(ABS(AA-AVEE))/AA
      IF ((IFPAV.EQ.2).OR.(IFPAV.GE.4)) GO TO 48
      IF (DIFF.LE.EXPECT) GO TO 64
   48 VSQSUM=VSQSUM-1
      IF (NT.EQ.0) PRINT 226,EXPECT
      NT=NT+1
      PRINT 227,J,JEO,NN,KN,KP,AA,AVEE,DIFF,   VSQSUM
   64 CONTINUE
      AS(INDEX)=AA
      DO 70 MI=1,19
      NH=NVAR(MI,IBN)
      IF (NH.EQ.0) GO TO 70
      AP(NH,INDEX)=AVEP(MI)
   70 CONTINUE
      IF (IFPAV.LT.3) GO TO 65
      IF (MT.EQ.0) PRINT 222
      MT=MT+1
      DO 58 LI=1,19
   58 AVEP(LI)=AVEP(LI)/AA
      PRINT 220,J,KN,KP,JEO,(AVEP(LI),LI=1,19)
      GO TO 65
  242 PRINT 240,INDEX,IND
   65 CONTINUE
      RETURN
  220 FORMAT (1X,3I3,I4,2X,15E8.1/(1X,10E8.1))
  222 FORMAT (*0  J KN KP JEO*6X*X/E      Y/E      Z/E     T1/E     T2/E
     1T3/E    T4/E     T5/E     T6/E     H1/E     H2/E     H3/E     H4/E     H5
     2/E     H6/E*)
  226 FORMAT (/*  J JEO NN KN KP   DIAGONAL ENERGY     AVERAGE ENERGY  DI
     1FF/ENERGY                *2X,12HU*U DIAG - 1*  DIFF GREATER THAN  *
     2E10.3)
  227 FORMAT (1X,5I3,2X,E16.9,2X,E16.9,3X,E10.3,3X,E10.3)
  240 FORMAT (/*INDEX OVERFLOW,  INDEX =*I7*   IND = *I7)
      END
```

```
      SUBROUTINE  SYMDIG (N,ITN)
C
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C THIS ROUTINE DIAGONALIZES THE SYMMETRIC MATRIX A AND COMPUTES ITS
C EIGENVECTORS, STORING THEM IN S. THE COLUMNS OF S ARE THE EIGENVECTORS
C CORRESPONDING TO THE EIGENVALUES WHICH ARE ALONG THE DIAGONAL OF A.
C   THE  ROUTINE USES ONLY THE UPPER RIGHT CORNER OF A FOR THE OFF DIAGONAL
C ELEMENTS OF A AND STORES THEIR SQUARES IN THE THE LOWER LEFT HAND CORNER.
C  THE ORDER OF ARITHMETIC OPERATIONS IS SET UP SUCH THAT THE METHOD OF DI
C IZATION WORKS ONLY WHEN THE DIFFERENCE OF THE DIAGONAL ELEMENTS IS NOT ZE
C AND WORKS BEST IF THAT DIFFERENCE IS GREATER THAN THE OFF DIAGONAL ELEM
C MAGNITUDE.
C  IF ITN IS NOT ZERO ON ENTRY THE MATRIX ELEMENTS ARE PRINTED BEFORE AND A
C DIAGONALIZATION.
C    WE WILL CALL B=A(I,J) AND B$=CONJG(A(I,J))
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C
      COMMON A(25,25),S(25,25),AS(600),JIN(2,2500),INDEX,NVAR(24,2),IBN
      TYPE DOUBLE BAB,R
C PRECN MUST BE APPROX = TO  2**(-N) WHERE N IS THE NUMBER OF BITS USED TO
C  THE FLOATING MANTISSA IN THE COMPUTER
      IPRT=ITN
      PRECN=1.0E-11
C ITN = NUMBER OF ITERATIONS THRU ALL OF A.
      ITN = 0
      IF (N.LE.0) RETURN
C INITIALIZE THE  S MATRIX
      DO 2 I = 1,N
      S(I,I) = 1.
      II=I+1
      DO 2 J=II,N
C NOTE I + 1 BECOMES LARGER THAN N
    2 S(I,J) = S(J,I) = 0.0
      IF (IPRT.EQ.0) GO TO 1
      PRINT 200,((A(J,I),I=1,11),J=1,N)
    1 CONTINUE
      IF (N.LE.1) RETURN
      BAVE = 0.0
C COMPUTE B=B$ AND STORE THEM  IN THE LOWER RIGHT OF A
      DO 4 I=1,N
      II=I+1
      DO 4 J=II,N
      TEMP = A(I,J)
      BB=TEMP*TEMP
      A(J,I) = BB
    4 BAVE = BAVE + BB
      FN = N
      BAVE=BAVE*(2. *FN/(FN-1.0))
      IF (N.LT.3) BAVE=0.
      FN=FN*FN
      INVER=0
      NM=N+1
      IF (A(2,1).LT.A(N,NM)) INVER=1
C THIS ENTRY SHOULD BE USED ONLY IF THE CALLING PROGRAM IS NOT SATISFIED WI
C THE DIAGONALIZATION AND WISHES TO CYCLE THRU MORE ITERATIONS ON THE SAM
C MATRIX.
```

```
      ENTRY DIGMOR
CNOTE...
C+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-
C BAVE SHOULD NOT BE ZERO UNLESS THE MATRIX T O BE DIAGONALIZED HAS ITS L
C ELEMENT IN THE UPPER  LEFT OR LOWER RIGHT OFF THE THE DIAGONAL AND THE
C OF THE THE ELEMENTS COME IN DECREASING ORDERUP OR DOWN AWAY FROM THE TH
C ONE
C+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-+-
      BAVE=0.0
      ITN=0
      IND = 1
C AFTER EACH ITERATION THRU THE WHOLE MATRIX, RETURN HERE
C COMPUTE THE AVERAGE VALUE OF THE SQUARES OF THE OFF DIAGONAL ELEMENTS
    6 BAVE = BAVE/FN
      IF (IBAVE.EQ. ) GO TO 7
      IF (IND.EQ. ) GO TO 6
    7 IBAVE=
      IND = 0
    8 M = 0
      ITN = ITN+1
      IF (ITN.GT.10 ) GO TO 5
   10 LL=
      M = M+1
      IF (M.GE.N) GO TO 6
C THE ROUTINE IS SET UP TO CHECK AND ROTATE MATRIX ELEMENTS SEQUENTIALLY
C PARALLEL TO THE DIAGONAL,WORKING DOWN AND TO THE RIGHT,
C OR WORKING UP AND TO THE LEFT WHEN INVER=1
   12 LL=LL+1
      L=LL
      IF (INVER.EQ.1) L=N-L
      K = L+M
      IF (L.LE.0) GO TO 1
      IF (L.GE.N) GO TO 1
      IF (K.GT.N)GO TO 12
      BAB = A(K,L)
C IF B*B$ IS LESS THAN THE AVERAGE B*B$ GO TO THE NEXT ELEMENT,OTHERWISE R
      IF (BAB.LT.BAVE) GO TO 12
      IBAVE=1
      IF (BAB.LT.PRECN) GO TO 12
      C1 = A(L,L)
      C2 = A(K,K)
      B = A(L,K)
      CDF = (C1-C2)/2.0
      R=CDF*(1.0-DSQRT(1. +BAB/(CDF*CDF)))
      IF (ABS(R).LT.PRECN) GO TO 12
      ALFA = 1.0/DSQRT(1.  + R*R/BAB)
      IF (ALFA.EQ.1.0) GO TO 12
C IND IS A FLAG WHICH IS SET WHEN A ROTATION IS DONE
C IND ALSO CONTAINS THE NUMBER OF ROTATIONS DONE AFTER EACH TIME THRU THE
      IND = IND+1
C A ROTATION WILL NOW BE DONE WHICH WILL SET THE VALUE OF A(L,K) TO ZERO
      BETA = (R*ALFA)/B
      DO 40 I = 1,N
C ROTATE THE UNITARY TRANSFORMATION MATRIX
      TEMP = ALFA*S(I,L) - S(I,K)*BETA
      S(I,K) = BETA*S(I,L) + S(I,K)*ALFA
```

```
      S(I,L) = TEMP
C  ROTATE THE HERMITIAN MATRIX
      IF (I-L) 20,24,28
   20 TEMP1 = ALFA*A(I,L) - A(I,K)*BETA
      A(I,K) = TEMP2 = BETA*A(I,L) + A(I,K)*ALFA
      A(I,L) = TEMP
C COMPUTE B**3S AND STORE THEM  IN THE LOWER RIGHT OF A
      A(L,I) = TEMP*TEMP
      A(K,I)=TEMP2*TEMP2
      GO TO 40
   24 A(L,L) = C1 - R
      A(K,K) = C2 + R
C WITHOUT ROUNDOFF ERRORS A(L,K) WOULD BE ZERO AS CALCULATED BY THE FOLLO
C WE SHALL SET IT EQUAL TO ZERO
C     TEMP=(ALFA*ALFA-BETA*BETA)*B+ALFA*(C1-C2)*BETA
C     A(L,K)=TEMP
C     A(K,L)=TEMP*CONJG(TEMP)
      A(L,K)=A(K,L)=0.0
      GO TO 40
   28 IF (I-K) 30,40,34
   30 TEMP1 = ALFA*A(L,I) - BETA*A(I,K)
      A(I,K) = TEMP2 = BETA*A(L,I)          + ALFA*A(I,K)
      A(L,I) = TEMP
      A(I,L) = TEMP*TEMP
      A(K,I) = TEMP2*TEMP2
      GO TO 40
   34 TEMP1 = ALFA*A(L,I) - BETA*A(K,I)
      A(K,I) = TEMP2 = A(L,I)*BETA          + ALFA*A(K,I)
      A(L,I) = TEMP
      A(I,L) = TEMP*TEMP
      A(I,K) = TEMP2*TEMP2
   40 CONTINUE
      GO TO 12
C THE ROTATION IS COMPLETED ,GET THE NEXT ELEMENT
C
   60 CONTINUE
C THE DIAGONALIZATION WAS COMPLETED TO THE DESIRED ACCURACY,
C THE FOLLOWING SORTS THE EIGENVALUES INTO DESCENDING ORDER
C THE EIGENVECTORS ARE ALSO SWITCHED TO CORRESPOND TO THEIR EIGENVALUE
      IF (IPRT.EQ.0) GO TO 11
C
   50 CONTINUE
C THE DIAGONALIZATION WAS NOT COMPLETED SATISFACTORILY AFTER 100 ITERATION
C THRU THE COMPLETE MATRIX,  THE CALLING PROGRAM MAY RETURN ENTERING AT D
C TO COMPLETE THE DIAGONALIZATION.
C
      PRINT 201,((A(J,I),I=1,11),J=1,N)
      PRINT 202,((S(J,I),I=1,11),J=1,N)
      PRINT 203,ITN
  203 FORMAT (///* ITN = *I8)
  110 M=N
  120 M=M/2
      IF (M) 130,140 ,130
  130 K=N-M
      J=1
  141 I=J
```

```
149 L=I+M
    B=A(I,I) $ B1=A(L,L)
    IF (B-B1)15 ,16 ,16
150 TEMP=A(I,I)
    A(I,I)=A(L,L) $ A(L,L)=TEMP
    DO 155 LL=1,N
    TEMP=S(LL,I) $ S(LL,I)=S(LL,L)
155 S(LL,L)=TEMP
    I=I-M
    IF (I-1) 16 ,149,149
160 J=J+1
    IF (J-4) 141,141,12
140 CONTINUE
    RETURN
200 FORMAT (*0A BEFORE DIAGONALIZATION*/( 1X,11E12.5))
201 FORMAT (*0A AFTER  DIAGONALIZATION*/( 1X,11E12.5))
202 FORMAT (*0S AFTER  DIAGONALIZATION*/( 1X,11E12.5))
    END
```

```
      SUBROUTINE WANGT (A,NN,JEO,JAGAIN,NMAX,PAR,AH,P,NP)
      DIMENSION PAR(19),P(19,4,NMAX),AH(4,NMAX),NP(3)
      DIMENSION A(25,25)
C
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C   THIS RDUTINE FORMS THE WANG TRANSFORMED HAMILTONIAN AND STORES IT INT
C IF JAGAIN =0,A NEW INTERMEDIATE HAM LTONIAN IS ALWAYS FORMED,IF NOT,THE
C  THE DIFFERENCE BETWEEN THE JEO=1 OR 2 AND JEO=3 OR 4 ARE MADE.
C JEO=1 ***K IS EVEN, USE SUM OF  THE BASIS FUNCTIONS
C JEO=2 ***K IS EVEN, USE DIFFERENCE OF  THE BASIS FUNCTIONS
C JEO=3 ***K IS ODD , USE DIFFERENCE OF  THE BASIS FUNCTIONS
C JEO=4 ***K IS ODD , USE SUM OF  THE BASIS FUNCTIONS
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
C
      J=NP(1)
      GO TO (10,1 ,12,12) JEO
   10 KEO=(J/2)*2
      GO TO 14
   12 KEO=((J+1)/2)*2-1
   14 N=(KEO/2+1
      IF (J.EQ.0) N=0
      NP(3)=N
      IF (N.LT.0) RETURN
      IF (J.LE.0) RETURN
      RT2=1.414213562
      IF (JAGAIN) 24,26
   24 GO TO (60,64,68,72)JEO
   60 JEO=1
      EO=2
      GO TO 30
   64 JEO=2
      EO=-2
      GO TO 31
   68 JEO=3
      EO=-2
      GO TO 40
   72 JEO=4
      EO=2
      GO TO 40
   26 CONTINUE
      NEND=4*NMAX
      DO 20 I=1,NEND
   20 AH(I)=0.0
C FORM THE HAMILTONIAN IN J,K SPACE
      DO 13 L=1,4
      DO 13 LL= 1,N
      DO 13 I=1,19
   13 AH(L,LL)=AH(L,LL)+PAR(I)*P(I,L,LL)
      GO TO (28,29,36,37) JEO
C FORM THE WANG TRANSFORMATION
   28 JEO=1
      EO=1
   30 I1=1
      DO 34 I=2,4
      AH(I,I)=RT2*AH(I,I)
   34 CONTINUE
```

```
      GO TO 32
   29 JEO=2
      EO=-1
   31 CONTINUE
      N=N-1
      NP(3)=N
      IF (N.EQ.0) RETURN
      I1=1
   32 CONTINUE
      AH(1,2)=AH(1,2)+EO*AH(3,2)
      AH(2,3)=AH(2,3)+EO*AH(4,3)
      GO TO 50
   36 JEO=3
      EO=-1
      GO TO 40
   37 JEO=4
      EO=1
   40 DO 42 I=1,3
      L=I+1
      AH(I,I)=AH(I,I) +EO*AH(L,I)
   42 CONTINUE
      AH(1,2)=AH(1,2)+EO*AH(4,2)
      I1=1
   50 CONTINUE
C STORE THE TRANSFORMED MATRIX INTO A
      DO 52 I=1,N
      II=NN+I
      DO 52 M=I,N
      IJ=M+I1
      L=M+NN
      K=M-I+1
      IF (K.GT.4) GO TO 51
      A(L,II)=AH(K,IJ)
      A(II,L)=AH(K,IJ)
      GO TO 52
   51 CONTINUE
      A(L,II)=A(II,L)=0.0
   52 CONTINUE
      NN=NN+N
      RETURN
      END
```

```
     FOR     :       0 HOURS      MINUTES    42.184 SECONDS
     OTHER   :       0 HOURS      MINUTES     0.623 SECONDS

 ELAPSED TIME:       0 HOURS      MINUTES    42.807 SECONDS
TOTAL COMPUTE COST AT REDUCED RATE  $    2.18
QUENCE NUMBER 042916:0 0  FINISHED AT 13337:7                    DATE  05/03/73
```

APPENDIX IV

POLYNOMIAL FITTING BY LEAST SQUARES*

Convolution of a function, f(x), (which here represents the spectral data), by a function, c(x), is given by

$$h(y) = \int f(x)c(y-x)\,dx$$

The function, c(x), generally, rapidly goes to zero, so the integral has a narrow range of integration. Numerically the integral becomes a summation, i.e.

