DETERMINATION OF A_0
FOR DEUTERATED METHYL HALIDES

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This is to certify that the

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ABSTRACT

DETERMINATION OF A_0 FOR DEUTERATED METHYL HALIDES

By

Richard Wayne Peterson

High resolution absorption spectra of the ν_4 and $2\nu_4$ vibration - rotation bands of CD_3I, CD_3Cl, and CD_3Br have been obtained with the Michigan State University near-infrared spectrometer.

Molecular parameters have been determined by least squares fits of observed frequencies to generalized frequency expressions for symmetric top molecules resulting from the theoretical work of Amat and Nielsen. A simultaneous analysis of the ν_4 and $2\nu_4$ bands of CD_3I led to a value of $A_0 = 2.5788 \pm 0.0004$ along with other molecular parameters. A similar analysis of the unperturbed lines of CD_3Cl yielded the value $A_0 = 2.5930 \pm 0.0006$. The A_0 values obtained for CD_3I and CD_3Cl were compared to those from zeta-sum work and were found to be an order of magnitude more precise. A_0 could not be obtained by a simultaneous analysis for CD_3Br because of the highly perturbed nature of $2\nu_4$; however a single-band fit of ν_4 resulted in values of D_0^K, α_4^A, α_4^B, and other linear combinations of parameters.

Systematic perturbations have been observed on the low frequency side of the ν_4 band of each molecule. Individual line shifts due to these perturbations have been listed in all cases

where definite assignments were possible. Other perturbations were observed in $2\nu_4(\parallel)$ of CD_3Cl and in $2\nu_4(\perp$ and $\parallel)$ of CD_3Br.

DETERMINATION OF A_0 FOR DEUTERATED METHYL HALIDES

By

Richard Wayne Peterson

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TO MY PARENTS

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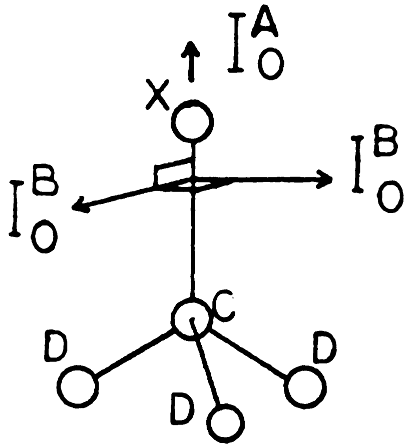
CHAPTER I

INTRODUCTION

The birth of quantum mechanics in the late 1920's led to a renewed interest in the near-infrared absorption spectra of small molecules. It was found that many features of infrared spectra could be predicted by a quantum mechanical model of the molecule consisting of a rigid rotator and a set of uncoupled harmonic oscillators. Symmetric top molecules (where $I_{xx} = I_{yy} \neq I_{zz}$) allow an exact determination of vibration-rotation energy levels for the zero-order model described above. Because of this, some of the first molecules studied experimentally and theoretically were the methyl halides.

The basic form of a deuterated methyl halide molecule (CD_3X, where $X = F$, Cl, Br, or I) is shown in Figure 1.1. In addition to their classification as symmetric tops, the methyl halides have C_{3v} symmetry, which means they have a threefold axis of symmetry and three vertical planes of symmetry. Figure 1.2 illustrates the atomic motions involved with each of the vibrational modes of a methyl halide molecule. The modes ν_4, ν_5, and ν_6 are doubly degenerate.

In Chapter II a summary is given of the modern quantum mechanical development of a fourth-order energy expression for a vibrating and rotating symmetric top molecule. This general model includes such effects as anharmonic forces, changes of moments of



$$A_0 = \frac{\hbar}{4\pi c\, I_0^A}$$

$$B_0 = \frac{\hbar}{4\pi c\, I_0^B}$$

FIG 1·1 CD_3X STRUCTURE

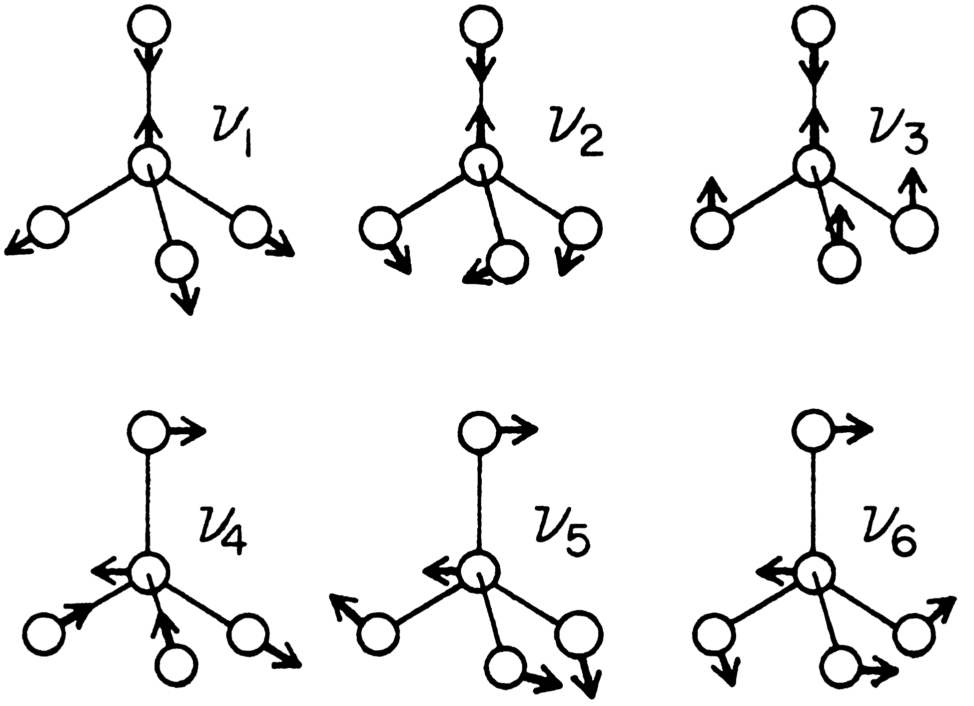


FIG 1·2 NORMAL MODES OF METHYL HALIDES

inertia with vibration, centrifugal distortion, and vibration-rotation interactions. Different frequency expressions of particular importance to this work are introduced and compared.

Because of the selection rules which govern symmetric top transitions, the determination of the ground-state constant $A_0 = \hbar/4\pi c\ I_0^A$ (where I_0^A is the principal moment of inertia about the unique symmetry axis) is a difficult but important problem. Chapter III describes and compares the two most commonly used methods of determining A_0. This work involves an application of the more accurate of the two methods to CD_3X molecules.

The experimental procedures used in recording the ν_4 and $2\nu_4$ bands of CD_3I, CD_3Cl, and CD_3Br are described in Chapter IV. Chapter V describes the computer programs used in determining accurate frequencies of spectral lines recorded and in obtaining molecular parameters, such as A_0, from the observed frequencies.

The remainder of the thesis describes the details of the analysis of the spectra for each of the three molecules. Molecular parameters obtained from the analysis are recorded and compared with those obtained from lower resolution spectra. In the cases of CD_3Cl and CD_3Br (Chapters VII and VIII) a number of spectral lines are found to correspond to transitions to perturbed upper-state energy levels. Whenever possible the magnitudes of these energy level shifts are determined.

The concluding chapter summarizes the molecular parameters determined for each molecule and includes suggestions for future work.

CHAPTER II

DEVELOPMENT OF SYMMETRIC TOP THEORY

Among the problems which confront the beginner in high resolution spectroscopy is the complexity of an accurate analytical expression which is able to specify the energy of the quantum levels of a vibrating and rotating polyatomic molecule. The situation is further complicated for the experimentalist by the variety of expressions which have been used to predict the frequencies of radiation which are absorbed when the molecule is excited to higher energy states. For example, some frequency expressions are convenient for the rapid computation of approximate molecular parameters from gross features of the spectra, others apply only to small portions of a given absorption band, and still others are general enough to allow a large scale computer analysis of more than one band under very high resolution. The goal of this chapter is to introduce a few of the frequency expressions which are presently used for symmetric tops and to facilitate their comparison.

A brief development of a general energy expression which results from the fourth-order Hamiltonian as developed by Amat and Nielsen is given first. After applying appropriate selection rules, the generalized frequency expression for symmetric top molecules is obtained. This complicated expression is then compared to frequency expressions which are commonly used experimentally at low to medium resolution.

The development of a correct quantum mechanical form of the Hamiltonian has been presented in detail by H.H. Nielsen (1) in his comprehensive paper of 1951. Details of this development have been given at Michigan State University in the lectures on molecular structure by P.M. Parker, and an excellent summary is given in Chapter I of a theoretical thesis by R.L. Dilling (2). The resultant Hamiltonian is commonly called the Darling-Dennison (D-D) Hamiltonian (3,4) and is written as follows:

$$\mathcal{H} = \frac{1}{2}\Big[\mu^{\frac{1}{4}} \sum_{\alpha\beta} (P_\alpha - p_\alpha)\mu^{-\frac{1}{2}}\mu_{\alpha\beta}(P_\beta - p_\beta)\mu^{\frac{1}{4}} \tag{2.1}$$

$$+ \frac{1}{2}\mu^{\frac{1}{4}} \sum_{s\sigma} p^{*}_{s\sigma}\mu^{-\frac{1}{2}} p_{s\sigma}\mu^{\frac{1}{4}}\Big] + V$$

Table 2.1 contains a brief description of each of the quantities used in the D-D Hamiltonian. More detailed information concerning the basic relationships between these constants may be found in references (1,2,3,4).