$$h_n = \sum_{i=-m}^{i=m} f_{n+i}c_{-i}$$

The summation formula yields only one data point, h_n, for each summation, so that it must be repeated incrementing n each time to convolute the entire spectrum.

Let us now derive the convolutes, c_i, which can be used to obtain the rth derivative by the method of least squares fitting to a polynomial of degree j over the range +m to -m points. If we represent a polynomial of of degree j by the equation

$$f(x) = b_{j0} + b_{j1}x + b_{j2}x^2 + \cdots + b_{jj}x^j \qquad \text{(A-IV-1)}$$

$$= \sum_{k=0}^{k=j} b_{jk}x^k$$

*Adapted from Whittaker and Robinson[38] pp.291-295.

The derivatives of f(x) are

$$\frac{\partial f}{\partial x} = b_{j1} + 2b_{j2}x + \cdots + jb_{jj}x^{j-1}$$

$$\partial^2 f/\partial x^2 = 2b_{j2} + 6b_{j3} + \cdots + j(j-1)b_{jj}x^{j-2}$$

$$\partial^r f/\partial x^r = r!b_{jr} + \cdots \qquad \text{(A-IV-2)}$$

By evluating Eq.(A-IV-2) at x=0, we obtain the derivative at that point, i.e.

$$\left.\frac{\partial^r f}{\partial x^r}\right|_{x=0} = r!b_{jr} = a_{jr} \qquad \text{(A-IV-3)}$$

Our goal is to fit the above functions by the method of least squares to our experimental lines and thereby obtain the values of the derivatives. That is, we wish to find b_{jr} such that

$$\frac{\partial}{\partial b_{jr}} \left[\sum_{i=-m}^{i=m} (f_i - y_i)^2 \right] = 0$$

where x takes on integer values, i, ranging from -m to +m. This step can only be done if the increments in x from point to point are the same. Substituting for f_i we get

$$\frac{\partial}{\partial b_{jr}} \left[\sum_{i=-m}^{i=m} \left(\sum_{k=0}^{k=j} b_{jk} i^k - y_i \right)^2 \right] = 0 \qquad \text{(A-IV-4)}$$

From Eq.(A-IV-4) we get

$$\sum_{i=-m}^{i=m} y_i i^r = \sum_{k=0}^{k=j} b_{jk} \sum_{i=-m}^{i=m} i^{k+r}$$

Let us define

$$S_{r+k} = \sum_{i=-m}^{i=m} i^{k+r}$$

$$F_r = \sum_{i=-m}^{i=m} y_i i^r$$

so that we have

$$F_r = \sum_{k=0}^{k=j} b_{jk} S_{r+k} \qquad \text{(A-IV-5)}$$

Note that:

r = order of derivative

±m = range of integral

i = running index of integral

j = degree of polynomial

k = degree of term in polynomial

The set of equations given by (A-IV-5), called the normal equations, can be solved for the b_{jk}, and from them the kth derivatives can be obtained.

The sum S_p for even p is given by

$$S_p = 2\left[\frac{m^{p+1}}{p+1} + \frac{m^p}{2} + \frac{p}{2!} B_1 m^{p-1} - \frac{p(p-1)(p-2)}{4!} B_2 m^{p-3} + \frac{p(p-1)(p-2)(p-3)(p-4)}{6!} B_3 m^{p-5} - \cdots\right]$$

where the B's are Bernoulli numbers, e.g. $B_1 = 1/6$, $B_2 = 1/30$, $B_3 = 1/42$, $B_4 = 1/30$, $B_5 = 5/66$. The sum S_p is zero for all odd values of p, which yields the interesting result that for all ℓ,

$$b_{2\ell,0} = b_{2\ell+1,0}$$

$$b_{2\ell-1,1} = b_{2\ell,1}$$

$$b_{2\ell,2} = b_{2\ell+1,2}$$

...

e.g. smoothing by least squares fitting to quadratic or

cubic polynomials are identical!

The solution of the normal equations for $f_0 = b_{j0} = a_{j0}$, where $j = 2\ell$ or $j = 2\ell+1$, may be written in determinate form as

$$f_0 = \frac{\begin{vmatrix} F_0 & F_2 & \cdots & F_{2\ell} \\ S_2 & S_4 & \cdots & S_{2\ell+2} \\ S_4 & S_6 & \cdots & S_{2\ell+4} \\ \vdots & \vdots & \ddots & \vdots \\ S_{2\ell} & S_{2\ell+2} & \cdots & S_{4\ell} \end{vmatrix}}{\begin{vmatrix} S_0 & S_2 & \cdots & S_{2\ell} \\ S_2 & S_4 & \cdots & S_{2\ell+2} \\ S_4 & S_6 & \cdots & S_{2\ell+4} \\ \vdots & \vdots & \ddots & \vdots \\ S_{2\ell} & S_{2\ell+2} & \cdots & S_{4\ell} \end{vmatrix}}$$

Since only the F's are a function of y_i, the determinate can be written as

$$f_0 = c_m y_m + c_{m-1} y_{m-1} + \cdots + c_{-m} y_{-m}$$

where the c's are constants whose values are determined by j and i. We see that this equation is identical in form of that at the beginning of this section, which is the integral equation of convolution.

If we choose the degree of the polynomial, j, to be equal to 2 or 3, then we will obtain the formula for the

convolutes, c_i required for fitting data by the method of least squares to a cubic polynomial, which is given by

$$c_i = 3 \cdot \frac{3m^2 + 3m - 1 - 5i^2}{(2m-1)(2m+1)(2m+3)} \qquad \text{(A-IV-6)}$$

We see that this method of obtaining the rth derivative requires the data to be linear in the abscissa values over the range of integration and that the range of integration is over an odd number of points.

APPENDIX V

FREQUENCY ASSIGNMENTS FOR THE (2,0,0) BAND OF HDTe

J	K-	K+	J	K-	K+	OBS	OBS-CALC	WT	ISOTOPE
11	10	1	12	11	2	3894.836	-0.031	0.01	130
10	10	0	11	11	1	3899.890	0.001	0.04	130
11	9	2	12	10	3	3908.061	-0.041	0.01	130
10	9	1	11	10	2	3913.140	0.002	0.10	130
12	8	4	13	9	5	3915.668	-0.071	0.00	130
9	9	0	10	10	1	3918.212	0.002	0.10	130
11	8	3	12	9	4	3920.655	-0.045	0.01	130
10	8	3	11	9	2	3925.705	-0.024	0.01	130
9	8	1	10	9	2	3930.799	-0.011	0.04	130
8	8	1	9	9	0	3935.931	0.005	2.00	130
10	7	4	11	8	3	3937.669	-0.026	0.02	130
9	7	2	10	8	3	3942.747	-0.014	0.10	130
11	6	6	12	7	5	3944.035	-0.032	0.01	130
8	7	2	9	8	1	3947.871	-0.007	2.00	130
10	6	5	11	7	4	3949.044	-0.017	0.04	130
10	6	4	11	7	5	3949.172	-0.018	0.02	130
7	7	0	8	8	1	3953.033	0.003	2.00	130
8	6	3	9	7	2	3959.182	-0.007	2.00	130
10	5	5	11	6	6	3961.121	-0.013	0.01	130
7	6	1	8	7	2	3964.333	-0.004	3.00	130
9	5	5	10	6	4	3964.683	-0.002	0.02	130
9	5	4	10	6	5	3965.309	-0.014	0.20	130
6	6	1	7	7	0	3969.517	-0.002	5.00	130
8	5	4	9	6	3	3969.852	-0.001	0.30	130
8	5	3	9	6	4	3970.050	0.006	0.01	130
18	0	18	19	1	19	3971.837	-0.008	0.20	130
18	1	18	19	0	19	3971.837	-0.008	0.20	130
17	2	16	18	1	17	3971.837	0.001	0.20	130
9	3	7	10	4	6	3972.203	0.008	0.01	130
9	4	6	10	5	5	3972.784	0.000	0.03	130
7	5	3	8	6	2	3974.997	-0.005	0.02	130
7	5	2	8	6	3	3975.038	-0.009	0.02	130
17	0	17	18	1	18	3977.183	-0.002	0.30	130
17	1	17	18	0	18	3977.183	-0.002	0.30	130
16	2	15	17	1	16	3977.183	-0.008	0.30	130
9	4	5	10	5	6	3978.490	-0.002	0.10	130
8	4	5	9	5	4	3979.107	0.001	0.30	130
6	5	2	7	6	1	3980.182	0.004	9.00	130
8	4	4	9	5	5	3981.635	-0.001	2.00	130
16	0	16	17	1	17	3982.465	0.005	0.10	130
16	1	16	17	0	17	3982.465	0.005	0.10	130
15	2	14	16	1	15	3982.465	-0.018	0.01	130
8	3	6	9	4	5	3982.586	0.001	0.01	130
7	4	4	8	5	3	3984.765	-0.005	1.00	130
5	5	0	6	6	1	3985.386	0.000	6.00	130
7	4	3	8	5	4	3985.685	-0.008	1.00	130
15	0	15	16	1	16	3987.673	0.001	0.10	130
15	1	15	16	0	16	3987.673	0.001	0.10	130
14	2	13	15	1	14	3987.714	0.003	0.02	130

J	K-	K+	J	K-	K+	OBS	OBS-CALC	WT	ISOTOPE
6	4	3	7	5	2	3990.132	0.003	3.00	130
6	4	2	7	5	3	3990.393	-0.001	0.40	130
7	3	5	8	4	4	3991.131	0.002	0.20	130
14	0	14	15	1	15	3992.816	-0.002	0.50	130
14	1	14	15	0	15	3992.816	-0.002	0.50	130
13	2	12	14	1	13	3992.871	-0.004	0.40	130
12	2	10	13	3	11	3993.149	-0.003	0.20	130
12	3	10	13	2	11	3993.584	-0.011	0.02	130
9	3	6	10	4	7	3994.215	0.008	0.01	130
5	4	2	6	5	1	3995.385	0.001	0.40	130
5	4	1	6	5	2	3995.435	-0.003	0.40	130
8	3	5	9	4	6	3996.164	-0.001	1.00	130
13	0	13	14	1	14	3997.902	0.003	0.50	130
13	1	13	14	0	14	3997.902	0.003	0.50	130
12	2	11	13	1	12	3997.973	-0.004	2.00	130
6	3	4	7	4	3	3998.188	-0.005	0.01	130
7	3	4	8	4	5	3998.527	0.002	0.04	130
4	4	1	5	5	0	4000.622	0.000	2.00	130
4	4	0	5	5	1	4000.622	-0.006	2.00	130
6	3	3	7	4	4	4001.503	0.000	3.00	130
10	2	8	11	3	9	4002.432	0.001	1.00	130
12	0	12	13	1	13	4002.914	-0.001	0.50	130
12	1	12	13	0	13	4002.914	-0.001	0.50	130
11	1	10	12	2	11	4002.979	0.005	0.20	130
11	2	10	12	1	11	4003.023	0.000	0.10	130
5	3	3	6	4	2	4004.288	-0.001	5.00	130
10	3	8	11	2	9	4004.602	-0.000	1.00	130
5	3	2	6	4	3	4005.539	0.003	2.00	130
11	0	11	12	1	12	4007.866	0.002	0.20	130
11	1	11	12	0	12	4007.866	0.001	0.20	130
5	2	4	6	3	3	4008.743	0.014	0.02	130
8	2	6	9	3	7	4009.597	0.003	3.00	130
4	3	2	5	4	1	4009.860	-0.003	1.00	130
4	3	1	5	4	2	4010.188	-0.001	3.00	130
9	3	7	10	2	8	4010.637	-0.010	0.01	130
7	2	5	8	3	6	4012.317	-0.000	3.00	130
10	0	10	11	1	11	4012.749	0.003	0.50	130
10	1	10	11	0	11	4012.749	0.000	0.50	130
9	2	8	10	1	9	4013.004	-0.006	0.01	130
6	2	4	7	3	5	4014.859	0.001	0.60	130
3	3	1	4	4	0	4015.209	0.000	0.40	130
3	3	0	4	4	1	4015.250	-0.006	0.40	130
6	5	2	6	6	1	4016.589	0.010	0.01	130
6	5	1	6	6	0	4016.589	0.003	0.01	130
4	2	3	5	3	2	4016.635	-0.000	1.00	130
8	5	4	8	6	3	4016.993	0.001	0.10	130
8	1	7	9	2	8	4017.320	-0.002	0.40	130
8	3	6	9	2	7	4017.320	0.001	0.40	130
9	0	9	10	1	10	4017.553	-0.006	0.05	130
9	1	9	10	0	10	4017.553	-0.014	0.01	130

J	K-	K+	J	K-	K+	OBS	OBS-CALC	WT	ISOTOPE
8	2	7	9	1	8	4018.043	-0.000	0.10	130
10	5	5	10	6	4	4019.126	-0.011	0.10	130
4	2	2	5	3	3	4020.816	-0.007	0.10	130
10	1	10	10	2	9	4021.204	-0.004	0.01	130
7	1	6	8	2	7	4021.646	0.001	4.00	130
8	0	8	9	1	9	4022.310	0.009	0.01	130
8	1	8	9	0	9	4022.310	-0.012	0.01	130
3	2	2	4	3	1	4023.240	-0.007	0.10	130
7	2	6	8	1	7	4023.240	0.006	0.10	130
3	2	1	4	3	2	4024.734	-0.003	2.00	130
11	3	9	11	4	8	4025.302	-0.001	0.04	130
6	1	5	7	2	6	4025.540	-0.002	3.00	130
3	1	3	4	2	2	4025.842	0.001	0.02	130
9	1	9	9	2	8	4026.086	-0.003	0.01	130
9	0	9	9	1	8	4026.397	-0.001	0.40	130
5	4	2	5	5	1	4026.698	-0.001	0.01	130
9	4	6	9	5	5	4026.774	-0.007	0.01	130
6	4	3	6	5	2	4026.826	-0.001	0.04	130
7	0	7	8	1	8	4026.967	0.003	0.10	130
7	4	4	7	5	3	4026.967	0.001	0.10	130
7	1	7	8	0	8	4027.013	-0.007	0.10	130
7	4	3	7	5	2	4027.758	-0.001	1.00	130
10	1	9	10	2	8	4027.978	0.008	0.10	130
6	2	5	7	1	6	4028.753	0.003	5.00	130
10	3	8	10	4	7	4028.857	0.004	1.00	130
5	1	4	6	2	5	4028.974	-0.002	0.40	130
2	2	1	3	3	0	4029.056	0.005	0.10	130
2	2	0	3	3	1	4029.357	0.001	0.40	130
9	2	8	9	3	7	4030.500	0.003	1.00	130
8	1	8	8	2	7	4030.830	-0.002	0.40	130
9	4	5	9	5	4	4031.162	-0.003	0.40	130
6	0	6	7	1	7	4031.525	-0.005	4.00	130
6	1	6	7	0	7	4031.672	-0.006	0.10	130
6	3	4	7	2	5	4032.497	-0.004	0.10	130
7	4	4	8	3	5	4033.577	0.005	0.10	130
8	3	6	8	4	5	4033.677	0.001	1.00	130
10	4	6	10	5	5	4033.773	0.002	0.40	130
9	1	8	9	2	7	4033.903	-0.003	0.10	130
8	2	7	8	3	6	4034.468	0.002	1.00	130
2	1	2	3	2	1	4034.575	-0.002	0.80	130
5	2	4	6	1	5	4034.760	0.007	0.01	130
7	3	5	7	4	4	4034.975	-0.002	0.20	130
3	1	2	4	2	3	4035.381	-0.006	0.10	130
7	1	7	7	2	6	4035.381	0.014	0.01	130
6	3	4	6	4	3	4035.685	-0.005	1.00	130
5	0	5	6	1	6	4035.961	-0.002	0.40	130
5	1	5	6	0	6	4036.334	0.004	0.40	130
7	0	7	7	1	6	4036.716	-0.000	0.01	130
5	3	2	5	4	1	4037.040	-0.004	0.10	130
7	2	6	7	3	5	4037.830	0.002	0.40	130

J	K-	K+	J	K-	K+	OBS	OBS-CALC	WT	ISOTOPE
10	2	8	10	3	7	4038.268	0.012	0.01	130
6	3	3	6	4	2	4038.377	0.003	1.00	130
2	1	1	3	2	2	4038.938	-0.002	1.60	130
6	1	6	6	2	5	4039.593	-0.001	1.00	130
8	1	7	8	2	6	4039.861	-0.001	0.10	130
4	0	4	5	1	5	4040.197	0.000	3.00	130
7	3	4	7	4	3	4040.262	-0.001	0.10	130
6	2	5	6	3	4	4040.493	0.001	0.01	130
4	1	4	5	0	5	4041.050	0.002	2.00	130
1	1	1	2	2	0	4041.756	-0.005	0.04	130
6	0	6	6	1	5	4042.046	-0.001	0.20	130
8	3	5	8	4	4	4042.210	0.009	0.01	130
5	2	4	5	3	3	4042.431	-0.001	0.10	130
1	1	0	2	2	1	4043.098	0.000	2.00	130
10	3	7	10	4	6	4043.184	0.001	0.60	130
9	2	7	9	3	6	4043.475	-0.001	0.10	130
4	2	3	4	3	2	4043.696	-0.004	0.04	130
3	0	3	4	1	4	4044.156	-0.002	1.00	130
7	1	6	7	2	5	4045.367	-0.003	3.00	130
3	2	1	3	3	0	4045.649	-0.002	0.10	130
3	1	3	4	0	4	4045.945	-0.002	2.00	130
4	1	4	4	2	3	4046.624	-0.003	0.60	130
4	2	2	4	3	1	4046.828	0.006	0.04	130
5	0	5	5	1	4	4047.305	-0.006	0.04	130
2	0	2	3	1	3	4047.884	-0.003	0.50	130
5	2	3	5	3	2	4048.177	-0.003	0.60	130
7	2	5	7	3	4	4048.886	0.001	1.00	130
6	2	4	6	3	3	4049.098	0.010	0.01	130
3	1	3	3	2	2	4049.215	-0.002	0.80	130
6	1	5	6	2	4	4049.840	-0.001	0.40	130
2	1	2	3	0	3	4051.132	-0.006	0.10	130
1	0	1	2	1	2	4051.638	-0.006	0.40	130
4	0	4	4	1	3	4052.085	0.004	0.40	130
5	1	4	5	2	3	4052.861	0.001	9.00	130
2	1	1	2	2	0	4054.194	-0.003	2.00	130
4	1	3	4	2	2	4054.391	0.005	0.10	130
3	1	2	3	2	1	4054.681	-0.006	0.60	130
0	0	0	1	1	1	4055.760	-0.001	1.00	130
3	0	3	3	1	2	4055.863	-0.001	4.00	130
1	1	1	2	0	2	4056.593	-0.001	0.20	130
2	0	2	2	1	1	4058.397	-0.003	5.00	130
1	0	1	1	1	0	4059.808	-0.001	3.00	130
1	1	0	1	0	1	4067.767	-0.000	7.00	130
2	1	1	2	0	2	4069.031	0.001	4.00	130
2	0	2	1	1	1	4070.834	-0.003	0.60	130
3	1	2	3	0	3	4071.251	0.003	1.00	130
3	2	1	3	1	2	4071.490	-0.011	0.01	130
4	2	2	4	1	3	4071.657	0.005	0.20	130
1	1	1	0	0	0	4071.821	0.005	0.10	130
2	2	0	2	1	1	4072.058	-0.001	0.10	130

J	K-	K+	J	K-	K+	OBS	OBS-CALC	WT	ISOTOPE
5	2	3	5	1	4	4072.807	0.001	3.00	130
4	1	3	4	0	4	4074.495	0.002	0.01	130
7	3	4	7	2	5	4074.572	0.002	0.10	130
6	3	3	6	2	4	4074.572	-0.007	0.10	130
6	2	4	6	1	5	4075.114	0.002	1.00	130
5	3	2	5	2	3	4075.499	0.004	0.30	130
8	3	5	8	2	6	4075.734	-0.004	0.10	130
2	1	2	1	0	1	4075.790	-0.001	0.10	130
3	0	3	2	1	2	4075.959	0.005	0.10	130
3	2	2	3	1	3	4076.607	-0.000	1.00	130
10	4	6	10	3	7	4076.728	0.004	0.04	130
9	4	5	9	3	6	4076.772	0.002	0.10	130
4	3	1	4	2	2	4076.927	0.003	0.60	130
4	1	3	3	2	2	4077.762	-0.001	1.00	130
8	4	4	8	3	5	4077.889	0.005	1.00	130
3	3	0	3	2	1	4077.986	-0.004	0.20	130
5	1	4	5	0	5	4078.478	0.007	0.10	130
3	3	1	3	2	2	4079.058	0.007	0.04	130
3	1	3	2	0	2	4079.265	0.007	0.10	130
4	3	2	4	2	3	4079.497	-0.007	0.01	130
7	4	3	7	3	4	4079.596	0.005	1.00	130
5	3	3	5	2	4	4080.388	0.004	1.00	130
12	4	8	12	3	9	4080.502	0.006	0.01	130
4	0	4	3	1	3	4080.608	-0.003	1.00	130
6	4	2	6	3	3	4081.279	0.006	0.10	130
10	5	5	10	4	6	4081.319	-0.005	0.01	130
5	2	4	5	1	5	4081.374	-0.003	0.10	130
6	3	4	6	2	5	4081.764	-0.001	0.30	130
4	1	4	3	0	3	4082.495	0.007	0.10	130
2	2	1	1	1	0	4083.149	-0.007	0.10	130
6	4	3	6	3	4	4083.300	-0.009	0.01	130
5	4	2	5	3	3	4083.300	0.003	0.01	130
4	4	1	4	3	2	4083.444	0.001	0.04	130
7	4	4	7	3	5	4083.619	0.003	0.10	130
8	4	5	8	3	6	4084.345	0.008	0.10	130
2	2	0	1	1	1	4084.503	0.007	0.40	130
5	0	5	4	1	4	4084.804	-0.002	2.00	130
8	5	3	8	4	4	4085.085	-0.010	0.01	130
9	4	6	9	3	7	4085.542	0.001	0.40	130
11	3	8	11	2	9	4085.673	0.005	0.01	130
5	1	5	4	0	4	4085.743	0.004	2.00	130
7	5	2	7	4	3	4086.254	-0.005	0.04	130
7	5	3	7	4	4	4086.778	-0.002	0.20	130
5	5	0	5	4	1	4087.460	-0.006	0.01	130
10	6	4	10	5	5	4088.098	-0.004	0.20	130
6	0	6	5	1	5	4088.676	0.005	5.00	130
6	1	6	5	0	5	4089.098	0.008	0.10	130
6	1	5	5	2	4	4089.731	-0.000	0.40	130
8	6	3	8	5	4	4090.058	-0.001	0.20	130
7	2	5	6	3	4	4090.228	-0.005	0.04	130

J	K-	K+	J	K-	K+	OBS	OBS-CALC	WT	ISOTOPE
4	2	3	3	1	2	4090.406	0.002	1.00	130
3	2	1	2	1	2	4091.591	0.000	3.00	130
7	0	7	6	1	6	4092.323	0.001	4.00	130
7	1	7	6	0	6	4092.503	0.005	0.10	130
5	2	4	4	1	3	4093.262	0.001	0.60	130
8	7	2	8	6	3	4093.333	0.011	0.00	130
7	7	0	7	6	1	4093.782	-0.000	0.01	130
9	1	8	9	0	9	4094.090	0.018	0.00	130
3	3	1	2	2	0	4094.255	-0.003	3.00	130
3	3	0	2	2	1	4094.533	-0.002	0.20	130
7	1	6	6	2	5	4094.630	-0.004	0.40	130
9	8	1	9	7	2	4095.438	0.001	0.01	130
6	2	5	5	1	4	4095.704	0.001	2.00	130
8	0	8	7	1	7	4095.833	-0.001	1.00	130
8	1	8	7	0	7	4095.905	0.001	0.10	130
10	9	1	10	8	2	4095.890	-0.005	0.01	130
8	2	6	7	3	5	4097.131	0.005	1.00	130
10	1	9	10	0	10	4097.484	-0.003	0.01	130
7	2	6	6	1	5	4098.081	-0.002	2.00	130
4	3	2	3	2	1	4098.805	0.002	1.00	130
8	1	7	7	2	6	4098.844	-0.006	0.10	130
4	3	1	3	2	2	4100.192	-0.008	0.10	130
4	2	2	3	1	3	4100.192	0.010	0.10	130
10	1	10	9	0	9	4102.576	0.000	0.04	130
10	0	10	9	1	9	4102.576	0.010	0.04	130
5	3	3	4	2	2	4102.622	-0.005	0.01	130
9	2	8	8	1	7	4103.433	-0.002	1.00	130
4	4	1	3	3	0	4104.356	-0.001	0.10	130
4	4	0	3	3	1	4104.387	-0.008	0.04	130
6	3	4	5	2	3	4105.649	0.000	5.00	130
11	1	11	10	0	10	4105.816	0.002	1.00	130
11	0	11	10	1	10	4105.816	0.005	1.00	130
10	2	9	9	1	8	4106.396	0.006	0.40	130
5	3	2	4	2	3	4106.687	0.002	0.20	130
13	1	12	13	0	13	4107.116	0.005	0.01	130
7	3	5	6	2	4	4107.954	0.001	2.00	130
12	0	12	11	1	11	4108.981	0.001	0.20	130
12	1	12	11	0	11	4108.986	0.004	0.20	130
11	1	10	10	2	9	4109.249	0.003	0.04	130
5	4	2	4	3	1	4109.294	-0.002	0.01	130
11	2	10	10	1	9	4109.413	0.006	0.01	130
5	4	1	4	3	2	4109.568	-0.001	0.10	130
8	3	6	7	2	5	4109.719	-0.002	0.01	130
9	3	7	8	2	6	4111.228	0.001	2.00	130
13	1	13	12	0	12	4112.073	-0.003	2.00	130
13	0	13	12	1	12	4112.073	-0.002	2.00	130
11	2	9	10	3	8	4112.174	0.000	0.60	130
12	1	11	11	2	10	4112.352	-0.002	0.10	130
12	2	11	11	1	10	4112.413	-0.007	0.00	130
10	3	8	9	2	7	4112.813	0.009	0.01	130

J	K-	K+	J	K-	K+	OBS	OBS-CALC	WT	ISOTOPE
5	5	0	4	4	1	4113.674	0.002	2.00	130
6	4	3	5	3	2	4113.898	0.004	0.10	130
6	3	3	5	2	4	4114.475	0.006	2.00	130
6	4	2	5	3	3	4114.972	-0.004	0.20	130
14	1	14	13	0	13	4115.095	-0.001	2.00	130
14	0	14	13	1	13	4115.095	-0.001	2.00	130
13	1	12	12	2	11	4115.369	0.004	0.01	130
12	2	10	11	3	9	4115.696	-0.005	0.60	130
12	3	10	11	2	9	4116.944	0.005	0.60	130
7	4	4	6	3	3	4117.848	0.002	2.00	130
6	5	2	5	4	1	4118.663	0.003	0.01	130
6	5	1	5	4	2	4118.700	-0.000	0.01	130
13	3	11	12	2	10	4119.423	-0.008	0.01	130