In principle, the D-D Hamiltonian is quite applicable to any type of molecule. It is unfortunately a grievous task to solve the Schroedinger equation for this complex Hamiltonian to high orders of accuracy. The usual systematic approach is to first expand H in the manner,

$$H = H_0 + H_1 + H_2 + H_3 + \ldots\ldots.$$

where expansions of V and $\mu_{\alpha\beta}$ are

$$V = V_0 + V_1 + V_2 + \ldots$$

$$V = \frac{1}{2}\sum_{s\sigma} \lambda_s Q_{s\sigma}^2 + \sum_{\substack{s\sigma \\ s'\sigma' \\ s''\sigma''}} K_{\substack{s\sigma \\ s'\sigma' \\ s''\sigma''}} Q_{s\sigma}Q_{s'\sigma'}Q_{s''\sigma''} + \ldots$$

Table 2.1

Parameters of the D-D Hamiltonian

Quantity	Description
$\mu_{\alpha\beta}$	the inverse moments of inertia matrix, $\mu \equiv \det(\mu_{\alpha\beta})$
α, β	range over (x,y,z) of the rotating coordinate system attached to the molecule in a manner subject to the Eckart conditions (4,5)
s, σ	(s) is an index ranging over all normal modes; (σ) ranges over the components of degenerate normal modes
$Q_{s\sigma}$	displacement of the σ component of the normal mode (s), does not appear explicitly in H
P_α	component of total angular momentum
P_α	component of internal angular momentum; (p_α) may be expressed as a linear combination of components of internal angular momentum as expressed in normal coordinate space: $p_\alpha = \sum_s \zeta^{\alpha}_{s1s2}\,\theta_{sz}$
$P^*_{s\sigma}$	momentum conjugate to $Q_{s\sigma}$ $p^*_{s\sigma} = -i\hbar \frac{\partial}{\partial Q_{s\sigma}}$
$V(Q_{s\sigma})$	potential energy of the molecule

and

$$\mu_{\alpha\beta} = \frac{1}{I_\alpha I_\beta}\left[\Omega^{(0)\alpha\beta} + \sum_{s\sigma} \Omega^{(1)\alpha\beta} Q_{s\sigma} + \ldots\right]$$

where, if x,y,z are principal axes,

$$\Omega^{(0)\alpha\beta} = I_\alpha \delta_{\alpha\beta}$$

With these, one can write for H_0 (1,2)

$$H_0 = H_R + H_V$$

$$= \frac{1}{2}\sum_\alpha \frac{P_\alpha^2}{I_\alpha} + \frac{1}{2}\sum_{s\sigma}\left[P_{s\sigma}^2 + \lambda_s Q_{s\sigma}^2\right] \tag{2.2}$$

This Hamiltonian of a rigid rotor (H_R) and a set of uncoupled harmonic oscillators (H_V) is very important in the development which follows. The Schroedinger equation of H_0 (where $I_{xx}^e = I_{yy}^e$) has the well-known eigenfunctions[a]

$$\Psi_T = \Psi_R \Psi_V$$

where

$$\Psi_R = |J\ K\ M\rangle$$

and

$$\Psi_V = |v_1\rangle|v_2\rangle \ldots |v_s \ell_s\rangle$$

where $v_1, v_2 \ldots v_s$ are the vibrational quantum numbers of the uncoupled harmonic oscillators, and J,K,M, and ℓ_s are angular momentum quantum numbers defined by

---

[a] The quantum mechanics problem of the rigid symmetric rotor was first solved by Dennison via matrix mechanics (6). Solutions by both wave mechanics and matrices are given in his paper of 1931 (7).

$$P^2\Psi_R = J(J+1)\hbar^2\Psi_R$$

$$P_z\Psi_R = K\hbar\Psi_R$$

(2.3) $$P_Z\Psi_R = M\hbar\Psi_R$$

$$\mathcal{P}_{s\sigma}\Psi_V = \ell_s\hbar\Psi_V$$

In the case of a symmetric top in zero order, v_s, J, and $|K|$ are considered primary quantum numbers since they determine distinct eigenvalues; ℓ_s, M, and the sign of K are secondary quantum numbers and in zero order only designate degeneracies.

A method of arriving at energies beyond zero order which has often been used is that of the contact transformation. This is essentially the perturbation approach as presented by Born, Heisenberg, and Jordan in 1926 (8,9), and it was applied by Van Vleck in 1929 to higher order terms of diatomic molecules (10). Shaffer, Nielsen, and Thomas were the first to use the technique in the case of polyatomic molecules (11), and in his paper of 1951 (1) Nielsen summarized first and second-order contributions to the energies of symmetric tops. One applies the transformation to the general D-D Hamiltonian as expanded to at least second-order,

$$\mathcal{H}' = T\mathcal{H}T^{-1} = \mathcal{H}_0' + \mathcal{H}_1' + \mathcal{H}_2' + \dots$$

and one attempts to choose T such that

$$(1)\ \mathcal{H}_0' = \mathcal{H}_0 \quad \text{and} \quad (2)\ \langle n|\mathcal{H}_1'|n'\rangle = 0 \quad \text{for} \quad n \neq n'$$

In this way the transformation does not invalidate the highly prized eigenfunctions of H_0, but does remove the off-diagonal elements of H_1'. Detailed application of the T transformation necessitates that the resulting terms be rearranged according to expected orders of magnitude. The rearranged matrix is written as

$$h' = \mathcal{H}_0 + h_1' + h_2' + \ldots$$

Then, since H_0 has known eigenfunctions $\Psi_n^{(0)}$, we may apply second-order perturbation theory which states that if

$$\mathcal{H}_0\Psi_n^{(0)} = E_n^{(0)}\Psi_n^{(0)}$$

then

$$E_n^{(0)} = \langle n|\mathcal{H}_0|n\rangle$$

$$E_n^{(1)} = \langle n|h_1'|n\rangle$$

$$E_n^{(2)} = \langle n|h_2'|n\rangle + \sum_n{}' \frac{|\langle n|h_1'|n''\rangle|^2}{E_n^{(0)} - E_{n''}^{(0)}}$$

but by virtue of the contact transformation,

$$\langle n|h_1'|n''\rangle = 0 \quad \text{for all} \quad n \neq n''$$

and therefore

$$E_n^{(2)} = \langle n|h_2'|n\rangle$$

Care must be taken in the case of degeneracies in $E_n^{(0)}$. In such a case, one must use perturbation-adapted zero-order wave functions to find $E_n^{(1)}$ before proceeding to $E_n^{(2)}$.

The above method is described in great detail in two papers by Nielsen, Amat, and Goldsmith (12,13). Amat and Nielsen (14,15,16) then went on to perform an analogous second contact transformation which removes the matrix elements off-diagonal in the principal quantum numbers v_s from h_2'. This procedure results (after no small amount of labor) in a doubly-transformed Hamiltonian,

$$\mathcal{H}^{\dagger} = T \mathcal{H}' T^{-1} = \mathcal{H}_0^{\dagger} + \mathcal{H}_1^{\dagger} + \mathcal{H}_2^{\dagger} + \mathcal{H}_3^{\dagger} + \mathcal{H}_4^{\dagger} + \cdots$$

$$= \mathcal{H}_0 + \mathcal{H}_1' + \mathcal{H}_2^{\dagger} + \mathcal{H}_3^{\dagger} + \mathcal{H}_4^{\dagger}$$

After another regrouping, the new Hamiltonian is written,

$$h^{\dagger} = \mathcal{H}_0 + h_1' + h_2^{\dagger} + h_3^{\dagger} + h_4^{\dagger}$$

with $\mathcal{H}_0 + h_1' + h_2^{\dagger}$ diagonal in the vibrational quantum numbers v_s, again in a representation which has as its zero-order wave functions, the eigenfunctions of $\mathcal{H}_0$. However, for a symmetric top, $h_2^{\dagger}$ is not diagonal in the angular momentum numbers ℓ_s and K, and therefore terms off-diagonal in these quantities can contribute to fourth-order energies, or even to lower order in the case of certain resonance perturbations.

Table 2.2 contains the energy expression from double contact transformation theory of an axially symmetric molecule complete through third-order, with partial contributions from fourth-order. The explicit form of the terms of the Hamiltonian may be found in the thesis by W.E. Blass (17). Table 2.3 is a list of all the new quantities which appear in the energy expression with their descriptions.

We are usually concerned with the energy absorbed as the molecule is excited from its ground vibrational state (all $v_s = 0$) to an upper state where some $v_s \neq 0$. This puts the range of radiation absorbed in the near-infrared region where our spectrometer operates. The general frequency expression is thus obtained by subtracting the ground-state energy expression from the upper-state energy.

Table 2.2

Axially Symmetric Energy Expression

$$E_0 = B_e J(J+1) + (A_e - B_e)K^2 + \Sigma_s \omega_s (v_s + g_s/2)$$

$$E_1 = -2A_e \Sigma_t \zeta_t^z \ell_t K$$

$$E_{21} = -D_e^J J^2 (J+1)^2 \quad -D_e^{JK} K^2 J(J+1) \quad -D_e^K K^4$$

$$E_{22} = -\Sigma_s \alpha_s^B (v_s + g_s/2) J(J+1) \quad -\Sigma_s (\alpha_s^A - \alpha_s^B)(v_s + g_s/2) K^2$$

$$E_{23} = \Sigma_{\substack{ss' \\ s\le s'}} x_{ss'} (v_s + g_s/2)(v_{s'} + g_{s'}/2) + \Sigma_{\substack{tt' \\ t\le t'}} x_{\ell_t \ell_{t'}} \ell_t \ell_{t'}$$

$$E_{31} = \Sigma_t \eta_t^J \ell_t J(J+1) K$$

$$E_{32} = \Sigma_t \eta_t^K \ell_t K^3 + \Sigma_t [\eta_t + \Sigma_s \eta_{t,s} (v_s + g_s/2)] \ell_t K$$

$$\begin{aligned} E_{41} = {} & \Sigma_s \beta_s^J (v_s + g_s/2) J^2 (J+1)^2 + \Sigma_s \beta_s^{JK} (v_s + g_s/2) K^2 J(J+1) \\ & + \Sigma_s \beta_s^K (v_s + g_s/2) K^4 \end{aligned}$$

$$\begin{aligned} E_{42} = {} & \{\Sigma_{\substack{ss' \\ s\le s'}} \gamma_{ss'}^B (v_s + g_s/2)(v_{s'} + g_{s'}/2) + \Sigma_{\substack{tt' \\ t\le t'}} \gamma_{\ell_t \ell_{t'}} \ell_t \ell_{t'} \\ & + \Delta B_e\}[J(J+1) - K^2] + \{\Sigma_{\substack{ss' \\ s\le s'}} \gamma_{ss'}^A (v_s + g_s/2)(v_{s'} + g_{s'}/2) \\ & + \Sigma_{\substack{tt' \\ t\le t'}} \gamma_{\ell_t \ell_{t'}} \ell_t \ell_{t'} + \Delta A_e\} K^2 \end{aligned}$$

$$E_{43} = H_0^J J^3 (J+1)^3 \quad + H_o^{JK} K^2 J^2 (J+1)^2 + H_0^{KJ} K^4 J(J+1) \quad + H_o^K K^6$$

$$\begin{aligned} E_{44} = {} & \Sigma_{\substack{ss's'' \\ s\le s'\le s''}} y_{ss's''} (v_s + g_s/2)(v_{s'} + g_{s'}/2)(v_{s''} + g_{s''}/2) \\ & + \Sigma_{\substack{stt' \\ t\le t'}} y_{s\ell_t \ell_{t'}} (v_s + g_s/2) \ell_t \ell_{t'} + \Sigma_s \Delta\omega_s (v_s + g_s/2) \end{aligned}$$

Table 2.3

Description of Energy Parameters

Quantity	Description
s,n,t	s is an index of a given vibrational mode. n will refer to a specifically non-degenerate mode; t, the degenerate modes.
B_e, A_e	$B_e = \frac{\hbar}{4\pi c I_x^e}$ where $I_x^e = I_y^e$ $A_e = \frac{\hbar}{4\pi c I_z^e}$ where z is the axis of symmetry
ω_s, g_s	designate a purely harmonic frequency ω_s of a normal mode s having degeneracy g_s.
ζ_t^z	coriolis coupling constant about the symmetry axis.
α_s^B, α_s^A	coefficients of vibrational corrections to B_e and A_e
D_e^J, D_e^{JK}, D_e^K	corrections due to centrifugal distortion of equilibrium configuration.
$X_{ss'}$, $X_{\ell_t \ell_{t'}}$	first-anharmonic corrections
$y_{ss'}$, $y_{s\ell_t \ell_{t'}}$	second-anharmonic corrections
β_s^J, β_s^{JK}, β_s^K	third-order changes in centrifugal terms due to vibration.
η_t^J, η_t^K	third-order corrections to ζ_t^z
$\gamma_{ss'}^A$, $\gamma_{\ell_t \ell_{t'}}^A$	fourth-order corrections to A_e
$\gamma_{ss'}^B$, $\gamma_{\ell_t \ell_{t'}}^B$	fourth-order corrections to B_e
H_0^J, H_0^{JK}, H_0^{KJ}, H_0^K	fourth-order corrections due to centrifugal distortion.
$\Delta\omega_s$	fourth-order correction to ω_s having the same quantum dependence as ω_s
ΔB_e, ΔA_e	fourth order corrections to A_e and B_e, having same quantum dependence at A_e and B_e

Table 2.4 is a general expression (including partial fourth-order terms) which gives the frequency (in cm^{-1}) of radiation absorbed as the molecule is excited from its ground vibrational state to an upper state where some of the set v_s are not zero. The vibrational terms have been grouped at the beginning of the expression and these will be constant for a given vibrational excitation. In the notation of the frequency expression, changes in the rotational quantum numbers K and J are specified by giving initial values (K,J) and their changes (ΔK and ΔJ). Particular transitions will therefore often be specified by the notation

$${}^{\Delta K}\Delta J_{|K|}(J) \quad \text{where } K \text{ and } J \text{ are initial values}$$

where P implies ΔK or $\Delta J = -1$

Q implies ΔK or $\Delta J = 0$

R implies ΔK or $\Delta J = +1$

For example, an ${}^{R}Q_3(4)$ transition implies $K_{\text{initial}} = 3$ $K_{\text{final}} = 4$

$J_{\text{initial}} = 4$ $J_{\text{final}} = 4$

The vibrational transition from (all $v_s = 0$) to (1,0,0,0,2,0) is called the band $\nu_1 + 2\nu_5$. This thesis is largely concerned with the analysis of the ν_4 and $2\nu_4$ bands of CD_3X molecules.

Three important substitutions have been made in going from the energy expression to the frequency expression. They consist of applications of the following definitions,

$$(2.4) \quad A_v = A_e - \sum_s \alpha_s^A (v_s + g_s/2) + \sum_{\substack{ss' \\ s \le s'}} \gamma_{ss'}^A (v_s + g_s/2)(v_{s'} + g_{s'}/2) + \sum_{\substack{tt' \\ t \le t'}} \gamma_{\ell_t \ell_{t'}}^A \ell_t \ell_{t'} + \Delta A_e$$

Table 2.4

Generalized Frequency Expression

$$(v_n, v_{n+1}, \ldots, v_t, \Delta\ell_t, v_{t+1}, \Delta\ell_{t+1}, \ldots)^{\Delta K}\Delta J_K(J) =$$

$$\Sigma_s(\omega_s + \Delta\omega_s)v_s +$$

$$\underset{s\le s'}{\Sigma_s\Sigma_{s'}} x_{ss'}[v_s+g_s/2)(v_{s'}+g_{s'}/2)-g_s g_{s'}/4] +$$

$$\underset{t\le t'}{\Sigma_t\Sigma_{t'}} x_{\ell_t\ell_{t'}}\Delta\ell_t\Delta\ell_{t'} +$$

$$\underset{s\le s'\le s''}{\Sigma_s\Sigma_{s'}\Sigma_{s''}} y_{ss's''}[(v_s+g_s/2)(v_{s'}+g_{s'}/2)(v_{s''}+g_{s''}/2)-g_s g_{s'} g_{s''}/8] +$$

$$\Sigma_s\underset{t\le t'}{\Sigma_t\Sigma_{t'}} y_{s\ell_t\ell_{t'}}(v_s+g_s/2)\Delta\ell_t\Delta\ell_{t'} +$$

$$A_0[(K+\Delta K)^2-K^2] +$$

$$B_0[(J+\Delta J)(J+1+\Delta J)-J(J+1) - (K+\Delta K)^2+K^2] +$$

$$[-2A_e\Sigma_t\zeta_t^z\Delta\ell_t+\Sigma_t\{\eta_t+\Sigma_s\eta_{ts}(v_s+g_s/2)\}\Delta\ell_t][K+\Delta K] +$$

$$-D_0^J[(J+\Delta J)^2(J+1+\Delta J)^2-J^2(J+1)^2] +$$

$$-D_0^{JK}[(K+\Delta K)^2(J+\Delta J)(J+1+\Delta J)-K^2J(J+1)] +$$

$$-D_0^K[(K+\Delta K)^4-K^4] +$$

$$[-\Sigma_s\alpha_s^A v_s+\underset{s\le s'}{\Sigma_s\Sigma_{s'}}\gamma^A_{ss'}(v_s v_{s'}+v_s g_{s'}/2+v_{s'} g_s/2)$$

$$+\underset{t\le t'}{\Sigma_t\Sigma_{t'}}\gamma^A_{\ell_t\ell_{t'}}\Delta\ell_t\Delta\ell_{t'}][(K+\Delta K)^2] +$$

(continued on next page)

Table 2.4 (cont.)

Generalized Frequency Expression

$$\Big[-\sum_s \alpha_s^B v_s + \underset{s\le s'}{\sum_s \sum_{s'}} \gamma_{ss'}^B (v_s v_{s'} + v_s g_{s'}/2 + v_{s'} g_s/2)$$

$$+ \underset{t\le t'}{\sum_t \sum_{t'}} \gamma_{\ell_t \ell_{t'}}^B \Delta\ell_t \Delta\ell_{t'}\Big]\big[(J+\Delta J)(J+1+\Delta J)-(K+\Delta K)^2\big] +$$

$$\sum_t \eta_t^J \Delta\ell_t \big[(K+\Delta K)(J+\Delta J)(J+1+\Delta J)\big] +$$

$$\sum_t \eta_t^K \Delta\ell_t \big[(K+\Delta K)^3\big] +$$

$$\sum_s \beta_s^J v_s \big[(J+\Delta J)^2 (J+1+\Delta J)^2\big] +$$

$$\sum_s \beta_s^{JK} v_s \big[(K+\Delta K)^2 (J+\Delta J)(J+1+\Delta J)\big] +$$

$$\sum_s \beta_s^K v_s \big[(K+\Delta K)^4\big] +$$

$$H_0^J \big[(J+\Delta J)^3 (J+1+\Delta J)^3 - J^3 (J+1)^3\big] +$$

$$H_0^{JK} \big[(K+\Delta K)^2 (J+\Delta J)^2 (J+1+\Delta J)^2 - K^2 J^2 (J+1)^2\big] +$$

$$H_0^{KJ} \big[(K+\Delta K)^4 (J+\Delta J)(J+1+\Delta J) - K^4 J(J+1)\big] +$$

$$H_0^K \big[(K+\Delta K)^6 - K^6\big]$$

$$(2.5)\quad B_v = B_e - \sum_s \alpha_s^B (v_s+g_s/2) + \sum_{\substack{ss' \\ s\le s'}} \gamma_{ss'}^B (v_s+g_s/2)(v_{s'}+g_{s'}/2) + \sum_{\substack{tt' \\ t\le t'}} \gamma_{\ell_t\ell_{t'}} \ell_t \ell_{t'} + \Delta B_e$$

$$(2.6)\quad D_v^m = D_e^m - \sum_s \beta_s^m (v_s+g_s/2) \quad \text{for} \quad m = J,K,JK$$

Substitutions have been made for A_0, B_0, and D_0^m since these ground-state effects each have distinct rotational quantum dependencies which are quite independent of the upper-state vibrational level. It will be noticed that the equilibrium constants A_e, B_e, and D_e^m still are not readily available even if their ground-state values are known.

Well-known selection rules (18) specify that for symmetric tops,

$\Delta K = 0$ for $\parallel$ bands

$\Delta K = \pm 1$ for $\perp$ bands

and for both types of bands

$\Delta J = 0, \pm 1$

except that $J = 0$ to $J = 0$ transitions do not occur.

In addition, selection rules on ℓ_t can be inferred from symmetry considerations. In particular, for ν_4

$\Delta\ell_4 = \Delta K = \pm 1$

and for $2\nu_4$

$\Delta\ell_4 = -2\Delta K = 0, \pm 2$

Table 2.5 (19) shows the form which the generalized frequency expression takes when it is applied to ν_4 or $2\nu_4$. The effect of the selection rule on $(\Delta\ell_t)$ has been put in terms of the parameter

Table 2.5

Single Band Frequency Expression for ν_4 or $2\nu_4$

$${}^{\Delta K}\Delta J_K(J) = +\{B_0[(J+\Delta J)(J+1+\Delta J)-J(J+1) - (K+\Delta K)^2+K^2]$$

$$-D_0^J[(J+\Delta J)^2(J+1+\Delta J)^2-J^2(J+1)^2]$$

$$-D_0^{JK}[(K+\Delta K)^2(J+\Delta J)(J+1+\Delta J)-K^2J(J+1)]\} +$$

$$\begin{bmatrix} \nu_0(\nu_4) & \text{or} \\ \nu_0(2\nu_4 \perp) & \text{or} \\ \nu_0(2\nu_4 \parallel) & \end{bmatrix} - [k(\Delta K)^2(A_e\zeta_4^z - 1/4\eta_4^K)] +$$

$$[A_0 - kA_e\zeta_4^z - 1/2k\eta_4^K][(K+\Delta K)^2-K^2] +$$

$$[-D_0^K - 1/4k\eta_4^K][(K+\Delta K)^4-K^4] +$$

$$[-\alpha_4^A + 3/2k\eta_4^K][(\Delta v_4)(K+\Delta K)^2] +$$

$$[-\alpha_4^B][(\Delta v_4)\{(J+\Delta J)(J+1+\Delta J) - (K+\Delta K)^2\}] +$$

$$[\eta_4^J][(k\Delta K)(K+\Delta K)(J+\Delta J)(J+1+\Delta J)] +$$

$$[\beta_4^J][(\Delta v_4)(J+\Delta J)^2(J+1+\Delta J)^2] +$$

$$[\beta_4^{JK}][\Delta v_4)(K+\Delta K)^2(J+\Delta J)(J+1+\Delta J)] +$$

$$[\beta_4^K][(\Delta v_4)(K+\Delta K)^4] +$$

$$[H_0^J][(J+\Delta J)^3(J+1+\Delta J)^3-J^3(J+1)^3] +$$

$$[H_0^{JK}][(K+\Delta K)^2(J+\Delta J)^2(J+1+\Delta J)^2-K^2J^2(J+1)^2] +$$

$$[H_0^{KJ}][(K+\Delta K)^4(J+\Delta J)(J+1+\Delta J)-K^4J(J+1)] +$$

$$[H_0^K][(K+\Delta K)^6-K^6]$$

$k = 1$ for ν_4

$k = -2$ for $2\nu_4$

(k), thus allowing the one expression to apply to both ν_4 and $2\nu_4$ ($\perp$ or $\parallel$). The expression is written in a form making it convenient for a large-scale computer fit of individual transition frequencies to obtain the unknown constants $(A_0 - kA_e\zeta_4^z, -D_0^K, -\alpha_4^A, -\alpha_4^B \ldots$ etc.). Chapter V covers the computerized analysis procedure in detail.