6	6	1	5	5	0	4122.275	0.001	6.00	130
7	5	3	6	4	2	4123.551	-0.000	2.00	130
11	4	8	10	3	7	4125.175	-0.003	2.00	130
12	4	9	11	3	8	4125.797	-0.007	0.50	130
18	1	18	17	0	17	4126.432	-0.001	0.04	130
13	4	10	12	3	9	4126.618	-0.001	0.20	130
17	1	16	16	2	15	4126.618	0.001	0.20	130
7	6	2	6	5	1	4127.216	-0.003	2.00	130
7	6	1	6	5	2	4127.222	-0.002	2.00	130
8	4	4	7	3	5	4127.929	0.001	0.30	130
8	5	4	7	4	3	4128.200	-0.004	0.01	130
8	5	3	7	4	4	4128.935	-0.008	4.00	130
7	7	0	6	6	1	4130.185	0.002	8.00	130
8	6	3	7	5	2	4132.135	0.010	0.00	130
8	6	2	7	5	3	4132.135	-0.021	0.00	130
9	5	4	8	4	5	4134.487	-0.002	2.00	130
8	7	2	7	6	1	4135.056	-0.001	4.00	130
10	5	6	9	4	5	4135.719	0.000	1.00	130
9	4	5	8	3	6	4136.395	-0.002	0.40	130
9	6	4	8	5	3	4136.956	-0.001	2.00	130
9	6	3	8	5	4	4137.089	-0.004	3.00	130
8	8	1	7	7	0	4137.403	0.010	0.04	130
12	5	8	11	4	7	4139.277	-0.007	0.02	130
13	5	9	12	4	8	4139.698	-0.000	0.04	130
9	7	2	8	6	3	4139.900	-0.006	8.00	130
10	5	5	9	4	6	4140.778	-0.004	1.00	130
10	6	5	9	5	4	4141.631	0.000	3.00	130
10	6	4	9	5	5	4142.101	0.001	1.00	130
9	8	1	8	7	2	4142.184	0.001	4.00	130
9	9	0	8	8	1	4143.896	-0.002	10.00	130
10	7	4	9	6	3	4144.719	0.006	4.00	130
11	6	6	10	5	5	4145.963	-0.006	2.00	130
10	4	6	9	3	7	4146.525	-0.004	0.01	130
9	3	6	8	2	7	4146.836	0.002	0.01	130
10	8	3	9	7	2	4145.948	0.002	10.00	130
11	6	5	10	5	6	4147.324	-0.005	2.00	130
11	5	6	10	4	7	4148.322	0.001	0.10	130

J	K-	K+	J	K-	K+	OBS	OBS-CALC	WT	ISOTOPE
10	9	2	9	8	1	4148.598	0.003	2.00	130
11	7	5	10	6	4	4149.466	-0.005	2.00	130
11	7	4	10	6	5	4149.556	0.000	1.00	130
10	10	1	9	9	0	4149.693	0.000	5.00	130
11	8	3	10	7	4	4151.683	-0.002	2.00	130
13	6	8	12	5	7	4152.422	-0.003	0.10	130
11	9	2	10	8	3	4153.268	0.004	2.00	130
12	7	6	11	6	5	4154.123	-0.003	1.00	130
11	10	1	10	9	2	4154.295	0.007	3.00	130
12	7	5	11	6	6	4154.406	-0.005	0.01	130
11	11	0	10	10	1	4154.767	-0.007	3.00	130
12	8	5	11	7	4	4156.396	0.007	3.00	130
12	9	4	11	8	3	4157.913	0.007	3.00	130
12	10	3	11	9	2	4158.863	0.010	0.04	130
12	11	2	11	10	1	4159.268	0.010	0.02	130
13	6	7	12	5	8	4159.754	-0.011	0.02	130
13	8	5	12	7	6	4161.110	0.002	0.01	130
13	9	4	12	8	5	4162.537	0.012	0.01	130
11	10	1	12	11	2	3895.041	-0.023	0.01	128
10	10	0	11	11	1	3900.092	0.005	0.10	128
11	9	2	12	10	3	3908.265	-0.035	0.01	128
10	9	1	11	10	2	3913.322	-0.016	0.02	128
12	8	4	13	9	5	3915.871	-0.066	0.00	128
9	9	0	10	10	1	3918.416	0.005	0.10	128
11	8	3	12	9	4	3920.856	-0.043	0.00	128
10	8	3	11	9	2	3925.903	-0.027	0.00	128
9	8	1	10	9	2	3931.062	-0.010	0.04	128
8	8	1	9	9	0	3936.130	0.001	2.00	128
10	7	4	11	8	3	3937.875	-0.023	0.10	128
9	7	2	10	8	3	3942.953	-0.012	0.20	128
8	7	2	9	8	1	3948.077	-0.006	1.00	128
10	6	5	11	7	4	3949.243	-0.021	0.01	128
10	6	4	11	7	5	3949.375	-0.019	0.01	128
7	7	0	8	8	1	3953.238	0.001	3.00	128
8	6	3	9	7	2	3959.389	-0.007	0.01	128
7	6	1	8	7	2	3964.545	0.000	4.00	128
9	5	5	10	6	4	3964.883	-0.008	0.01	128
9	5	4	10	6	5	3965.520	-0.009	0.10	128
6	6	1	7	7	0	3969.729	0.001	5.00	128
18	0	18	19	1	19	3972.047	-0.002	0.10	128
9	4	6	10	5	5	3972.986	-0.003	0.01	128
7	5	3	8	6	2	3975.208	-0.003	0.01	128
7	5	2	8	6	3	3975.251	-0.005	0.01	128
17	0	17	18	1	18	3977.394	0.004	1.00	128
9	4	5	10	5	6	3978.701	-0.000	0.02	128
8	4	5	9	5	4	3979.316	0.002	0.10	128
6	5	2	7	6	1	3980.392	0.004	4.00	128
8	4	4	9	5	5	3981.851	0.006	0.40	128
16	0	16	17	1	17	3982.665	-0.001	0.20	128
7	4	4	8	5	3	3984.981	0.001	0.50	128

J	K-	K+	J	K-	K+	OBS	OBS-CALC	WT	ISOTOPE
5	5	0	6	6	1	3985.593	-0.004	5.00	128
15	0	15	16	1	15	3987.882	0.003	0.04	128
14	2	13	15	1	14	3987.919	0.002	0.01	128
6	4	3	7	5	2	3990.346	0.005	0.20	128
6	4	2	7	5	3	3990.607	0.002	0.40	128
7	3	5	8	4	4	3991.343	0.005	0.20	128
14	0	14	15	1	15	3993.028	0.001	0.40	128
13	2	13	14	1	13	3993.083	0.004	0.20	128
5	4	2	6	5	1	3995.598	0.001	0.40	128
5	4	1	6	5	2	3995.643	-0.008	0.10	128
8	3	5	9	4	6	3996.380	0.003	0.40	128
13	0	13	14	1	14	3998.113	0.004	1.00	128
6	3	4	7	4	3	3998.405	0.000	0.04	128
6	2	5	7	3	4	3999.356	0.003	0.01	128
4	4	1	5	5	0	4000.836	0.000	9.99	128
6	3	3	7	4	4	4001.819	0.003	2.00	128
10	2	8	11	3	9	4002.648	0.007	0.40	128
12	0	12	13	1	13	4003.125	-0.000	1.00	128
11	1	10	12	2	11	4003.187	0.003	0.20	128
11	2	10	12	1	11	4003.234	0.001	0.01	128
5	3	3	6	4	2	4004.499	-0.003	2.00	128
5	3	2	6	4	3	4005.756	0.006	1.00	128
11	0	11	12	1	12	4008.074	-0.002	0.40	128
5	2	4	6	3	3	4008.941	-0.000	1.00	128
8	2	6	9	3	7	4009.816	0.009	0.10	128
4	3	2	5	4	1	4010.076	-0.002	1.00	128
4	3	1	5	4	2	4010.405	0.001	5.00	128
9	3	7	10	2	8	4010.356	-0.001	1.00	128
7	2	5	8	3	6	4012.541	0.009	1.00	128
10	0	10	11	1	11	4012.962	0.003	1.00	128
6	2	4	7	3	5	4015.077	0.004	1.00	128
3	3	1	4	4	0	4015.425	-0.000	0.20	128
3	3	0	4	4	1	4015.465	-0.007	0.04	128
4	2	3	5	3	2	4016.842	-0.008	0.02	128
10	5	5	10	6	4	4019.352	-0.003	0.04	128
4	2	2	5	3	3	4021.038	-0.002	0.40	128
12	3	10	12	4	9	4021.320	0.002	0.10	128
7	1	6	8	2	7	4021.862	0.002	2.00	128
8	0	8	9	1	9	4022.524	0.008	0.01	128
8	1	8	9	0	9	4022.524	-0.013	0.01	128
3	2	2	4	3	1	4023.455	-0.009	0.10	128
3	2	1	4	3	2	4024.953	-0.002	1.00	128
6	1	5	7	2	6	4025.758	0.000	4.00	128
9	0	9	9	1	8	4026.614	0.001	0.01	128
7	0	7	8	1	8	4027.182	0.002	0.10	128
7	1	7	8	0	8	4027.231	-0.005	0.20	128
5	1	4	6	2	5	4029.197	0.004	0.10	128
2	2	1	3	3	0	4029.277	0.008	0.01	128
2	2	0	3	3	1	4029.573	-0.001	0.10	128
9	2	8	9	3	7	4030.718	0.005	0.40	128

J	K-	K+	J	K-	K+	OBS	OBS-CALC	WT	ISOTOPE
8	1	8	8	2	7	4031.050	0.001	0.20	128
4	1	3	5	2	4	4032.357	-0.004	0.40	128
9	4	5	9	5	4	4031.390	0.004	0.20	128
6	0	6	7	1	7	4031.741	-0.006	0.10	128
6	1	6	7	0	7	4031.890	-0.004	1.00	128
10	4	6	10	5	5	4033.995	0.003	0.10	128
9	1	8	9	2	7	4034.125	0.005	0.01	128
8	2	7	8	3	6	4034.695	0.011	0.10	128
7	3	5	7	4	4	4035.201	0.004	0.20	128
3	1	2	4	2	3	4035.601	-0.005	1.00	128
5	0	5	6	1	6	4036.183	0.002	0.40	128
7	2	6	7	3	5	4038.056	0.009	0.20	128
10	2	8	10	3	7	4038.476	0.006	0.04	128
6	3	3	6	4	2	4038.595	-0.000	1.00	128
2	1	1	3	2	2	4039.207	-0.002	3.00	128
6	1	6	6	2	5	4039.813	-0.000	0.06	128
8	1	7	8	2	6	4040.080	0.002	0.10	128
4	0	4	5	1	5	4040.417	0.001	1.00	128
6	2	5	6	3	4	4040.717	0.006	0.01	128
4	1	4	5	0	5	4041.266	-0.001	2.00	128
1	1	1	2	2	0	4041.975	-0.006	1.00	128
6	0	6	6	1	5	4042.267	0.002	0.10	128
5	2	4	5	3	3	4042.654	0.002	0.01	128
1	1	0	2	2	1	4043.319	0.001	0.20	128
4	2	3	4	3	2	4043.918	-0.003	0.10	128
3	0	3	4	1	4	4044.382	0.004	0.04	128
7	1	6	7	2	5	4045.589	0.001	1.00	128
3	2	1	3	3	0	4045.879	0.006	0.10	128
3	1	3	4	0	4	4046.170	0.003	2.00	128
5	0	5	5	1	4	4047.530	-0.000	0.10	128
2	0	2	3	1	3	4048.101	-0.007	0.20	128
5	2	3	5	3	2	4048.403	0.001	0.60	128
6	2	4	6	3	3	4049.317	0.008	0.10	128
3	1	3	3	2	2	4049.441	0.003	0.10	128
6	1	5	6	2	4	4050.062	0.002	0.20	128
2	1	2	2	2	1	4051.355	0.012	0.01	128
2	1	2	3	0	3	4051.355	-0.004	0.01	128
1	0	1	2	1	2	4051.858	-0.007	1.00	128
4	0	4	4	1	3	4052.304	0.003	1.00	128
5	1	4	5	2	3	4053.084	0.003	2.00	128
4	1	3	4	2	2	4054.609	0.000	0.20	128
3	1	2	3	2	1	4054.905	-0.004	1.00	128
0	0	0	1	1	1	4055.986	0.003	0.20	128
3	0	3	3	1	2	4056.088	0.002	2.00	128
1	1	1	2	0	2	4056.819	0.003	0.10	128
2	0	2	2	1	1	4058.619	-0.003	3.00	128
1	0	1	1	1	0	4060.031	-0.001	2.00	128
1	1	0	1	0	1	4067.994	0.003	5.00	128
2	1	1	2	0	2	4069.257	0.002	1.00	128
3	2	1	3	1	2	4071.717	-0.008	0.10	128

J	K-	K+	J	K-	K+	OBS	OBS-CALC	WT	ISOTOPE
4	2	2	4	1	3	4071.877	0.001	0.40	128
2	2	0	2	1	1	4072.281	-0.002	0.10	128
5	2	3	5	1	4	4073.034	0.003	4.00	128
4	1	3	4	0	4	4074.722	0.003	0.40	128
7	3	4	7	2	5	4074.799	0.006	0.10	128
6	3	3	6	2	4	4074.799	-0.003	0.10	128
6	2	4	6	1	5	4075.340	0.003	2.00	128
2	1	2	1	0	1	4076.008	-0.008	0.01	128
3	0	3	2	1	2	4076.189	0.008	0.04	128
10	4	6	10	3	7	4076.950	0.004	0.04	128
9	4	5	9	3	6	4076.995	0.003	0.10	128
4	3	1	4	2	2	4077.053	0.006	0.20	128
8	4	4	8	3	5	4078.108	0.002	0.04	128
4	3	2	4	2	3	4079.726	-0.002	0.40	128
7	4	3	7	3	4	4079.824	0.011	0.04	128
12	4	8	12	3	9	4080.725	0.004	1.00	128
4	0	4	3	1	3	4080.836	-0.002	0.10	128
6	4	2	6	3	3	4081.505	0.009	0.10	128
10	5	5	10	4	6	4081.549	0.005	0.04	128
10	3	7	10	2	8	4081.852	-0.010	0.01	128
6	3	4	6	2	5	4081.990	0.000	0.10	128
4	1	4	3	0	3	4082.717	0.002	0.40	128
8	4	5	8	3	6	4084.572	0.010	0.01	128
2	2	0	1	1	1	4084.727	0.004	0.20	128
5	0	5	4	1	4	4085.035	0.001	1.00	128
8	5	3	8	4	4	4085.315	-0.002	0.04	128
11	3	8	11	2	9	4085.905	0.010	0.01	128
5	1	5	4	0	4	4085.970	0.010	0.01	128