One form of the single-band frequency expression which is often used at lower resolution is that in which $\Delta J = 0$, and third and fourth-order terms are ignored (20,21,22). This expression allows an approximate analysis from the Q branches of perpendicular bands ($\Delta K = \pm 1$) from symmetric top molecules. If, in addition, centrifugal distortion is ignored, the second-order frequency expression for these ${}^RQ_K$ and ${}^PQ_K$ lines is

$$\begin{aligned}\nu(J,K,\Delta K) = \nu_0 &+ (B_v - B_0)J(J+1) \\ &+ 2[A_v(1 - \zeta_v) - B_v]K\Delta K \\ &+ [(A_v - A_0) - (B_v - B_0)]K^2\end{aligned}$$

where the small second term determines the extent of the spreading of the unresolved lines. The usual approach is to fit the Q branch peak to the formula,

$$\begin{aligned}\nu(K,\Delta K) = \nu_0 &+ 2[A_v(1 - \zeta_v) - B_v]K\Delta K \\ &+ [(A_v - A_0) - (B_v - B_0)]K^2\end{aligned} \tag{2.7}$$

where ν_0 contains all the non-rotational terms.

A careful comparison of this expression for Q branch peaks with the general single-band expression as applied to ν_4 or $2\nu_4$ (Table 2.5) indicates that the two are compatible. Unfortunately, coefficients obtained from fits of the two forms are very difficult to compare. For example, ν_0 of (2.7) contains all the terms which have constant quantum coefficients involving $\Delta K = \pm 1$; the generalized ν_0 has put some of these $(\Delta K)^2$ terms in the coefficients of α_4^A and α_4^B. Likewise, the coefficient of $K\Delta K$ contains effects which become part of the coefficients of $A_0 - A_e\zeta_4^z$, α_4^A, and α_4^B in the generalized equation. The third term of (2.7) is equal to $(\alpha_4^B - \alpha_4^A)$, but does not allow a determination of α_4^A or α_4^B separately. Such mixing of terms requires that great care be taken in comparing results of fits using the two forms.

Two combination relationships from $(K, \Delta K)$ are often used in Q branch analyses. These result directly from the ΔK dependence of the second term. They are

$$\begin{aligned} {}^RQ_K + {}^PQ_K &= 2[\nu_0 + A_v(1 - \zeta_v)^2 - B_v] \\ &\quad + 2[(A_v - A_0) - (B_v - B_0)]K^2 \\ {}^RQ_K - {}^PQ_K &= 4[A_v(1 - \zeta_v) - B_v]K \end{aligned} \tag{2.8}$$

These combination relationships are most commonly found in papers written before the computer era, since they allow a simple graphical determination of approximate molecular constants.

Analysis of the parallel bands $(\Delta K = 0)$ of symmetric tops is usually a difficult process due to difficulties in assigning the overlapping lines. The most common approach has been to measure series of ${}^QR_K(J)$ and ${}^QP_K(J)$ lines without attempting to identify the (hopefully) constant K value of the particular series (21,22). The resultant frequency expressions for ${}^QP_K(J)$ and ${}^QR_K(J)$ are

$$^{Q}P_K(J) = \nu_0 + (A_v - A_0 - B_v + B_0)K^2$$
$$- (B_v + B_0 - 2K^2D_{JK})J + (B_v - B_0)J^2 + 4D_{JJ}J^3$$

$$^{Q}R_K(J) = \nu_0 + (A_v - A_0 - B_v + B_0)K^2 + B_v$$
$$+ (3B_v - B_0)J + (B_v - B_0)J^2 - 4(J+1)^3D_{JJ} - 2K^2(J+1)D_{JK}$$

If a given K series is followed (K = constant), then the two equations can be put in compact form, viz.,

(2.9) $$\nu(J) = a_1 + b_1m + c_1m^2 + d_1m^3$$

where $m = -J$ for the P branch

$m = J + 1$ for the R branch

and $a_1 = \nu_0 + (A_v - A_0 - B_v + B_0)K^2$

$b_1 = B_v + B_0 - 2K^2D_{JK}$

$c_1 = B_v - B_0 = \alpha_v^B$ for fundamentals

$d_1 = -4D_{JJ}$

The $^{Q}Q_K(J)$ lines $(\Delta J = 0, \Delta K = 0)$ in the center of a parallel band are seldom completely resolved because of the small magnitude of α_v^B for the methyl halides; but, because of a much larger α_v^A, often they can be identified in K. This allows them to be described by the equation,

(2.10) $$\nu(K) = a_2 + b_2K^2$$

where $a_2 = \nu_0 + (B_v - B_0)J(J+1)$

$b_2 = (A_v - A_0 - B_v + B_0)$

$= \alpha_v^B - \alpha_v^A$ for fundamentals.

Thus from a complete analysis of a parallel band one can determine α_v^A, α_v^B, and $\nu_0(\|)$.

Equations (2.7 - 2.10) have all been used extensively for moderate resolution spectra where it is difficult to resolve the ${}^RR_K(J)$, ${}^PP_K(J)$ lines of $\perp$ bands and ${}^QP_K(J)$ and ${}^QR_K(J)$ lines of $\|$ bands. They can also be usefully applied where computer facilities are minimal, or where approximate molecular constants are desired without spending much time and effort assigning individual lines. When it is possible to resolve the individual ${}^RR_K(J)$, ${}^PP_K(J)$, ${}^QP_K(J)$, ${}^QR_K(J)$ lines, it is best to use the appropriate form of the generalized frequency expression. The latter approach has been used exclusively in this work, except where a comparison of accuracies with previous work and differing methods has been made.

The next chapter is concerned with differing methods of finding the ground-state constant A_0. Two methods are treated in detail: the first uses a generalized frequency expression, the second uses the peak Q branch formula (2.7) and some of its equivalent forms.

CHAPTER III

METHODS OF A_0 DETERMINATION

A definition of A_0 in terms of A_e is given in Eq. (2.4), and this definition is then used in a development of a single-band frequency expression as applied to ν_4 or $2\nu_4$ (Table 2.5). The expression shows clearly that A_0 cannot be determined from a single band. Two methods of obtaining A_0 are the main topic of this chapter. The first involves the use of frequencies of a fundamental band and its first overtone (e.g. ν_4 and $2\nu_4$); the second uses information from the three fundamental perpendicular bands of a methyl halide (i.e. ν_4, ν_5, and ν_6). In the analysis chapters which follow, a statistical study is included from experimental applications of both methods.

If single-band fits of ν_4 and $2\nu_4$ are made, the particular combination of $A_0 - A_e\zeta_4^z$ and $A_0 + 2A_e\zeta_4^z$ can be obtained. These constants can then be combined to determine a value of A_0. An alternative approach is to fit the bands simultaneously to a frequency expression generalized to include both bands. This simultaneous equation has been given by T.L. Barnett (19) and is contained in Table 3.1. Barnett and Edwards applied the simultaneous fit approach to find A_0 for CH_3Br and CH_3I (23,24,25). Barnett has also shown that A_0 can be obtained by fitting a combination band of the form $\nu_t + \nu_n$ simultaneously with $2\nu_t$ (19). The simultaneous approach has a number of advantages over the method of combining two single-band fits. These advantages are discussed in

Table 3.1

Frequency Expression for a Simultaneous Fit of ν_4 and $2\nu_4$

$$
\begin{aligned}
{}^{\Delta K}\Delta J_K(J) - \{ & B_0[(J+\Delta J)(J+1+\Delta J)-J(J+1)-(K+\Delta K)^2+K^2] \\
& -D_0^{J}[(J+\Delta J)^2(J+1+\Delta J)^2-J^2(J+1)^2] \\
& -D_0^{JK}[(K+\Delta K)^2(J+\Delta J)(J+1+\Delta J)-K^2J(J+1)]\} =
\end{aligned}
$$

$$
\left[\begin{array}{ll}
\nu_0(\nu_4) & \text{or} \\
\nu_0(2\nu_4\ \perp) & \text{or} \\
\nu_0(2\nu_4\ \|) &
\end{array}\right]
$$

$$
\begin{aligned}
& [A_0][(K+\Delta K)^2-K^2] + \\
& [-2A_e\zeta_4^{\,z}+\eta_4][(\Delta\ell_4)(K+\Delta K)] + \\
& [-D_0^{K}][(K+\Delta K)^4-K^4] + \\
& [-\alpha_4^{A}][(\Delta v_4)(K+\Delta K)^2] + \\
& [-\alpha_4^{B}][(\Delta v_4)\{(J+\Delta J)(J+1+\Delta J)-(K+\Delta K)^2\}] + \\
& [\eta_4^{K}][(\Delta\ell_4)(K+\Delta K)^3] + \\
& [\eta_{44}][(\Delta v_4+1)(\Delta\ell_4)(K+\Delta K)] + \\
& [\eta_4^{J}][(\Delta\ell_4)(K+\Delta K)(J+\Delta J)(J+1+\Delta J)] + \\
& [\beta_4^{J}][(\Delta v_4)(J+\Delta J)^2(J+1+\Delta J)^2] + \\
& [\beta_4^{JK}][(\Delta v_4)(K+\Delta K)^2(J+\Delta J)(J+1+\Delta J)] + \\
& [\beta_4^{K}][(\Delta v_4)(K+\Delta K)^4] + \\
& [H_0^{K}][(K+\Delta K)^6-K^6] + \\
& [H_0^{J}][(J+\Delta J)^3(J+1+\Delta J)^3-J^3(J+1)^3] + \\
& [H_0^{JK}][(K+\Delta K)^2(J+\Delta J)^2(J+1+\Delta J)^2-K^2J^2(J+1)^2] + \\
& [H_0^{KJ}][(K+\Delta K)^4(J+\Delta J)(J+1+\Delta J)-K^4J(J+1)] + \\
& [\gamma_{44}^{A}][(\Delta v_4)(\Delta v_4+2)(K+\Delta K)^2] + \\
& [\gamma_{\ell_4\ell_4}^{A}][(\Delta\ell_4)^2(K+\Delta K)^2] + \\
& [\gamma_{44}^{B}][(\Delta v_4)(\Delta v_4+2)\{(J+\Delta J)(J+1+\Delta J)-(K+\Delta K)^2\}] + \\
& [\gamma_{\ell_4\ell_4}^{B}][(\Delta\ell_4)^2\{(J+\Delta J)(J+1+\Delta J)-(K+\Delta K)^2\}]
\end{aligned}
$$

the chapters involving the A_0 determination of CD_3I and CD_3Cl.

The method of a simultaneous analysis of individual transitions of a well-resolved ν_t and $2\nu_t(\perp)$ is believed to be the most accurate way to determine A_0 for axially symmetric moelcules. However, for purposes of comparing statistical accuracy and methodology, one needs to consider the time-honored procedure of obtaining A_0 from the zeta-sum rule.

Historically, for accidentally symmetric-top molecules, it was possible to predict infrared spectra without consideration of vibration-rotation interaction. The classic paper of D.M. Dennison (7), published in 1931, summarized the theoretical work up to that time which was done without considering Coriolis interactions. In 1934, E. Teller (26) pointed out that many features of the perpendicular bands of true symmetric tops can be explained if one considers the Coriolis interaction between rotation and the vibrational motions of degenerate normal modes. Since the eigenvalues of internal angular momentum are not necessarily integers, Teller introduced the constant ζ as a proportionality factor in the expression for the component of internal angular momentum which results as a consequence of degenerate vibrations,

$$p_z|\ell_s v_s\rangle = \ell_s \hbar \zeta^z_{s1s2} |\ell_s v_s\rangle$$

Teller then presented a theorem which states that the sum of the ζ's for all the degenerate first-excited vibrational states is a function of only the individual masses and their relative distances in the molecule. Most important, Teller succeeded in showing that this sum is not a function of the force field which binds the atoms in the molecule. By using this result, Johnson and Dennison (27) were able to show that in the harmonic approximation,

$$\sum_t \zeta_t^z = (\#\text{ of atoms on symmetry axis}) - 2 + B_e/2A_e$$

or for methyl halides,

$$\sum_t \zeta_t^z = B_e/2A_e \tag{3.1}$$

The theory behind the zeta-sum rule has since been more rigorously developed by Boyd and Longuet-Higgins (28).

Most zeta-sum work with the methyl halides has involved an application of an equation of the form (2.7), utilizing only the Q branches of ν_4, ν_5, and ν_6. Eq. (2.7) can be put in the form,

$$\nu = C_1(v) + C_2(v)K\Delta K + C_3(v)K^2 \tag{3.2}$$

where $C_1(v)$ = all terms independent of K

$$C_2(v) = 2[A_v(1 - \zeta_v^z) - B_v]$$

$$C_3(v) = [(A_v - A_0) - (B_v - B_0)]$$

If Q branches of ν_4, ν_5, ν_6, are fit, the constants $C_i(v)$ for $v = 4,5,6$, can be obtained.

Then,

$$\sum_v C_2(v) = 2\sum_v [A_v - A_v\zeta_v^z - B_v]$$

This sum can be approximated as

$$\sum_v C_2(v) \simeq 2\sum_v [A_v - B_0 - A_0\zeta_v^z] \tag{3.3a}$$

or can be approximated still further as

$$\sum_v C_2(v) \simeq 2\sum_v [A_0 - B_0 - A_0\zeta_v^z] \tag{3.3b}$$

First consider the form (3.3a) which has been used in recent work on the methyl halides (20,21). It requires further information from $C_3(v)$ in order to arrive at A_0,

$$\sum_v C_3(v) \simeq \sum_v A_v - 3A_0 = -\sum_v \alpha_v^A;$$

substituting into (3.3a),

$$\sum_v C_2(v) = 2[\sum_v C_3(v) + 3A_0 - 3B_0 - A_0 \sum_v \zeta_v^z] .$$

but the zeta-sum rule may be approximated as

$$\sum_v \zeta_v^z = \frac{B_e}{2A_e} \simeq \frac{B_0}{2A_0}$$

and thus,

$$A_0 = \frac{1}{6}[\sum_v C_2(v) - 2\sum_v C_3(v) + 7B_0] \tag{3.4}$$

The further approximation (3.3b)was used in earlier work on the methyl halides and is presented in standard reference books on the subject (18,29). The older treatments often obtained the value of C_2 for each band by means of the combination relations (2.8) and graphical techniques. The expression for A_0 which results from (3.3b) is identical to Eq. (3.4) if $\sum_v C_3(v) = 0$. This approximation corresponds to a change in A_0 of about 0.005 cm^{-1}. Approximations involved in arriving at Eq. (3.3a) are not as large as that described above. For example, in the case of CD_3X molecules, the error in A_0 which results is approximately 0.0002 cm^{-1}.

There is one other important source of error (apart from the harmonic approximation of the zeta-sum rule itself) and this involves the problem of where to measure Q branch peaks. Y. Morino and J. Nakamara consider this problem in their zeta-sum paper (20).

In Appendix I of that paper, an estimate of the change in J_{max} corresponding to a Q branch peak is given as a function of the K. The uncertainty caused by this dependence is further complicated by the slit function of the instrument. They were only able to estimate the maximum effect on $C_2(5)$ to be $\pm$ 0.04 cm^{-1} for CD_3Cl ν_5 (which was the poorest band they analyzed). Such a change in $C_2(5)$ corresponds to a change in A_0 of $\pm$ .006 cm^{-1}. Morino and Nakamura concluded they could ignore any J_{max} dependence on K since in most cases this systematic error would be less than their random experimental error.

In summary, a zeta-sum determination of A_0 under low to moderate resolution depends on the following approximations:

(1) The zeta-sum rule is derived in the harmonic approximation.

(2) The approximation,

$$\sum_v A_v \zeta_v^z = A_0 \sum_v \zeta_v^z$$

is made in obtaining Eq. (3.3a).

(3) In all applications to CH_3X or CD_3X, J_{max} has been assumed not to be a function of K.

The approximations (2) and (3) above could be removed by a high resolution study of ν_4, ν_5, and ν_6. Such a single-band analysis would yield the constants:

$$A_0 - A_e\zeta_4^z = C_4$$
$$A_0 - A_e\zeta_5^z = C_5 \quad \text{or} \quad 3A_0 - A_e(\zeta_4^z + \zeta_5^z + \zeta_6^z) = C_4 + C_5 + C_6$$
$$A_0 - A_e\zeta_6^z = C_6$$

Therefore, by summing these terms and by making the very small approximation $B_0 \simeq B_e$, a value of A_0 would be immediately available. However, the harmonic approximation (1) would remain; indeed a high resolution study of ν_4, ν_5, and ν_6 could provide a measure of the magnitude of this approximation if the resultant A_0 were compared to that obtained from a simultaneous analysis.

It is apparent that even though the zeta-sum technique could gain accuracy under high resolution, it would still be subject to a source of systematic error which currently cannot be estimated. In comparison, the accuracy of A_0 from simultaneous fits of unperturbed bands is largely determined by the resolving power of the spectrometer which is used.

In much of this chapter the assumption has been made that unperturbed spectra are available. In practice, the chances of finding a pair of ν_t and $2\nu_t$ bands which are completely unperturbed is slight (likewise for ν_4, ν_5, and ν_6). Accidental resonances are found to play a critical role not only in determining whether A_0 can be obtained by a given method, but also in determining the accuracy of its value when it can be found. Examples of the effects of perturbations in particular cases are given in Chapters VII and VIII.

CHAPTER IV

EXPERIMENTAL PROCEDURE

High resolution spectra of the ν_4 (4.5μ) and $2\nu_4$ (2.2μ) regions of CD_3I, CD_3Cl, and CD_3Br have been recorded on the Michigan State University near infrared spectrometer. Experimental conditions for the individual runs are given in Tables 4.1, 4.2, and 4.3. Two or three spectra were recorded for each of the six bands. The averaging procedures and results of individual calibrations will be discussed for each of the molecules individually in the analysis chapters (VI, VII, and VIII).

The Michigan State University spectrometer has continually been improved during the past 15 years, and consequently it bears the imprints of many contributors. The present state of the instrument has been particularly affected by the work of former graduate students, J.L. Aubel and D.B. Keck. The most current report on the major features of this instrument is given in the thesis of D.B. Keck (30), which includes references to earlier work. In this chapter a summary of recent changes made on the instrument is given, along with a description of some of the problems unique to this work.

Because of the expense of samples of CD_3X gases, great care had to be exercised in handling them. If ordinary freeze-out procedures failed, the gases were slowly pumped out of the absorption cell through a liquid nitrogen cold trap. Memories of these freeze-out difficulties are less than fond, since they often

Table 4.1

Experimental Conditions - CD_3I

	ν_4 (44° - 38°)	$2\nu_4$ (45° - 39.5°)
Grating	300 grooves/mm 1st Order - S.P. @500/1	300 grooves/mm 2nd Order - S.P. @500/1
Calibration	CO (1-0) N_2O (1,2,0)	CO (2-0) N_2O (2,0,1)
Paper Speed	4"/min	4"/min
Detector	PbSe - Type E1 @77°K	PbS - Type 0 @77°K
Date of Runs	Chart #1 - 7/11/68 Chart #2 - 11/23/68	Chart #1 - 6/20/68 Chart #2 - 7/24/68 Chart #3 - 12/11/68
Rod Current	#1 - 360 amps #2 - 375 amps	#1 - 360 amps #2 - 360 amps #3 - 380 amps
Pressures (torr)	#1 - 19 #2 - 19,10,20	#1 - 20 #2 - 19 #3 - 25,19,30
Path lengths	#1 - 3.2 m #2 - 6.4 m	#1 - 9.6 m #2 - 9.6 m #3 - 9.6 m
Slits (approx. width)	#1 - 60 microns #2 - 35 microns	#1 - 16 microns #2 - 11 microns #3 - 8 microns
Best Chart Resolution	#2 - .05 cm^{-1}	#3 - .04 cm^{-1}