7	5	3	7	4	4	4087.001	-0.003	0.10	128
3	2	2	2	1	1	4087.352	0.005	0.40	128
5	5	0	5	4	1	4087.700	0.009	0.01	128
6	0	6	5	1	5	4088.902	0.003	1.00	128
6	1	6	5	0	5	4089.319	0.001	0.40	128
6	1	5	5	2	4	4089.961	0.001	0.10	128
8	6	3	8	5	4	4090.282	-0.000	0.01	128
4	2	3	3	1	2	4090.696	0.005	0.01	128
3	2	1	2	1	2	4091.818	-0.001	2.00	128
7	0	7	6	1	6	4092.550	-0.001	0.10	128
7	1	7	6	0	6	4092.732	0.005	1.00	128
5	2	4	4	1	3	4093.490	0.001	0.40	128
9	1	8	9	0	9	4094.314	0.013	0.00	128
3	3	1	2	2	0	4094.490	0.004	0.20	128
7	1	6	6	2	5	4094.857	-0.007	0.40	128
8	0	8	7	1	7	4095.061	-0.002	1.00	128
8	1	8	7	0	7	4096.131	-0.002	0.10	128
8	2	6	7	3	5	4097.364	0.006	0.10	128
7	2	6	6	1	5	4098.313	0.002	4.00	128
4	3	2	3	2	1	4099.036	0.004	0.40	128
8	1	7	7	2	6	4099.080	0.001	0.10	128
4	3	1	3	2	2	4100.424	-0.005	0.01	128

J	K-	K+	J	K-	K+	OBS	OBS-CALC	WT	ISOTOPE
4	2	2	3	1	3	4100.424	0.011	0.01	128
5	2	3	4	1	4	4110.535	0.000	0.04	128
8	2	7	7	1	6	4100.875	0.006	0.40	128
10	1	10	9	0	9	4102.805	-0.001	0.10	128
9	2	8	8	1	7	4103.665	0.000	0.40	128
4	4	0	3	3	1	4104.622	-0.002	0.01	128
6	3	4	5	2	3	4105.878	-0.000	0.10	128
10	2	9	9	1	8	4106.620	-0.001	0.40	128
5	3	2	4	2	3	4106.916	0.001	0.20	128
13	1	12	13	0	13	4107.351	0.009	0.10	128
7	3	5	6	2	4	4108.181	-0.001	2.00	128
5	4	2	4	3	1	4109.526	-0.000	0.01	128
5	4	1	4	3	2	4109.804	0.005	0.01	128
8	3	6	7	2	5	4109.949	-0.001	0.10	128
9	3	7	8	2	6	4111.458	0.002	2.00	128
13	1	13	12	0	12	4112.305	-0.003	1.00	128
10	3	8	9	2	7	4113.034	0.001	0.10	128
5	5	0	4	4	1	4113.898	-0.005	0.10	128
6	4	2	5	3	3	4115.202	-0.005	0.80	128
12	2	10	11	3	9	4115.938	0.005	0.10	128
12	3	10	11	2	9	4117.174	0.004	0.20	128
6	5	2	5	4	1	4118.894	0.003	0.01	128
13	3	11	12	2	10	4119.660	-0.003	0.10	128
6	6	1	5	5	0	4122.508	0.003	8.00	128
9	4	6	8	3	5	4123.252	-0.008	2.00	128
11	4	8	10	3	7	4125.410	0.003	0.10	128
12	4	9	11	3	8	4126.033	-0.001	0.20	128
17	1	16	16	2	15	4126.856	0.005	0.40	128
7	6	1	6	5	2	4127.453	-0.003	2.00	128
8	5	4	7	4	3	4128.430	-0.007	0.02	128
8	5	3	7	4	4	4129.177	0.001	4.00	128
19	1	19	18	0	18	4129.311	-0.003	0.00	128
7	7	0	6	6	1	4130.416	0.001	6.00	128
9	5	4	8	4	5	4134.722	-0.001	2.00	128
8	7	2	7	6	1	4135.290	0.001	3.00	128
10	5	6	9	4	5	4135.950	-0.001	0.04	128
9	4	5	8	3	6	4136.633	-0.001	0.00	128
9	6	4	8	5	3	4137.183	-0.008	1.00	128
9	6	3	8	5	4	4137.327	0.001	0.10	128
8	8	1	7	7	0	4137.629	0.004	2.00	128
11	5	7	10	4	6	4138.253	-0.004	0.60	128
12	5	8	11	4	7	4139.513	-0.002	0.01	128
9	7	2	8	6	3	4140.131	-0.009	6.00	128
10	5	5	9	4	6	4141.019	0.001	0.10	128
10	6	5	9	5	4	4141.861	-0.004	0.80	128
10	6	4	9	5	5	4142.337	0.002	0.20	128
9	8	1	8	7	2	4142.415	-0.001	3.00	128
9	9	0	8	8	1	4144.130	-0.001	9.90	128
10	7	4	9	6	3	4144.953	0.006	1.00	128
11	6	6	10	5	5	4146.195	-0.008	0.40	128

J	K-	K+	J	K-	K+	OBS	OBS-CALC	WT	ISOTOPE
10	4	6	9	3	7	4146.779	0.010	0.01	128
10	8	3	9	7	2	4147.178	-0.002	6.00	128
11	6	5	10	5	6	4147.555	-0.009	0.01	128
10	9	2	9	8	1	4148.827	-0.002	4.00	128
11	7	4	10	6	5	4149.781	-0.010	0.10	128
10	10	1	9	9	0	4149.927	0.000	2.00	128
11	8	3	10	7	4	4151.917	-0.003	3.00	128
13	6	8	12	5	7	4152.655	-0.003	0.01	128
11	9	2	10	8	3	4153.501	0.002	1.00	128
12	7	6	11	6	5	4154.363	0.002	0.01	128
11	10	1	10	9	2	4154.525	0.002	2.00	128
11	11	0	10	10	1	4155.011	0.003	0.40	128
12	8	5	11	7	4	4156.632	0.008	0.04	128
12	5	7	11	4	8	4157.752	0.003	0.01	128
12	9	4	11	8	3	4158.145	0.004	0.04	128
12	10	3	11	9	2	4159.096	0.008	0.04	128
12	11	2	11	10	1	4159.503	0.010	0.01	128
13	7	6	12	6	7	4159.633	-0.003	0.00	128
13	6	7	12	5	8	4160.011	0.006	0.01	128
13	9	4	12	8	5	4162.772	0.011	0.00	128
10	10	0	11	11	1	3900.298	0.006	0.01	126
11	9	2	12	10	3	3908.467	-0.038	0.00	126
10	9	1	11	10	2	3913.532	-0.012	0.10	126
9	9	0	10	10	1	3918.625	0.006	0.02	126
11	8	3	12	9	4	3921.070	-0.036	0.01	126
10	8	3	11	9	2	3926.116	-0.022	0.01	126
9	8	1	10	9	2	3931.215	-0.007	0.04	126
8	8	1	9	9	0	3936.344	0.004	0.10	126
10	7	4	11	8	3	3938.089	-0.018	0.20	126
9	7	2	10	8	3	3943.163	-0.013	0.01	126
8	7	2	9	8	1	3948.293	-0.002	1.00	126
10	6	4	11	7	5	3949.584	-0.021	0.00	126
7	7	0	8	8	1	3953.453	0.002	1.00	126
8	6	3	9	7	2	3959.610	0.001	0.01	126
7	6	1	8	7	2	3964.761	0.001	1.00	126
9	5	5	10	6	4	3965.097	-0.008	0.01	126
9	5	4	10	6	5	3965.735	-0.008	0.02	126
6	6	1	7	7	0	3969.951	0.007	1.00	126
17	0	17	18	1	18	3977.005	0.003	0.01	126
9	4	5	10	5	6	3978.925	0.007	0.02	126
8	4	5	9	5	4	3979.533	0.004	0.01	126
8	4	4	9	5	5	3982.064	0.002	0.20	126
16	0	16	17	1	17	3982.877	-0.003	0.01	126
7	4	4	8	5	3	3985.203	0.006	0.10	126
5	5	0	6	6	1	3985.815	-0.001	5.00	126
7	4	3	8	5	4	3986.125	0.004	0.04	126
15	0	15	16	1	16	3988.100	0.007	0.01	126
6	4	3	7	5	2	3990.565	0.006	0.01	126
6	4	2	7	5	3	3990.823	-0.001	0.04	126
7	3	5	8	4	4	3991.550	-0.004	0.10	126

J	K-	K+	J	K-	K+	OBS	OBS-CALC	WT	ISOTOPE
14	0	14	15	1	15	3993.240	-0.002	1.00	126
13	2	13	14	1	13	3993.285	-0.009	1.00	126
12	3	10	13	2	11	3994.014	-0.003	0.01	126
5	4	2	6	5	1	3995.821	0.004	0.04	126
5	4	1	6	5	2	3995.875	0.004	0.04	126
8	3	5	9	4	6	3996.607	0.011	0.01	126
13	0	13	14	1	14	3998.330	0.004	0.40	126
6	3	4	7	4	3	3998.628	0.004	0.01	126
6	2	5	7	3	4	3999.588	0.018	0.01	126
4	4	1	5	5	0	4001.056	-0.001	4.00	126
6	3	3	7	4	4	4002.039	0.002	1.00	126
12	0	12	13	1	13	4003.343	-0.000	1.00	126
11	1	10	12	2	11	4003.405	0.003	0.01	126
11	2	10	12	1	11	4003.454	0.004	0.01	126
5	3	3	6	4	2	4004.725	0.002	1.00	126
5	3	2	6	4	3	4005.981	0.010	0.01	126
11	0	11	12	1	12	4008.297	0.002	0.10	126
5	2	4	6	3	3	4009.161	0.000	0.50	126
4	3	2	5	4	1	4010.301	0.001	1.00	126
9	3	7	10	2	8	4011.084	0.010	0.40	126
10	0	10	11	1	11	4013.183	0.004	0.10	126
3	3	1	4	4	0	4015.649	0.000	0.20	126
3	3	0	4	4	1	4015.691	-0.005	0.04	126
4	1	4	5	2	3	4015.872	0.001	0.04	126
4	2	3	5	3	2	4017.076	0.003	0.01	126
8	2	7	9	1	8	4018.473	-0.004	1.00	126
4	2	2	5	3	3	4021.264	0.001	0.10	126
12	3	10	12	4	9	4021.352	0.015	0.04	126
7	1	6	8	2	7	4022.083	0.000	0.40	126
8	0	8	9	1	9	4022.745	0.007	0.01	126
8	1	8	9	0	9	4022.745	-0.014	0.01	126
7	2	6	8	1	7	4023.676	0.006	0.01	126
3	2	2	4	3	1	4023.676	-0.012	0.01	126
7	3	5	8	2	6	4025.101	0.003	0.01	126
3	2	1	4	3	2	4025.177	-0.002	1.00	126
6	1	5	7	2	6	4025.984	0.003	0.40	126
7	0	7	8	1	8	4027.404	0.001	0.10	126
7	1	7	8	0	8	4027.458	-0.001	0.20	126
5	1	4	6	2	5	4029.420	0.003	0.10	126
2	2	0	3	3	1	4029.793	-0.007	2.00	126
9	2	8	9	3	7	4030.940	0.004	0.10	126
8	1	8	8	2	7	4031.269	-0.004	0.02	126
6	0	6	7	1	7	4031.970	-0.001	0.40	126
4	1	3	5	2	4	4032.591	0.004	2.00	126
9	1	8	9	2	7	4034.350	0.008	0.02	126
3	1	2	4	2	3	4035.826	-0.006	0.01	126
7	1	7	7	2	6	4035.826	0.016	0.01	126
5	0	5	6	1	6	4036.409	0.002	0.60	126
5	3	2	5	4	1	4037.493	-0.000	0.02	126
10	2	8	10	3	7	4038.694	0.002	0.02	126

J	K-	K+	J	K-	K+	OBS	OBS-CALC	WT	ISOTOPE
6	3	3	6	4	2	4038.825	0.001	0.01	126
2	1	1	3	2	2	4039.435	-0.001	1.00	126
6	1	6	6	2	5	4040.048	0.009	0.01	126
4	0	4	5	1	5	4040.648	0.006	0.20	126
4	1	4	5	0	5	4041.487	-0.006	4.00	126
5	2	4	5	3	3	4042.882	0.002	1.00	126
1	1	0	2	2	1	4043.547	0.001	0.20	126
3	2	2	3	3	1	4044.853	-0.014	0.00	126
7	1	6	7	2	5	4045.819	0.006	0.04	126
3	1	3	4	0	4	4046.395	0.001	2.00	126
5	0	5	5	1	4	4047.759	0.002	0.01	126
2	0	2	3	1	3	4048.330	-0.005	0.01	126
5	2	3	5	3	2	4048.036	0.005	0.10	126
6	2	4	6	3	3	4049.543	0.005	0.10	126
6	1	5	6	2	4	4050.285	-0.002	1.00	126
2	1	2	2	2	1	4051.582	0.009	0.01	126
4	0	4	4	1	3	4052.528	-0.001	1.00	126
5	1	4	5	2	3	4053.312	0.003	2.00	126
4	1	3	4	2	2	4054.839	0.001	0.10	126
3	1	2	3	2	1	4055.134	-0.005	4.00	126
0	0	0	1	1	1	4056.214	0.001	1.00	126
3	0	3	3	1	2	4056.319	0.004	2.00	126
1	1	1	2	0	2	4057.046	0.001	0.01	126
2	0	2	2	1	1	4058.851	-0.001	1.00	126
1	0	1	1	1	0	4060.260	-0.002	2.00	126
1	1	0	1	0	1	4068.219	-0.003	4.00	126
2	1	1	2	0	2	4069.485	-0.001	0.20	126
3	2	1	3	1	2	4071.357	0.001	0.40	126
4	2	2	4	1	3	4072.101	-0.006	0.01	126
2	2	0	2	1	1	4072.518	0.004	0.40	126
5	2	3	5	1	4	4073.264	0.002	3.00	126
6	3	3	6	2	4	4075.029	-0.003	0.40	126
6	2	4	6	1	5	4075.572	0.002	0.40	126
2	1	2	1	0	1	4076.245	-0.004	0.01	126
3	0	3	2	1	2	4076.420	0.006	0.02	126
10	4	6	10	3	7	4077.188	0.012	0.01	126
9	4	5	9	3	6	4077.226	0.005	0.01	126
4	3	1	4	2	2	4077.286	0.008	0.01	126
8	4	4	8	3	5	4078.340	0.005	0.01	126
4	3	2	4	2	3	4079.960	-0.000	0.20	126
7	4	3	7	3	4	4080.050	0.007	0.10	126
4	0	4	3	1	3	4081.077	0.005	0.10	126
6	3	4	6	2	5	4082.221	-0.001	0.10	126
4	1	4	3	0	3	4082.950	0.001	0.04	126
2	2	0	1	1	1	4084.957	0.000	0.10	126
5	0	5	4	1	4	4085.270	0.001	0.40	126
11	3	8	11	2	9	4086.144	0.014	0.01	126
7	5	3	7	4	4	4087.229	-0.006	0.40	126
3	2	2	2	1	1	4087.574	-0.007	0.10	126
5	5	0	5	4	1	4087.945	0.023	0.00	126

J	K-	K+	J	K-	K+	OBS	OBS-CALC	WT	ISOTOPE
10	6	4	10	5	5	4088.560	0.006	0.02	126
6	0	6	5	1	5	4089.130	-0.004	0.01	126
6	1	6	5	0	5	4089.554	0.001	0.01	126
6	1	5	5	2	4	4090.202	0.005	0.01	126
3	2	1	2	1	2	4092.053	-0.002	0.01	126
7	0	7	6	1	6	4092.782	-0.005	0.10	126
7	1	7	6	0	6	4092.970	0.007	2.00	126
5	2	4	4	1	3	4093.729	0.005	0.40	126
3	3	0	2	2	1	4095.000	0.002	0.01	126
7	1	6	6	2	5	4095.100	-0.000	0.40	126
8	0	8	7	1	7	4096.297	-0.003	2.00	126
8	2	6	7	3	5	4097.606	0.010	0.01	126
7	2	6	6	1	5	4098.543	-0.004	3.00	126
8	1	7	7	2	6	4099.314	-0.003	0.01	126
8	2	7	7	1	6	4101.109	0.003	1.00	126
10	0	10	9	1	9	4103.041	0.007	0.01	126
10	1	10	9	0	9	4103.041	-0.003	0.01	126
5	3	3	4	2	2	4103.096	0.004	0.04	126
9	2	8	8	1	7	4103.902	0.000	0.40	126
4	4	0	3	3	1	4104.863	0.002	0.01	126
6	3	4	5	2	3	4106.109	-0.005	0.01	126
10	2	9	9	1	8	4106.866	0.008	0.10	126
5	3	2	4	2	3	4107.149	-0.004	0.01	126
7	3	5	6	2	4	4108.418	-0.000	1.00	126
5	4	1	4	3	2	4110.037	0.000	0.20	126
9	3	7	8	2	6	4111.693	0.000	1.00	126
10	3	8	9	2	7	4113.278	0.008	0.10	126
5	5	0	4	4	1	4114.137	-0.003	0.01	126
6	4	3	5	3	2	4114.376	0.014	0.01	126
6	4	2	5	3	3	4115.444	-0.001	0.02	126
12	2	10	11	3	9	4116.179	0.007	0.01	126
12	3	10	11	2	9	4117.419	0.011	0.02	126
6	5	2	5	4	1	4119.128	-0.001	0.01	126
6	5	1	5	4	2	4119.162	-0.008	0.01	126
6	6	1	5	5	0	4122.744	0.001	9.00	126
7	5	2	6	4	3	4124.219	-0.007	0.01	126
7	3	4	6	2	5	4124.310	-0.002	0.01	126
11	4	8	10	3	7	4125.651	0.007	0.20	126
17	1	16	16	2	15	4127.099	0.008	0.20	126
7	6	1	6	5	2	4127.690	-0.005	1.00	126
8	5	4	7	4	3	4128.668	-0.008	0.10	126
8	5	3	7	4	4	4129.415	-0.001	2.00	126
7	7	0	6	6	1	4130.560	0.006	7.00	126
8	6	3	7	5	2	4132.604	0.006	0.01	126
9	5	5	8	4	4	4132.843	0.003	0.20	126
9	5	4	8	4	5	4134.968	0.003	0.10	126
8	7	2	7	6	1	4135.529	-0.000	5.00	126
10	5	6	9	4	5	4136.184	-0.007	0.01	126
9	6	3	8	5	4	4137.569	0.002	0.04	126
8	8	1	7	7	0	4137.867	0.002	2.00	126

J	K-	K+	J	K-	K+	OBS	OBS-CALC	WT	ISOTOPE
11	5	7	10	4	6	4138.484	-0.012	0.01	126
9	7	2	8	6	3	4140.377	-0.004	5.00	126
10	5	5	9	4	6	4141.262	0.000	1.00	126
10	6	4	9	5	5	4142.576	-0.000	0.04	126
9	8	1	8	7	2	4142.656	-0.001	2.00	126
9	9	0	8	8	1	4144.367	-0.004	4.00	126
10	7	4	9	6	3	4145.195	0.006	1.00	126
11	6	6	10	5	5	4146.438	-0.007	0.01	126
10	8	3	9	7	2	4147.423	0.002	2.00	126
11	6	5	10	5	6	4147.805	-0.002	0.01	126
10	9	2	9	8	1	4149.068	-0.002	1.00	126
10	10	1	9	9	0	4150.166	-0.001	2.00	126
11	8	3	10	7	4	4152.161	-0.001	4.00	126
11	9	2	10	8	3	4153.743	0.003	0.60	126
11	11	0	10	10	1	4155.249	0.000	0.04	126
12	8	5	11	7	4	4156.376	0.009	1.00	126
12	9	4	11	8	3	4158.393	0.009	0.40	126
13	6	7	12	5	8	4160.253	0.002	0.01	126
13	9	4	12	8	5	4163.015	0.011	0.01	126
9	9	0	10	10	1	3918.723	-0.003	0.01	125
8	8	1	9	9	0	3936.449	0.000	0.01	125
10	7	4	11	8	3	3938.193	-0.022	0.01	125
9	7	2	10	8	3	3943.272	-0.012	0.01	125
8	7	2	9	8	1	3948.400	-0.004	0.01	125
7	7	0	8	8	1	3953.567	0.007	1.00	125
6	5	2	7	6	1	3980.720	0.003	0.01	125
6	4	2	7	5	3	3990.942	0.006	0.01	125
5	4	1	6	5	2	3995.984	0.001	0.01	125
6	2	5	7	3	4	3999.682	0.001	0.01	125
4	4	1	5	5	0	4001.170	-0.000	0.04	125
4	4	0	5	5	1	4001.170	-0.006	0.04	125
11	0	11	12	1	12	4008.409	0.002	0.01	125
9	3	7	10	2	8	4011.184	-0.002	0.04	125
10	0	10	11	1	11	4013.287	-0.005	0.01	125
3	3	1	4	4	0	4015.756	-0.007	0.01	125
3	3	0	4	4	1	4015.807	-0.003	0.01	125
9	0	9	10	1	10	4018.099	-0.009	0.01	125
8	2	7	9	1	8	4018.588	-0.002	0.04	125
7	1	6	8	2	7	4022.264	0.008	0.01	125
8	0	8	9	1	9	4022.864	0.012	0.01	125
8	1	8	9	0	9	4022.864	-0.009	0.01	125
3	2	2	4	3	1	4023.793	-0.010	0.01	125
7	2	6	8	1	7	4023.793	0.010	0.01	125
7	0	7	8	1	8	4027.511	-0.006	0.01	125
7	1	7	8	0	8	4027.563	-0.011	0.01	125
2	2	0	3	3	1	4029.906	-0.009	0.04	125
6	3	4	7	2	5	4033.056	0.008	0.01	125
4	1	4	5	0	5	4041.608	-0.000	2.00	125
3	0	3	4	1	4	4044.723	0.002	0.10	125
3	2	2	3	3	1	4044.977	-0.007	0.00	125

J	K-	K+	J	K-	K+	OBS	OBS-CALC	WT	ISOTOPE
3	1	3	4	0	4	4046.510	0.000	0.40	125
5	2	3	5	3	2	4048.759	0.011	0.01	125
6	1	5	6	2	4	4050.411	0.008	0.01	125
1	0	1	2	1	2	4052.213	0.002	0.01	125
5	1	4	5	2	3	4053.428	0.002	0.04	125
3	1	2	3	2	1	4055.254	-0.003	0.40	125
3	0	3	3	1	2	4056.440	0.008	0.01	125
2	0	2	2	1	1	4058.967	-0.003	0.10	125
1	0	1	1	1	0	4060.374	-0.006	0.01	125
1	1	0	1	0	1	4068.341	0.000	0.01	125
2	1	1	2	0	2	4069.599	-0.006	0.04	125
5	2	3	5	1	4	4073.380	-0.001	0.02	125
4	0	4	3	1	3	4081.195	0.003	0.10	125
6	3	4	6	2	5	4082.339	-0.002	0.01	125
4	1	4	3	0	3	4083.068	-0.001	0.02	125
5	0	5	4	1	4	4085.389	0.000	1.00	125
5	1	5	4	0	4	4086.322	0.001	0.10	125
5	5	0	5	4	1	4088.036	-0.005	0.01	125
6	0	6	5	1	5	4089.257	0.002	0.10	125
7	0	7	6	1	6	4092.914	0.006	0.01	125
7	1	7	6	0	6	4093.077	-0.006	0.04	125
5	2	4	4	1	3	4093.841	-0.003	0.01	125
7	1	6	6	2	5	4095.225	0.004	0.01	125
8	1	8	7	0	7	4096.487	-0.004	0.10	125
7	2	6	6	1	5	4098.670	0.002	0.04	125
9	1	9	8	0	8	4099.840	-0.018	0.00	125
10	1	10	9	0	9	4103.161	-0.005	0.01	125
10	2	9	9	1	8	4106.977	-0.003	0.01	125
5	3	2	4	2	3	4107.283	0.008	0.01	125
9	3	7	8	2	6	4111.819	0.005	0.01	125
5	5	0	4	4	1	4114.269	0.008	2.00	125
7	7	0	6	6	1	4130.781	0.004	4.00	125
8	5	4	7	4	3	4128.802	0.003	0.01	125
8	7	2	7	6	1	4135.654	0.002	0.04	125
9	7	2	8	6	3	4140.495	-0.009	0.40	125
7	6	1	6	5	2	4127.810	-0.008	0.10	125
7	6	2	6	5	1	4127.810	-0.002	0.10	125
6	6	1	5	5	0	4122.868	0.003	1.00	125
9	8	1	8	7	2	4142.771	-0.009	0.02	125
9	9	0	8	8	1	4144.494	-0.000	0.40	125
10	7	4	9	6	3	4145.312	-0.000	0.02	125
10	9	2	9	8	1	4149.194	0.000	0.01	125
10	10	1	9	9	0	4150.284	-0.007	0.02	125
11	8	3	10	7	4	4152.281	-0.005	0.01	125
11	9	2	10	8	3	4153.865	0.001	0.01	125
12	8	5	11	7	4	4157.001	0.010	0.01	125
10	8	3	11	9	2	3926.329	-0.025	0.01	124
10	7	4	11	8	3	3938.302	-0.022	0.01	124
9	7	2	10	8	3	3943.384	-0.010	0.01	124
8	7	2	9	8	1	3948.507	-0.008	0.01	124

J	K-	K+	J	K-	K+	OBS	OBS-CALC	WT	ISOTOPE
7	7	0	8	8	1	3953.676	0.004	0.01	124
7	6	1	8	7	2	3964.975	-0.007	0.01	124
6	6	1	7	7	0	3970.175	0.007	0.04	124
6	5	2	7	6	1	3980.830	-0.001	0.04	124
5	5	0	6	5	1	3986.043	0.001	0.02	124
4	4	1	5	5	0	4001.283	-0.002	0.02	124
4	4	0	5	5	1	4001.283	-0.009	0.02	124
3	3	1	4	4	0	4015.872	-0.007	0.01	124
3	3	0	4	4	1	4015.929	0.003	0.01	124
8	2	7	9	1	8	4018.711	0.006	0.01	124
4	2	2	5	3	3	4021.491	-0.003	0.01	124
8	0	8	9	1	9	4022.986	0.018	0.01	124
8	1	8	9	0	9	4022.986	-0.002	0.01	124
7	2	6	8	1	7	4023.912	0.013	0.01	124
3	2	2	4	3	1	4023.912	-0.007	0.01	124
3	2	1	4	3	2	4025.414	0.003	0.01	124
7	0	7	8	1	8	4027.634	0.001	0.10	124
7	1	7	8	0	8	4027.589	-0.001	0.20	124
2	2	0	3	3	1	4030.027	-0.006	0.04	124
4	1	3	5	2	4	4032.822	0.003	0.01	124
4	0	4	5	1	5	4040.881	0.006	0.04	124
4	1	4	5	0	5	4041.722	-0.004	0.01	124
5	1	4	5	2	3	4053.548	0.003	0.01	124
4	1	3	4	2	2	4055.038	0.014	0.01	124
2	0	2	2	1	1	4059.090	0.001	0.01	124
5	2	3	5	1	4	4073.507	0.006	0.04	124
6	1	6	5	0	5	4089.793	-0.003	0.00	124
5	2	4	4	1	3	4093.972	0.006	0.01	124
9	1	9	8	0	8	4099.949	-0.032	0.10	124
9	3	7	8	2	6	4111.952	0.015	0.02	124
6	6	1	5	5	0	4122.993	0.004	0.00	124
8	5	3	7	4	4	4129.075	0.012	0.00	124
7	7	0	6	6	1	4130.901	0.000	0.04	124
9	5	5	8	4	4	4133.105	0.018	0.00	124
8	7	2	7	6	1	4135.776	-0.001	0.04	124
8	8	1	7	7	0	4138.112	-0.000	0.10	124
9	7	2	8	6	3	4140.623	-0.006	0.04	124
9	8	1	8	7	2	4142.902	-0.003	0.01	124
10	7	4	9	6	3	4145.430	-0.008	0.01	124
10	9	2	9	8	1	4149.318	-0.001	0.01	124
10	10	1	9	9	0	4150.412	-0.003	0.01	124
11	9	2	10	8	3	4153.982	-0.008	0.01	124

APPENDIX VI

FREQUENCY ASSIGNMENTS FOR THE (1,0,0) AND (0,0,1) BANDS OF H_2S

J	K_-	K_+	J	K_-	K_+	OBS	OBS-CALC	WT	BAND
0	0	0	1	1	1	2599,326	0,002	0,01	100
1	0	1	2	1	2	2589,682	0,016	0,01	100
1	1	1	2	0	2	2591,243	-0,017	0,00--	100
2	1	2	3	0	3	2580,716	-0,001	0,12	100
2	0	2	3	1	3	2580,418	0,007	0,01	100
3	0	3	4	1	4	2570,607	0,001	0,06	100
4	1	4	5	0	5	2560,554	-0,001	0,25	100
5	0	5	6	1	6	2550,377	0,033	0,00--	100
6	1	6	7	0	7	2540,003	0,000	0,00--	100
7	0	7	8	1	8	2528,528	-1,005	0,00--	100
1	1	0	2	2	1	2578,350	0,004	0,01	100
2	2	1	3	1	2	2573,676	-0,003	0,01	100
2	1	1	3	2	2	2568,411	-0,012	0,00--	100
3	2	2	4	1	3	2561,234	0,018	0,00--	100
3	1	2	4	2	3	2559,743	0,065	0,00--	100