Table 4.2

Experimental Conditions - CD_3Cl

	ν_4 (44° - 38°)	$2\nu_4$ (45° - 39.5°)
Grating	300 groves/mm 1st Order - S.P. @500/1	300 grooves/mm 2nd Order - S.P. @500/1
Calibration	CO (1-0) N_2O (1,2,0)	CO (2-0) N_2O (2,0,1)
Paper Speed	4"/min	4"/min
Detector	PbSe - Type El @ 77°K	PbS - Type 0 @77°K
Date of Runs	Chart #1 - 7/12/68 Chart #2 - 11/25/68	Chart #1 - 6/19/68 Chart #2 - 7/24/68 Chart #3 - 12/11/68
Rod Current	#1 - 360 amps #2 - 375 amps	#1 - 360 amps #2 - 360 amps #3 - 375 amps
Pressure (torr)	#1 - 8,4,8 #2 - 15,9,15	#1 - 18 #2 - 24,18,24 #3 - 25,19,25
Path Lengths	#1 - 3.2 m #2 - 3.2 m	#1 - 9.6 m #2 - 9.6 m #3 - 9.6 m
Slits (approx. width)	#1 - 62 microns #2 - 35 microns	#1 - 16 microns #2 - 11 microns #3 - 8 microns
Best Chart Resolution	#2 - .05 cm^{-1}	#3 - .04 cm^{-1}

Table 4.3

Experimental Conditions - CD_3Br

	ν_4 (44° - 38°)	$2\nu_4$ (45° - 39.5°)
Grating	300 grooves/mm 1st Order - S.P. @500/1	300 grooves/mm 2nd Order - S.P. @500/1
Calibration	CO (1-0) N_2O (1,2,0)	CO (2-0) N_2O (2,0,1)
Paper Speed	4"/min	4"/min
Detector	PbSe - Type E1 @77°K	PbS - Type 0 @77°K
Date of Runs	Chart #1 - 8/19/68 Chart #2 - 11/25/68	Chart #1 - 8/09/68 Chart #2 - 10/30/68
Rod Currents	#1 - 360 amps #2 - 375 amps	#1 - 360 amps #2 - 375 amps
Pressures (torr)	#1 - 21,15,9,15 #2 - 20,15,20	#1 - 25,40 #2 - 20,40
Path Lengths	#1 - 3.2 m #2 - 3.2 m	#1 - 12.8 m #2 - 9.6 m
Slits (approx. width)	#1 - 54 microns #2 - 35 microns	#1 - 13 microns #2 - 9 microns
Best Chart Resolution	#2 - .05 cm^{-1}	#2 - .05 cm^{-1}

resulted in rather frantic glassware assemblage in the small time available between CD_3X removal and calibration gas insertion.

Initially a study of CD_3F was to be included in this work, but it was found that the only sample of this very expensive gas which remained in the laboratory was very small and impure. Moderate resolution runs were made using that sample, but a new sample arrived too late for any more runs during the winter of 1969. Future plans do include a study of ν_4 and $2\nu_4$ of CD_3F. Samples of CD_3CN have also been obtained and could be studied in the future.

The source of near infrared radiation in both wavelength regions was an ohmic-heated carbon rod. The associated assembly has been described by D.B. Keck. The only changes were in the operation of the source:

(1) It was found that the use of #17 copper wire for holding the carbon rods provided trouble free starting.

(2) If the rod being used had been exposed to the atmosphere, it was beneficial to flush the rod housing with argon after the rod has been heated for 10 or 15 minutes. This rids the chamber of the CO and CO_2 which are formed soon after the rod is heated. CO lines, which were used in the calibration of both bands, could be seen to be considerably broadened by CO in the housing. The lines immediately narrowed after flushing with argon.

The White type multiple traverse cell as described by T.H. Edwards (31) was completely disassembled and cleaned. The spherical mirrors were stripped and realuminized by Liberty Mirror (anti-corrosive quartz finish No. 749). The foreoptics and cell system were then carefully realigned and focused on the entrance slit of the monochromator.

All of the spectra eventually used were recorded with the monochromator in a single-pass configuration, using the 300 groves/mm grating between 45° and 38° (first-order for ν_4 and second-order for $2\nu_4$). The calibration fringes were an immense problem in this region. An apparent grating anomaly causes a sharp decrease in the intensity of ninth-order fringes between 43.5° and 43° and a similar effect in the case of eighth-order fringes between 42.7° and 42.3°. This effect has been noticed by others and was certainly verified far too many times in the course of this work. Fortunately the bad fringes occurred in a region lying largely between our low-frequency calibration and the CD_3X region. It did however cause some "only fair" fringes on the extreme low-frequency side of a few charts. This fringe problem was much worse in the case of double passing the grating. The already weak fringes became much weaker and could not be used. The infrared double-pass resolution was very good in the $2\nu_4$ region and so these spectra were run without fringes as high resolution references - if needed.

The problems associated with the previous detector system were described by Keck. A new detector housing was designed which allows a mounting of three detectors simultaneously in a manner allowing a rapid transition from one to another while maintaining a temperature of 77°K. The three detectors were mounted on a triangular head attached to the bottom of the liquid N_2 dewar. The dewar assembly can be rotated at least 120° left or right of the center position. The dewar is supported by a knurled stainless steel top which keeps the critical top O-ring seal as isolated as possible from the N_2. The cold O-ring maintains a good seal under rotation from one detector to another, but does stick and cause a difficult transition from one detector to another if it is not lubricated periodically (approximately every 10 cold turns). Whenever possible, the detector should be changed before cooling.

Sketches of the assembly are shown in Figure 4.1 along with the variable bias system (Figure 4.2) which was constructed to allow the choice of a bias resistance to match the impedance of the detector currently in use. Although it is advisable to periodically check and record the cold detector resistances, the correct choice of bias resistance can be simply made by maximizing the recorder signal. Even though the recorder signal seems greatly dependent upon bias choice, it should be realized that the effect on S/N is quite small.

Heat shields have been designed to limit the field of view of each of the mounted detectors. The shields slide into the large circular apertures in front of each detector and provide an adjustable rectangular opening. They have been found to be particularly necessary for the type E detectors; typically raising the cold resistance from around 3 $M\Omega$ to 10 $M\Omega$ and significantly increasing the detectivity.

The detectors which are currently available are the same types that are described by Keck. A new type E (PbSe) detector has been purchased from Kodak; however, its detectivity does not seem to match that of the previously used E type. The tri-detector system as described should be operated with a set of detectors to cover the entire 1 to 6 micron region. This can be accomplished by means of an N or O type in one position (1 to 2.8μ), a P type in another (2.8 to 4.2μ), and a type E (4 to 6μ) in the third position. Such

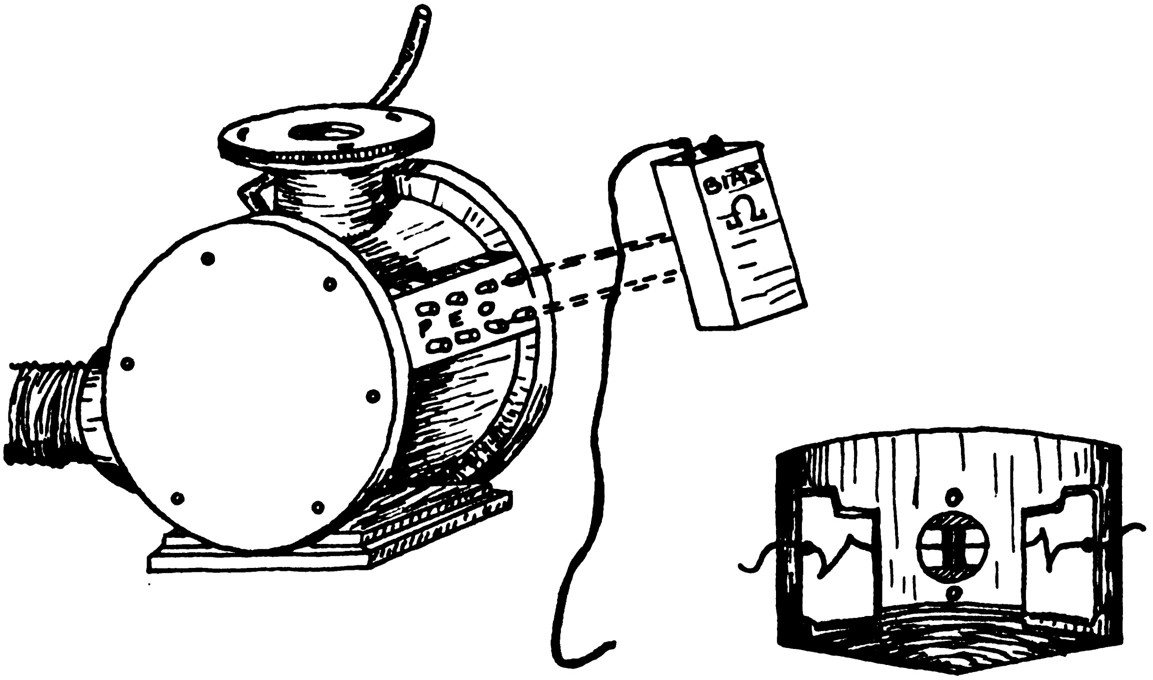


Figure 4.1 Detector Assembly

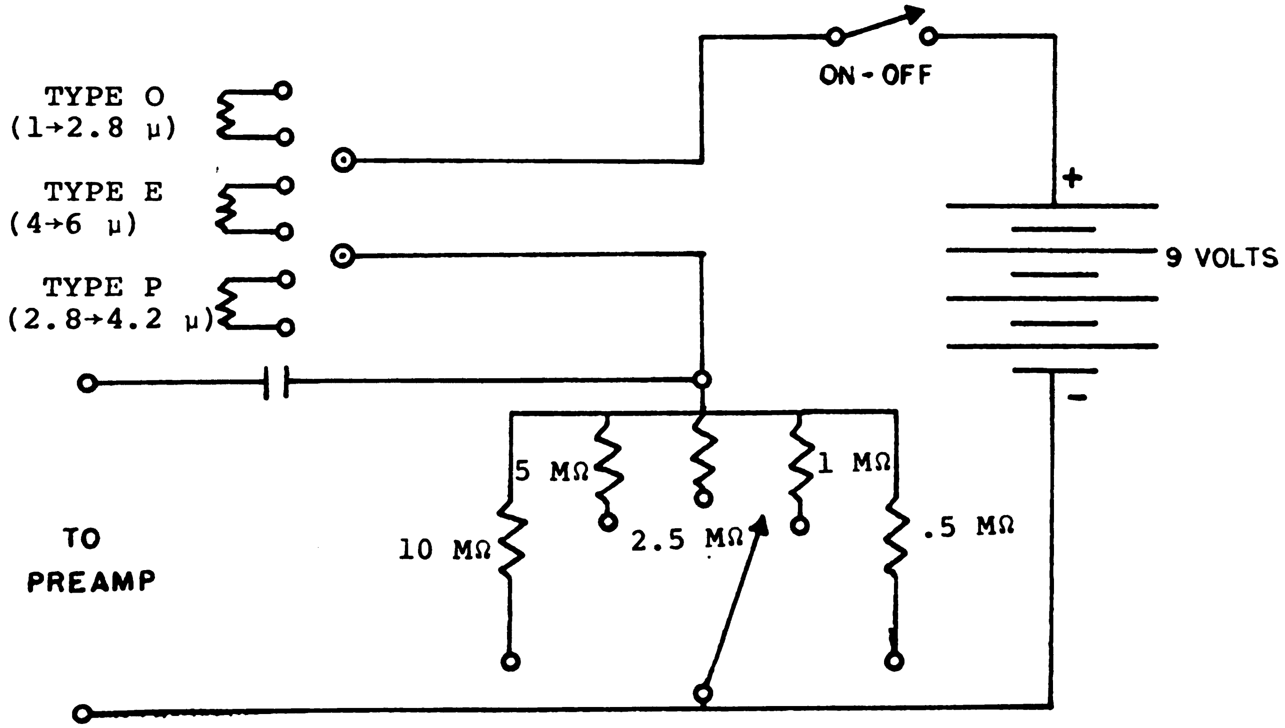


Figure 4.2 Bias Circuit

a system was used during the summer and fall of 68' and allowed runs of emission spectra in the 1μ region by L.E. Bullock, separated only by hours from some of these absorption runs around 4.5μ.

Plans are being made for the purchase of an InSb detector which operates with peak detectivity in the 4 to 6 micron region. The present type E PbSe detector for that region has a significantly lower detectivity than any of our PbS devices or the InSb. The new detector should allow excellent resolution in the 5 micron region in comparison to the present maximum of 0.05 to 0.07 cm^{-1}. Unfortunately, the new detector will necessarily be mounted in an evacuated dewar which will not have immediate compatibility with the present system.

Other plans for the near future include an improvement in the fringe detection system. Professor C.D. Hause's plans include use of a newly introduced phototube, the corresponding power supply, and a more sophisticated preamp. In addition Professor T.H. Edwards is investigating a tunable lock-in amplifier for the IR signal along with a digital voltmeter which will sample at least four channels of information and record them on magnetic tape. The advantages of such a data acquisition system would be numerous. Some of these advantages are discussed briefly in the first part of the next chapter which summarizes our current data analysis system.

CHAPTER V

ANALYSIS OF DATA

After a high resolution spectrum has been obtained from the spectrometer, a large amount of data reduction must be completed before observed frequencies are available from the chart. Part of this process involves an analog to digital conversion of the information on the chart; the rest involves obtaining observed frequencies from this digital data. Thus it is the first step of this process which could be almost eliminated with a digital voltmeter to magnetic tape data acquisition system.

Presently our data is digitized to five-place accuracy by the HYDEL system. A description of this process has been given by T.L. Barnett (19) and briefly by L.E. Bullock (32). The encoders, which are the heart of this digital process, were often unreliable during the past year. They were carefully cleaned a number of times but still cannot be completely trusted. Since the system had already seen considerable use when first acquired by this laboratory in the early 60's, the encoders may in fact simply be worn out. The tight financial situation has made overhauling the system quite infeasible at the present time. The state of the HYDEL system is thus another reason the magnetic tape system currently seems very inviting.

The computer program SHAFT as developed by D.B. Keck (30) and L.E. Bullock (32) has been very helpful in this work. Its major purpose is to help obtain the best possible set of observed frequencies from many records of HYDEL digital data output. SHAFT takes the recorded line and fringe positions, along with the input calibration frequencies, and from these determines the coefficients (A and B) of the linear equation,

$$\text{Line Frequency (cm}^{-1}\text{)} = \text{A (Fringe \#)} + \text{B}$$

Observed frequencies are calculated for all measurements of chart lines, and these are then averaged and output in formats useable in our other programs. The other options available in SHAFT are manifold and their usefulness is matched only by the initial complications in using them. However, for anyone who is about to start a project which involves many charts and measurements, learning to use the program is time well spent.

Two HYDEL measurements were made of two individual charts for each of the six bands. Thus, four sets of data were available for each band. Unfortunately, the first charts which were run during June and July 68' were almost invariably significantly poorer in resolution. Only in the case of $2\nu_4$ of CD_3Br was it possible to average frequencies between charts without reducing frequency accuracy. In each case, however, the two HYDEL measurements were averaged. Because of the unreliable condition of the HYDEL system during the past year, the two HYDEL measurements were very necessary since the occasional HYDEL errors were erratic and usually ranged from 0.04 to 0.07 cm^{-1}.

The observed (averaged) frequencies are then ready to be fit by a frequency expression given in terms of molecular constants, quantum numbers, and changes in these quantum numbers. The frequency expressions which have been used most extensively in this work are the single-band frequency expression (Table 2.5), the simultaneous ν_4 and $2\nu_4$ expression (Table 3.1), and to a much lesser degree, the Q branch frequency expression (Equation 2.7). Program SYMFIT has been written to conveniently provide for the above fits. The remainder of this chapter is devoted to a description of this program and instructions for its use.

The major goals in the construction of SYMFIT were:

(1) It must be a general symmetric top fitting program - thus it must fit single bands, subbands, double bands, Q branches, etc.

(2) SYMFIT should operate with formats compatible with the inputs and outputs to program SHAFT.

(3) It should be able to perform fits in less than 45 seconds (Priority 5 on the CDC 3600 at MSU).

(4) For the convenience of other researchers, SYMFIT should utilize subroutine STEPFIT in order to lessen confusion when comparisons are made to other fitting programs currently in use in this laboratory.

(5) SYMFIT should be compatible with the CDC 3600 and 6500.

A simplified block diagram of the final SYMFIT version which accomplishes these goals is shown in Figure 5.1. A listing of SYMFIT along with a typical data set is given in Appendix A.

The set up of a SYMFIT deck is described below. After a Fortran IV or binary copy of SYMFIT (and the associated control cards), the following cards are read:

(1) <u>Option card</u> - reads the variable IBAND in the last 8 columns (73-80)

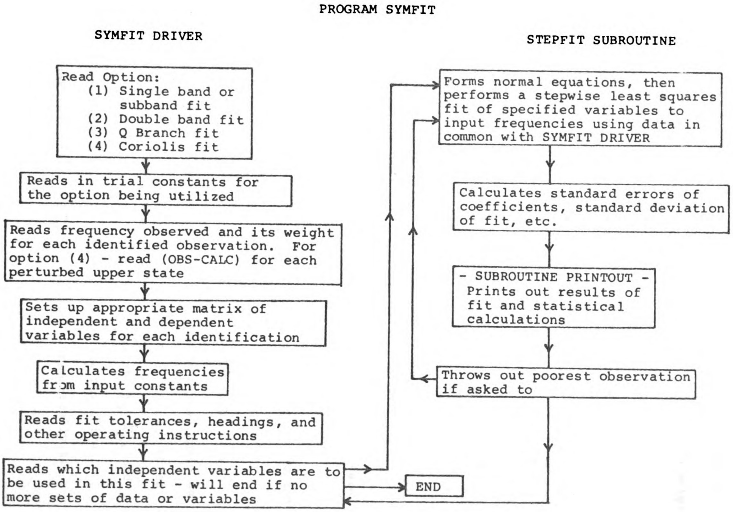


Figure 5.1 Block Diagram of SYMFIT

(a) If IBAND = 8HSINGLEBD[a], the program assumes it is to use the single band frequency expression of Table 2.5. The expression also will allow a fit of subbands when the only variables put into fit are α_4^B and the subband origin.

(b) If IBAND = 8HDOUBLEBD, the simultaneous frequency expression is assumed (Table 3.1).

(c) If IBAND = 8HQ BRANCH, a fit is made to the expression of Eq. 2.7.

(d) If IBAND = 8HCORIOLIS, a residual analysis of the type described by W.E. Blass (33) is performed.

(2) Constant card - if a card reading CONSTANT in the last 8 columns (73-80) is read next, the program assumes initial values of some variables will be read into the fit.

(3) END HEAD card - if a CONSTANT card was provided, the opportunity to insert a heading to describe these constants is provided. The program will print a heading until a card with END HEAD in the last 8 columns (73-80) is found.

(4) Initial values of constants are then expected to follow the END HEAD card. These are read in the order indicated by their quantum dependencies as shown in their respective Tables or in the Fortran listing. Values are read until an END CONST is found in columns (73-80). Thus if only three values are read in (e.g. microwave values of B_0, D_0^J, and D_0^{JK}), then the END CONST card should follow the third constant (all other initial values are automatically set = 0.0).

(5) Next, a NEW DATA card will start the reading of sets of Δv, ΔK, ΔJ,K,J, observed frequency, and line weight for

---

[a] The Fortran notation, IBAND = 8HSINGLEBD implies the variable IBAND contains the 8 characters SINGLEBD.

each identified transition. The identification format used in SYMFIT is compatible with the identification format of SHAFT. This format is given in statement 185 of the SYMFIT listing.

(6) An F in column 10 will stop the reading of frequencies and identifications.

(7) The next card reads in control data for the fitting subroutine STEPFIT. Variables read in here are: INF01, INF02, INF03, NDELMAX, XDEVMAX, TOL, EFIN, EFOUT, and ILEVEL. The format here is specified in statement 190. Definitions of these terms and their functions have been given in the MSU IR Laboratory writeup of STEPFIT and are given by Keck (30).

(8) The next card reads in values of the one-dimensional array NK(I). NK(I) = 0 unless the Ith variable is to be varied in the fit, in which case NK(I) = 1. The associated format is given in statement 195.

(9) END HEAD - Another heading may be read in at this point. Headings are listed until END HEAD is found in columns (73-80).

After reading the END HEAD card, the subroutine STEPFIT is called, and a least squares fit is performed. STEPFIT performs a stepwise least squares regression, in which variables are individually entered or removed from the fit after they are tested for statistical significance. Appendix B briefly describes the method used in this fit and the manner in which the associated statistics are calculated.

(10) After the fit is performed, STEPFIT will perform a refit after removing the poorest line depending upon its instructions on card (7). After performing the correct number of refits and corresponding line throwouts, control is restored to the driver program. If a LAST FIT card (last 8 columns) is found, the entire program will terminate.

(11) If a refit using a new set of variables (using the same data) is desired, the LAST FIT card should be replaced by a new card (8) which gives the new NK(I) array. Another END HEAD card (9) will then start the next fitting sequence.

(12) If an entirely new set of data is to be fit, the LAST FIT should be replaced by a NEW DATA card (5) followed by the sequence of cards: (6), (7), (8), and (9). This is most commonly used in the SINGLEBD option for subband fits in which each set of subband data is separated by cards (5), (6), (7), (8), and (9).