4	2	3	5	1	4	2550,377	-0,035	0,00--	100
4	1	3	5	2	4	2550,122	0,003	0,00--	100
2	2	0	3	3	1	2556,636	0,009	0,00--	100
3	3	1	4	2	2	2557,600	0,002	0,00--	100
3	2	1	4	3	2	2546,268	0,006	0,01	100
4	3	2	5	2	3	2542,378	0,004	0,01	100
3	3	0	4	4	1	2534,578	0,005	0,00--	100
1	1	1	0	0	0	2629,276	0,002	0,25	100
2	0	2	1	1	1	2636,767	-0,016	0,01	100
2	1	2	1	0	1	2638,392	-0,000	1.00	100
3	0	3	2	1	2	2646,474	-0,010	0,06	100
3	1	3	2	0	2	2646,803	0,001	0.70	100
4	1	4	3	0	3	2655,462	-0.012	0.06	100
5	0	5	4	1	4	2664,114	0,001	0.06	100
6	1	6	5	0	5	2672,636	0,001	1.00	100
7	0	7	6	1	6	2681,010	0,006	0.70	100
8	1	8	7	0	7	2689,225	0,002	1,00	100
9	0	9	8	1	8	2697,291	0,001	1.00	100
10	1	10	9	0	9	2705,202	-0,000	1.00	100
11	0	11	10	1	10	2712,960	0,001	1.00	100
12	1	12	11	0	11	2720,561	0,002	1.00	100
13	0	13	12	1	12	2728,010	0.010	1,00	100
14	1	14	13	0	13	2735,288	0,007	1.00	100
15	0	15	14	1	14	2742,414	0,011	1,00	100
16	1	16	15	0	15	2749,377	0.013	0,25	100
17	0	17	16	1	16	2756,173	0,007	0,06	100
2	2	1	1	1	0	2649,356	-0,002	1,00	100
3	1	2	2	2	1	2652,942	0,010	0,25	100
3	2	2	2	1	1	2658,217	0,003	0,25	100
4	2	3	3	1	2	2665,572	0,002	1,00	100
5	1	4	4	2	3	2673,108	-0,002	0.70	100
5	2	4	4	1	3	2673,498	0,002	1,00	100
6	2	5	5	1	4	2681,618	-0,015	0.06	100
7	1	6	6	2	5	2689,807	0.005	0.06	100
8	2	7	7	1	6	2697,859	0,001	1.00	100
9	2	8	8	2	7	2705,754	-0,003	1.00	100
10	2	9	9	1	8	2713,513	0,010	1,00	100
11	1	10	10	2	9	2721,103	0,010	1.00	100
12	2	11	11	1	10	2728,533	0,008	0,25	100
13	1	12	12	2	11	2735,802	0,004	1,00	100
14	2	13	13	1	12	2742,924	0.015	0,25	100
15	1	14	14	2	13	2749,877	0.018	0,25	100
16	2	15	15	1	14	2756,670	0,024	0.06	100
17	1	16	16	2	15	2763,308	0.037	0.01	100
3	3	1	2	2	0	2669,568	0,003	0.70	100

J	K_-	K_+	J	K_-	K_+	OBS	OBS-CALC	WT	BAND
4	2	2	3	3	1	2666,955	0,001	0,06	100
4	3	2	3	2	1	2678,361	0,012	0,10	100
5	2	3	4	3	2	2680,251	-0,001	1,00	100
5	3	3	4	2	2	2684,819	0,004	1,00	100
6	2	4	5	3	3	2690,160	-0,005	1,00	100
6	3	4	5	2	3	2691,405	0,005	1,00	100
7	2	5	6	3	4	2698,593	-0,021	0,01	100
7	3	5	6	2	4	2698,877	0,001	0,25	100
8	2	6	7	3	5	2706,601	0,035	0,01	100
8	3	6	7	2	5	2706,730	0,113	0,00--	100
9	2	7	8	3	6	2714,300	0,004	1,00	100
10	3	8	9	2	7	2721,860	-0,002	1,00	100
11	2	9	10	3	8	2729,264	-0,004	1,00	100
12	3	10	11	2	9	2736,519	0,001	1,00	100
13	2	11	12	3	10	2743,610	0,002	0,25	100
14	3	12	13	2	11	2750,544	0,006	0,25	100
15	2	13	14	3	12	2757,306	0,002	0,01	100
16	3	14	15	2	13	2763,916	0,009	0,01	100
5	3	2	4	4	1	2678,688	-0,001	0,06	100
6	4	3	5	3	2	2704,595	0,003	0,70	100
7	3	4	6	4	3	2706,235	-0,002	0,70	100
6	3	3	5	4	2	2694,673	-0,005	0,06	100
7	4	4	6	3	3	2709,745	0,003	0,25	100
8	3	5	7	4	4	2715,084	0,000	0,25	100
8	4	5	7	3	4	2716,017	0,002	1,00	100
9	3	6	8	4	5	2722,884	-0,001	0,70	100
9	4	6	8	3	5	2723,098	-0,002	0,25	100
10	4	7	9	3	6	2730,340	-0,010	0,01	100
11	3	8	10	4	7	2737,522	0,005	0,25	100
12	4	9	11	3	8	2744,570	-0,000	0,25	100
13	3	10	12	4	9	2751,458	-0,002	0,06	100
14	4	11	13	3	10	2758,115	-0,077	0,00--	100
15	3	12	14	4	11	2764,792	0,031	0,00--	100
5	5	1	4	4	0	2710,253	-0,004	0,25	100
6	5	2	5	4	1	2717,968	0,000	1,00	100
7	4	3	6	5	2	2706,731	-0,017	0,00--	100
7	5	3	6	4	2	2724,658	0,004	0,00--	100
8	5	4	7	4	3	2728,731	0,003	0,25	100
9	4	5	8	5	4	2730,727	0,009	1,00	100
9	5	5	8	4	4	2733,355	-0,003	0,06	100
10	4	6	9	5	5	2738,667	0,009	0,02	100
10	5	6	9	4	5	2739,385	0,001	0,70	100
11	4	7	10	5	6	2745,860	0,020	0,01	100
11	5	7	10	4	6	2745,999	-0,025	0,00--	100
12	5	8	11	4	7	2752,728	-0,028	0,25--	100
13	4	9	12	5	8	2759,435	0,046	0,06	100
14	5	10	13	4	9	2765,918	0,010	0,01	100
15	4	11	14	5	10	2772,278	0,018	0,00--	100
16	5	12	15	4	11	2778,483	0,030	0,00--	100
6	6	1	5	5	0	2728,974	-0,015	0,00--	100
7	6	2	6	5	1	2740,930	-0,013	0,02	100
8	5	3	7	6	2	2716,197	-0,109	0,00--	100
8	6	3	7	5	2	2744,296	0,006	0,70	100
9	5	4	8	6	3	2733,112	0,020	0,00--	100
10	5	5	9	6	4	2745,073	0,028	0,00--	100
10	6	5	9	5	4	2751,307	0,010	0,25	100
11	5	6	10	6	5	2753,709	0,038	0,00--	100
11	6	6	10	5	5	2755,736	0,006	0,01	100
12	5	7	11	6	6	2760,845	0,017	0,01	100
12	6	7	11	5	6	2761,472	0,042	0,00--	100
7	7	1	6	6	0	2747,177	-0,309	0,25	100

J	K_-	K_+	J	K_-	K_+	OBS	OBS-CALC	WT	BAND
8	8	1	7	7	0	2764,792	0,019	0,00--	100
9	7	3	8	6	2	2761,472	-0,055	0,00--	100
1	0	1	1	1	0	2608,566	0,001	0,70	100
2	1	1	2	2	0	2606,441	-0,004	0,25	100
3	2	1	3	3	0	2602,834	-0,001	0,70	100
4	3	1	4	4	0	2597,640	0,006	0,01	100
5	4	1	5	5	0	2591,155	0,003	0,01	100
5	5	1	6	6	0	2483,995	-6,231	0,00--	100
7	6	1	7	7	0	2576,865	-0,054	0,00--	100
2	0	2	2	1	1	2600,722	-0,012	0,00--	100
2	1	2	2	2	1	2597,003	0,025	0,01	100
3	1	2	3	2	1	2600,722	-0,004	0,01	100
3	2	2	3	3	1	2594,018	0,003	0,00--	100
4	2	2	4	3	1	2599,645	-0,001	0,06	100
5	3	2	5	4	1	2597,003	-0,009	0,00--	100
5	4	2	5	5	1	2581,106	+3,995	0,00--	100
6	4	2	6	5	1	2592,547	0,004	0,00--	100
7	5	2	7	6	1	2586,248	-0,006	0,03	100
3	0	3	3	1	2	2589,682	-0,044	0,00--	100
3	1	3	3	2	2	2588,424	+0,003	0,00--	100
4	2	3	4	3	2	2586,661	-0,000	0,01	100
5	2	3	5	3	2	2590,479	0,002	0,06	100
5	3	3	5	4	2	2583,988	+0,058	0,00--	100
6	3	3	6	4	2	2590,356	0,005	0,00--	100
6	4	3	6	5	2	2580,424	-0,023	0,00--	100
7	4	3	7	5	2	2588,879	-0,002	0,25	100
8	5	3	8	6	2	2585,477	0,004	0,00--	100
9	6	3	9	7	2	2579,860	-0,005	0,01	100
4	0	4	4	1	3	2578,747	-0,007	0,01	100
4	1	4	4	2	3	2578,499	0,017	0,05	100
5	1	4	5	2	3	2578,203	0,020	0,01	100
6	2	4	6	3	3	2578,051	0,011	0,00--	100
6	3	4	6	4	3	2575,379	0,002	0,01	100
7	3	4	7	4	3	2578,350	-0,024	0,06	100
7	4	4	7	5	3	2572,881	+0,008	0,00--	100
5	0	5	5	1	4	2568,071	+0,004	0,01	100
5	1	5	5	2	4	2568,029	0,001	0,00--	100
6	2	5	6	3	4	2566,712	0,009	0,01	100
7	2	5	7	3	4	2565,884	0,003	0,01	100
7	3	5	7	4	4	2565,110	+0,014	0,00--	100
8	4	5	8	5	4	2563,168	+0,007	0,02	100
9	4	5	9	5	4	2565,110	+0,016	0,00--	100
6	1	6	6	2	5	2557,397	0,019	0,00--	100
7	1	6	7	2	5	2555,957	0,033	0,00--	100
8	3	6	8	4	5	2554,238	0,075	0,00--	100
9	3	6	9	4	5	2552,905	-0,024	0,00--	100
7	0	7	7	1	6	2546,620	0,021	0,03	100
1	1	0	1	0	1	2619,759	+0,001	0,70	100
2	2	0	2	1	1	2620,825	+0,001	0,10	100
3	3	0	3	2	1	2622,862	+0,004	0,70	100
4	4	0	4	3	1	2625,984	+0,006	0,06	100
5	5	0	5	4	1	2629,869	+0,008	0,25	100
6	6	0	6	5	1	2633,882	+0,016	0,00--	100
7	7	0	7	6	1	2637,416	+0,013	0,00--	100
9	9	0	9	8	1	2641,722	+0,152	0,00--	100
2	1	1	2	0	2	2626,798	0,001	0,01	100
2	2	1	2	1	2	2630,435	+0,002	0,25	100
3	2	1	3	1	2	2625,170	+0,001	1,00	100
3	3	1	3	2	2	2631,541	+0,002	0,00--	100
4	3	1	4	2	2	2624,092	+0,009	0,00--	100
4	4	1	4	3	2	2632,376	+0,019	0,06	100

J	K_-	K_+	J	K_-	K_+	OBS	OBS-CALC	WT	BAND
5	5	1	5	4	2	2635,954	-0,000	0,06	100
6	5	1	6	4	2	2625,435	-0,008	0,00--	100
6	5	1	6	5	2	2637,776	-0,005	0,01	100
7	5	1	7	5	2	2628,127	-0,020	0,02	100
7	7	1	7	6	2	2639,709	0,030	0,01	100
8	8	1	8	7	2	2641,390	0,077	0,00--	100
9	8	1	9	7	2	2635,294	-0,067	0,00--	100
3	1	2	3	0	3	2636,767	0,097	0,00--	100
3	2	2	3	1	3	2637,885	-0,006	0,01	100
4	2	2	4	1	3	2634,156	0,001	0,06	100
4	3	2	4	2	3	2637,299	-0,002	0,00--	100
5	3	2	5	2	3	2631,008	0,000	0,70	100
5	4	2	5	3	3	2636,767	-0,046	0,00--	100
6	4	2	6	3	3	2627,919	0,003	0,01	100
6	5	2	6	4	3	2635,944	0,003	0,01	100
7	5	2	7	4	3	2625,670	-0,003	0,25	100
7	6	2	7	5	3	2639,434	-0,030	0,00--	100
8	6	2	8	5	3	2624,868	-0,026	0,00--	100
4	2	3	4	1	4	2646,474	0,024	0,00--	100
5	2	3	5	1	4	2643,999	-0,004	0,25	100
5	3	3	5	2	4	2644,889	-0,001	0,06	100
6	3	3	6	2	4	2640,862	-0,004	0,06	100
7	4	3	7	3	4	2636,767	0,012	0,00--	100
7	5	3	7	4	4	2641,390	-0,028	0,00--	100
8	5	3	8	4	4	2632,101	0,004	0,01	100
8	6	3	8	5	4	2639,329	0,006	0,00--	100
5	1	4	5	0	5	2655,198	0,014	0,01	100
5	2	4	5	1	5	2655,198	-0,024	0,00--	100
6	2	4	6	1	5	2652,942	-0,021	0,00--	100
6	3	4	6	2	5	2653,138	-0,005	0,25	100
7	3	4	7	2	5	2650,123	-0,003	0,25	100
7	4	4	7	3	5	2650,737	0,001	0,01	100
8	5	4	8	4	5	2649,086	0,011	0,06	100
7	2	5	7	1	6	2661,417	0,009	0,25	100
7	3	5	7	2	6	2661,417	-0,023	0,00--	100
8	3	5	8	2	6	2658,477	0,018	0,01	100
8	4	5	8	3	6	2658,592	0,000	0,06	100
9	4	5	9	3	6	2654,970	0,023	0,01	100
10	5	5	10	4	6	2650,737	0,056	0,00--	100
10	6	5	10	5	6	2651,880	0,033	0,01	100
7	1	6	7	0	7	2672,440	0,013	0,25	100
8	3	6	8	2	7	2669,568	-0,027	0,00--	100
9	3	6	9	2	7	2666,359	0,016	0,01	100
10	5	6	10	4	7	2662,780	0,031	0,01	100
8	2	7	8	1	8	2680,810	0,018	0,06	100
9	2	7	9	1	8	2677,575	0,003	0,02	100
10	4	7	10	3	8	2673,979	0,013	0,06	100
11	4	7	11	3	8	2669,954	0,014	0,00--	100
9	1	8	9	0	9	2688,959	-0,035	0,00--	100
10	3	8	10	2	9	2685,384	0,013	0,01	100
11	3	8	11	2	9	2681,398	0,036	0,00--	100
12	5	8	12	4	9	2677,036	0,072	0,00--	100
10	2	9	10	1	10	2697,050	0,013	0,01	100
11	2	9	11	1	10	2692,992	0,002	0,06	100
12	4	9	12	3	10	2688,600	0,039	0,00--	100
11	1	10	11	0	11	2704,923	0,000	0,01	100
12	3	10	12	2	11	2700,433	-0,003	0,00--	100
12	2	11	12	1	12	2712,636	-0,018	0,00--	100
1	1	1	2	2	0	2570,920	0,013	0,02	100
2	2	1	3	3	0	2551,320	-0,023	0,00--	100
4	4	1	5	5	0	2509,675	-0,009	0,00--	100

J	K_-	K_+	J	K_-	K_+	OBS	OBS-CALC	WT	BAND
2	1	2	3	2	1	2544.779	0.007	0.00--	100
3	0	3	4	3	2	2510.904	0.087	0.02**	100
2	2	0	1	1	1	2656.877	0.002	0.06	100
3	3	0	2	2	1	2675.071	-0.001	1.00	100
4	4	0	3	3	1	2693.292	-0.006	0.25	100
5	5	0	4	4	1	2711.543	-0.011	0.00--	100
6	6	0	5	5	1	2729.540	-0.143	0.00--	100
7	7	0	6	6	1	2747.507	-0.008	1.00	100
8	8	0	7	7	1	2764.934	0.013	0.06	100
3	3	1	2	0	2	2689.807	-0.110	0.00--	100
3	2	1	2	1	2	2681.928	-0.001	0.12	100
4	4	1	3	1	2	2711.317	0.013	0.01	100
4	3	1	3	2	2	2698.043	-0.003	0.01	100
5	5	1	4	2	2	2736.717	-0.006	0.06	100
5	4	1	4	3	2	2713.860	-0.003	0.25	100
6	6	1	5	3	2	2761.912	-0.013	0.01	100
6	5	1	5	4	2	2729.699	-0.070	0.00--	100
7	6	1	6	5	2	2745.999	-0.015	0.00--	100
8	8	1	7	5	2	2816.037	0.037	0.00--	100
4	2	2	3	1	3	2710.787	-0.043	0.00--	100
5	4	2	4	1	3	2733.112	0.047	0.00--	100
5	3	2	4	2	3	2725.935	0.000	0.01	100
6	4	2	5	3	3	2740.040	-0.001	0.00--	100
7	6	2	6	3	3	2776.296	-0.020	0.01	100
7	5	2	6	4	3	2753.533	-0.004	0.40	100
8	6	2	7	5	3	2766.908	0.003	0.06	100
9	8	2	8	5	3	2823.117	-0.738	0.00--	100
9	7	2	8	6	3	2780.623	-0.002	0.25	100
5	3	3	4	0	4	2740.930	-0.051	0.00--	100
5	2	3	4	1	4	2740.040	-0.002	0.06	100
6	4	3	5	1	4	2758.155	0.037	0.00--	100
6	3	3	5	2	4	2755.514	-0.007	0.01	100
7	5	3	6	2	4	2775.185	0.016	0.02	100
7	4	3	6	3	4	2769.485	-0.003	0.25	100
8	6	3	7	3	4	2792.170	0.007	0.02	100
8	5	3	7	4	4	2781.886	-0.092	0.00--	100
6	3	4	5	0	5	2768.403	0.002	0.01	100
6	2	4	5	1	5	2768.210	-0.002	0.00--	100
7	4	4	6	1	5	2784.662	-0.003	0.01	100
8	5	4	7	2	5	2800.477	-0.002	0.06	100
7	3	4	6	2	5	2783.997	-0.006	0.06	100
8	4	4	7	3	5	2798.627	0.007	0.01	100
9	5	4	8	4	5	2811.697	0.035	0.06	100
10	6	4	9	5	5	2822.975	0.096	0.00--	100
7	3	5	6	0	6	2795.823	-0.024	0.01	100
7	2	5	6	1	6	2795.823	0.010	0.01	100
8	4	5	7	1	6	2811.531	-0.011	0.00--	100
8	3	5	7	2	6	2811.430	0.031	0.01	100
9	5	5	8	2	6	2826.679	0.064	0.00--	100
9	4	5	8	3	6	2826.151	0.016	0.01	100
10	5	5	9	4	6	2839.833	0.080	0.00--	100
10	6	5	9	3	6	2841.157	0.039	0.01	100
4	0	4	5	0	5	2574.891	0.059	0.00--	001
2	1	1	3	1	2	2583.998	-0.024	0.00--	001
3	2	2	4	2	3	2574.889	-0.021	0.00--	001
3	1	2	4	1	3	2574.208	-0.022	0.00--	001
4	2	3	5	2	4	2564.555	0.035	0.00--	001
4	1	3	5	1	4	2464.422	-99.989	0.00--	001
3	3	1	4	3	2	2567.766	-0.088	0.00--	001
3	2	1	4	2	2	2564.311	-0.007	0.01	001
4	3	2	5	3	3	2555.111	-0.007	0.01	001

J	K_-	K_+	J	K_-	K_+	OBS	OBS-CALC	WT	BAND
4	2	2	5	2	3	2553,437	-0,003	0,20	001
5	3	3	6	3	4	2544,081	0,019	0,01	001
5	2	3	6	2	4	2543,679	-0,001	0,01	001
6	3	4	7	3	5	2533,575	0,066	0,00--	001
6	2	4	7	2	5	2533,484	0,028	0,00--	001
3	3	0	4	3	1	2561,243	-0,082	0,00--	001
4	4	1	5	4	2	2549,501	-0,110	0,00--	001
4	3	1	5	3	2	2545,875	0,010	0,20	001
5	4	2	6	4	3	2535,568	-0,002	0,03	001
5	3	2	6	3	3	2532,761	0,015	0,01	001
6	4	3	7	4	4	2523,597	0,033	0,00--	001
6	3	3	7	3	4	2522,587	-0,025	0,10	001
7	4	4	8	4	5	2512,690	0,039	0,00--	001
4	4	0	5	4	1	2544,514	-0,109	0,00--	001
5	4	1	6	4	2	2525,755	0,026	0,00--	001
6	5	2	7	5	3	2516,304	-0,016	0,00--	001
6	4	2	7	4	3	2513,265	0,006	0,20	001
7	5	3	8	5	4	2503,219	0,023	0,01	001
2	1	2	1	1	1	2651,195	0,031	0,01	001
2	0	2	1	0	1	2651,880	-0,434	0,00--	001
3	1	3	2	1	2	2660,612	-0,108	0,00--	001
3	0	3	2	0	2	2661,090	0,111	0,00--	001
4	0	4	3	0	3	2669,568	-0,183	0,00--	001
5	1	5	4	1	4	2678,358	-0,139	0,00--	001
6	0	6	5	0	5	2687,096	-0,060	0,04 *	001
7	1	7	6	1	6	2695,695	-0,010	0,25	001
8	0	8	7	0	7	2704,154	0,004	0,25	001
9	1	9	8	1	8	2712,493	-0,001	0,06	001
10	0	10	9	0	9	2720,561	-0,177	0,00--	001
11	1	11	10	1	10	2728,731	-0,152	0,00--	001
12	0	12	11	0	11	2736,717	-0,210	0,00--	001
3	2	2	2	2	1	2668,134	-0,029	0,02	001
3	1	2	2	1	1	2671,270	0,042	0,00--	001
4	2	3	3	2	2	2678,358	-0,033	0,00--	001
4	1	3	3	1	2	2679,477	-0,092	0,01	001
5	2	4	4	2	3	2687,496	0,066	0,00--	001
5	1	4	4	1	3	2687,643	-0,045	0,00--	001
4	3	2	3	3	1	2684,158	-0,010	0,01	001
4	2	2	3	2	1	2689,378	-0,036	0,00--	001
5	3	3	4	3	2	2695,262	0,020	0,06	001
5	2	3	4	2	2	2698,249	-0,012	0,00--	001
6	2	4	5	2	3	2705,617	0,027	0,00--	001
7	3	5	6	3	4	2713,124	-0,013	0,00--	001
4	3	1	3	3	0	2692,224	0,011	0,06	001
5	4	2	4	4	1	2699,270	-0,004	0,25	001
5	3	2	4	3	1	2706,601	-0,012	0,00--	001
6	4	3	5	4	2	2711,147	0,020	0,01	001
6	3	3	5	3	2	2716,721	-0,029	0,01	001
7	4	4	6	4	3	2721,281	0,114	0,00--	001
5	4	1	4	4	0	2704,372	0,014	0,05	001
6	4	2	5	4	1	2723,098	-0,052	0,00--	001
7	5	3	6	5	2	2726,041	0,011	0,00--	001
6	5	1	5	5	0	2717,313	0,008	0,25	001
7	5	2	6	5	1	2734,097	0,031	0,00--	001
8	5	3	7	6	2	2740,040	0,013	0,00--	001
10	5	5	9	5	4	2765,617	0,102	0,00--	001
8	5	2	7	6	1	2746,961	0,031	0,00--	001
9	7	3	8	7	2	2753,533	0,317	0,00--	001
9	6	3	8	6	2	2768,884	-0,083	0,00--	001
10	7	4	9	7	3	2765,291	0,233	0,00--	001
8	7	1	7	7	0	2741,719	0,037	0,00--	001

J	K_-	K_+	J	K_-	K_+	OBS	OBS-CALC	WT	BAND
10	7	3	9	7	2	2774,906	-0,099	0,00--	001
2	1	2	2	1	1	2615,077	-0,038	0,00--	001
2	0	2	2	2	1	2614,852	3,951	0,00--	001
3	2	2	3	2	1	2615,936	-0,021	0,01	001
4	3	2	4	3	1	2616,858	-0,002	0,00--	001
4	2	2	4	4	1	2601,125	0,004	0,00--	001
3	1	3	3	1	2	2603,961	-0,002	0,06	001
3	0	3	3	2	2	2602,580	-0,025	0,02	001
4	2	3	4	2	2	2604,467	0,021	0,01	001
5	3	3	5	3	2	2605,488	0,021	0,05	001
6	4	3	6	4	2	2606,834	0,033	0,00--	001
6	3	3	6	5	2	2592,551	-0,054	0,00--	001
7	5	3	7	5	2	2608,140	-0,023	0,02	001
4	1	4	4	1	3	2593,084	0,046	0,01	001
4	0	4	4	2	3	2592,802	0,043	0,04	001
5	2	4	5	2	3	2592,550	0,047	0,00--	001
5	1	4	5	3	3	2591,481	0,045	0,00--	001
6	3	4	6	3	3	2592,550	0,034	0,00--	001
7	4	4	7	4	3	2593,288	-0,016	0,01	001
5	1	5	5	1	4	2582,545	0,087	0,01	001
6	2	5	6	2	4	2581,418	0,069	0,01	001
6	1	5	6	3	4	2581,191	0,072	0,04**	001
7	3	5	7	3	4	2580,426	0,023	0,00--	001
7	2	5	7	4	4	2579,603	0,003	0,00--	001
8	4	5	8	4	4	2580,038	0,100	0,00--	001
8	3	5	8	5	4	2577,728	0,016	0,00--	001
6	0	6	6	2	5	2572,058	0,159	0,00--	001
7	2	6	7	2	5	2570,617	0,095	0,00--	001
8	3	6	8	3	5	2569,101	-0,025	0,00--	001
8	2	6	8	4	5	2568,899	-0,039	0,01	001
9	4	6	9	4	5	2567,766	-0,114	0,00--	001
2	1	1	2	1	2	2640,727	-0,053	0,01	001
4	3	1	4	3	2	2635,644	0,004	0,02	001
5	4	1	5	4	2	2630,010	-0,046	0,01	001
3	2	2	3	0	3	2651,880	-0,022	0,00--	001
4	2	2	4	2	3	2648,354	-0,013	0,01	001
5	3	2	5	3	3	2644,889	0,018	0,00--	001
5	4	2	5	2	3	2651,587	-0,006	0,01	001
6	4	2	6	4	3	2641,120	-0,002	0,01	001
4	1	3	4	1	4	2660,454	0,005	0,02	001
4	2	3	4	0	4	2660,612	0,001	0,00--	001
5	3	3	5	1	4	2659,009	0,017	0,01	001
6	4	3	6	2	4	2657,315	-0,001	0,00--	001
7	5	3	7	3	4	2656,048	0,012	0,01	001
6	2	4	6	2	5	2667,340	0,007	0,01	001
6	3	4	6	1	5	2667,468	0,029	0,00--	001
7	3	4	7	3	5	2664,593	-0,064	0,00--	001
7	4	4	7	2	5	2665,038	-0,017	0,01	001
9	5	4	9	4	5	2660,159	0,108	0,00--	001
7	3	5	7	1	6	2675,940	0,010	0,00--	001
6	6	0	5	4	1	2760,845	0,043	0,01	001
3	2	1	2	0	2	2696,636	-0,001	0,01	001
3	3	1	2	1	2	2703,570	0,049	0,00--	001
4	3	1	3	1	2	2714,532	-0,017	0,00--	001
5	5	1	4	3	2	2745,686	0,245	0,00--	001
6	5	1	5	3	2	2750,247	0,006	0,01	001
4	2	2	3	0	3	2725,350	-0,009	0,01	001
5	3	2	4	1	3	2741,113	-0,010	0,01	001
5	4	2	4	2	3	2746,522	0,002	0,01	001
6	4	2	5	2	3	2757,143	-0,002	0,25	001
6	5	2	5	3	3	2765,291	-0,007	0,02	001

J	K_-	K_+	J	K_-	K_+	OBS	OBS-CALC	WT	BAND
5	2	3	4	0	4	2754,422	-0,004	0,00--	001
5	3	3	4	1	4	2755,040	0,009	0,01	001
6	3	3	5	1	4	2770,239	-0,037	0,01	001
6	4	3	5	2	4	2771,983	0,012	0,00--	001
7	4	3	6	2	4	2784,931	-0,087	0,00--	001
8	5	3	7	3	4	2799,293	-0,143	0,00--	001
6	2	4	5	0	5	2782,601	0,010	0,00--	001
6	3	4	5	1	5	2782,708	0,020	0,00--	001
7	3	4	6	1	5	2798,627	0,040	0,00--	001
6	3	4	7	3	5	2533,575	0,066	0,00--	001
6	3	4	6	1	5	2667,468	0,029	0,00--	001
6	3	4	5	1	5	2782,708	0,020	0,00--	001
3	2	2	2	2	1	2668,134	-0,029	0,01	001
3	2	2	4	4	1	2527,641	-0,023	0,01	001