The program is designed to print out the fit results in formats corresponding to the various options. Single-band fits of 200 to 300 lines require 10 to 15 seconds per fit (fitting with 5 or 6 independent variables). Double-band fits of 400 or 500 lines require 30 to 40 seconds each (fitting with 7 or 8 independent variables). The very simple fits of options 3 and 4 require only 3 to 5 seconds each.

The next four chapters include applications of various SYMFIT options to the cases of CD_3I, CD_3Cl, CD_3Br and to studies of the accuracy of molecular constants obtained for each of them.

CHAPTER VI

ANALYSIS OF ν_4 AND $2\nu_4$ OF CD_3I

Consideration of which molecule to study first is important in light of the experience which is necessarily gained from the first bands analyzed. In this case CD_3I was chosen because it was known to have a relatively unperturbed $2\nu_4$, and because its ν_4 band showed no obvious perturbations. This chapter summarizes previous work on CD_3I, and then presents the results of this work under high resolution. Since many steps of the CD_3I analysis procedure are the same for the other two molecules, many of the details are given in this chapter.

Infrared absorption spectra of CD_3I have been studied by a number of workers at lower resolution. Morino and Nakamura (20) included CD_3I in their comprehensive study of the degenerate fundamentals of CH_3X and CD_3X molecules at a resolution ranging from 0.6 to 0.8 cm^{-1}. In addition, Jones, Popplewell, and Thompson (21) studied many bands of CD_3I between 3 and 20μ at a resolution of approximately 0.2 cm^{-1}. In each of the above studies, a value of A_0 was calculated by a zeta-sum analysis of unresolved Q branches of the three perpendicular type fundamental bands.

$2\nu_4$ of CD_3I is the only one of the six bands under investigation which has previously been studied under high resolution. Joffrin, Van Thanh, and Barchewitz (22) studied the unresolved Q branch structure of the perpendicular component along with the parallel component at a stated resolution limit of 0.07 cm^{-1}. However, it does not appear that their path length was sufficiently long to resolve any non - Q branch lines of the perpendicular component. J. W. Boyd (34) studied $2\nu_4$ of CD_3I at sufficient resolution ($\simeq$ 0.07 cm^{-1}) and path length (8 m) to resolve many of the ${}^PP_K(J)$ and ${}^RR_K(J)$ lines of the perpendicular component. Boyd's original charts are present in the laboratory and provided useful checks on $2\nu_4$ assignments for the lines which he was able to resolve.

Experimental conditions for the recorded spectra of CD_3I are given in Table 4.1. The spectra were calibrated and frequencies were averaged by use of program SHAFT in the manner described in Chapter V. The standard deviations of the calibration fits are 0.002 and 0.003 cm^{-1} for ν_4 and $2\nu_4$ respectively. Survey spectra of the two regions are shown in Figure 6.1. A series of CO_2 lines is in evidence on the high-frequency side of ν_4, but under high resolution these lines are far enough apart to allow identification and use of most of the CD_3I lines in the region. The ν_4 and $2\nu_4$ surveys of CD_3I exhibit low intensity "secondary Q branches" which can be attributed to the hot bands $\nu_4 + \nu_6 - \nu_6$ and $2\nu_4 + \nu_6 - \nu_6$.

A number of characteristics of symmetric top spectra aid in the initial assignment of spectral lines. For example, subband identification is greatly aided by the $J \geq K$ requirement which gives rise to a number of "missing lines". In addition, nuclear spin statistics for CD_3X molecules predict that all spectral lines involving transitions from levels having ground state K values which are any integral multiple of 3 will be 11/8 times as strong as the other lines. Thus every third Q branch is noticeably more intense, even though the change in intensity is considerably less than the 2/1 ratio for CH_3X molecules. An excellent diagram of the expected intensities in a perpendicular band of a symmetric top molecule (disregarding the above mentioned spin statistics) is given by Herzberg (36). It will be noticed that $^{R}R_{K}(J)$ and $^{P}P_{K}(J)$ lines tend to dominate the fine structure for high K, but for very low K values one can expect to find both R and P branches of a given subband (e.g. $^{R}R_{0}(J)$ and $^{R}P_{0}(J)$).

With a basic knowledge of the above spectral features it is possible for even the beginner to assign a number of lines of a band such as $2\nu_4$ of CD_3I. In $2\nu_4$, 70 to 80 $^{R}R_{K}(J)$ lines had obvious assignments, and these lines were immediately put into a single-band fit. Such a fit was used to predict more $^{R}R_{K}(J)$ lines (by giving the unidentified transitions zero weights) and then the list of observed frequencies was searched for lines which are predicted by the fit. By such an iterative process most of the $^{R}R_{K}(J)$ lines of $2\nu_4$ were assigned. It was expected that with most of these $^{R}R_{K}(J)$ lines already assigned, one would be able to predict $^{P}P_{K}(J)$ lines to a high degree of accuracy. However, this was not the case, because, in order to accurately determine the set of constants $A_0 + 2A_e\zeta_4^z$, α_4^A, and D_0^K (all of which have quantum coefficients which are dependent only on K and ΔK), it is imperative that some lines with a negative ΔK be included in the fit. By further inspection of the chart, some $^{P}P_{1}(J)$ and $^{P}P_{2}(J)$ lines were found along with a few $^{P}P_{9}(J)$ lines on the low-frequency side of the parallel component. Once these were found, the fit was able to predict more $^{P}P_{10}$ and $^{P}P_{11}$ lines. It was later discovered that much time and trouble can usually be saved in this assignment process if a few Q branch frequencies are initially included in the fit in order to help determine more accurate values of the terms having coefficients dependent on only K and ΔK. In all the fits which were done after $2\nu_4$ of CD_3I, rough Q branch frequencies were included during the initial assigning process.

Once the perpendicular component of $2\nu_4$ was successfully fit, it was found that the resultant constants could be used to predict the frequencies of the parallel component which overlaps the $K\Delta K = -8, -7, -6, -5, -4$, and -3 subbands of the perpendicular component. Three distinct series of lines can be seen in the parallel component, although many of the lines are too broad to be included in the fit. The broad lines are the result of the overlapping of transitions of differing K values. For example the $K = 2$, $K = 6$, and $K = 10$ subbands all overlap. Over 60 narrow lines from the parallel component were included in the final $2\nu_4$ fit, and were given weights appropriate to the line shape and expected intensity of the assigned K value. For example, the series of lines formed by overlapping of the $K = 3$ and $K = 5$ subbands were assigned as $K = 3$ lines because this series is approximately twice as strong as that made up of $K = 5$ lines. A study of the single-band frequency expression shows that parallel component lines of high J are very valuable in determining a precise value of α_4^B, and in the case of $2\nu_4$ of CD_3I this effect was very apparent. The final single-band fit of $2\nu_4$ had a standard deviation of 0.007 cm^{-1} and determined the most precise set of constants of all the bands analyzed. The results of this fit are given in Table 6.1 along with the results from previous work on CD_3I. The microwave values of B_0, D_0^J, and D_0^{JK} which have been used in all the CD_3I fits are included in Table 6.2.

Many ${}^R R_K(J)$ lines of the ν_4 band could be immediately identified. However, the low-frequency side of this band was characterized by an overlapping of lines from different subbands. For example, the ${}^P P_9(J)$ lines fall on top of ${}^P P_8(J + 10)$ lines. This greatly limited the number of negative ΔK lines which could be included in the fit. In addition, it was found that the ${}^P P_{12}$, ${}^P P_{10}$, and ${}^P P_9$ lines which could be identified did not fit well with the rest of the band. These lines were therefore suspected of being perturbed and were given zero weights. The results of the ν_4 fit of unperturbed lines is given in Table 6.1, and the precision of the respective constants as determined by the two single-band fits may be compared. The wide range of $K\Delta K$ values available in the $2\nu_4$ perpendicular component together with α_4^A and α_4^B information from the parallel component are the major reasons for the greater precision of constants found in the fit of $2\nu_4$.

At this point in the analysis procedure, one must try to decide how to determine the best value of A_0 from the available data. As Chapter III points out, the results of single-band fits of ν_4 and $2\nu_4$ can be combined directly to obtain A_0. In this case,

$$A_0 - A_e\zeta_4^z = 2.1324 \quad \text{from } \nu_4$$

$$A_0 + 2A_e\zeta_4^z = 3.4726 \quad \text{from } 2\nu_4$$

and thus

$$3A_0 = 7.7374$$

$$A_0 = 2.5791 \text{ cm}^{-1}$$

Table 6.1

Molecular Constants of CD_3I

Obtained from Single Band Fits (in cm^{-1})

This work:

	$\nu_4(k=1)$	$2\nu_4(k=-2)$
$\nu_0-k(\Delta K)^2A_e\zeta_4^z$	2298.087 ± 0.006[a]	4581.387 ± 0.005 ($\perp$) 4546.115 ± 0.006 ($\parallel$)
$A_0-kA_e\zeta_4^z$	2.1324 ± 0.0005	3.4726 ± 0.0005
D_0^K	$(23\pm10) \times 10^{-6}$	$(36\pm2) \times 10^{-6}$
α_4^A	$(13.5\pm0.4) \times 10^{-3}$	$(12.89\pm.04) \times 10^{-3}$
α_4^B	$(86\pm10) \times 10^{-6}$	$(82\pm3) \times 10^{-6}$

[a] Quoted uncertainties are 95% s.c.i. (See Table IV)

Previous work:

(A) Morino and Nakamura (20)

$\nu_0(\nu_4) = 2298.1$

$\alpha_4^A = 0.014$

$A_0 = 2.586$

$\zeta_4^z = 0.178$

(B) Jones, Popplewell, and Thompson (21)

$\nu_0(\nu_4) = 2298.53$

$\alpha_4^A - \alpha_4^B = 0.015$ (from ν_4)

$\alpha_4^A - \alpha_4^B = 0.012$ (from $2\nu_4$)

$A_0 = 2.586$

$\zeta_4^z = 0.178$

(C) Joffrin, N. Van Thanh, and Barchewitz (22)

$\nu_0(2\nu_4)\perp = 4580.23$

$\nu_0(2\nu_4)\parallel = 4546.10$

$\alpha_4^A = 0.013\pm0.003$

$\alpha_4^B = 0.00017\pm0.00001$

$\zeta_4^z = 0.206$

(D) J. W. Boyd (34)

$\nu_0(2\nu_4)\perp = 4581.397$

$\nu_0(2\nu_4)\parallel = 4546.14$

$A_0(1+2\zeta_4^z) = 3.472$

$\alpha_4^A - \alpha_4^B = 0.01268$

$D_0^K = 0.000038$

$\alpha_4^B = 0.000091$

Table 6.2

Molecular Constants Resulting from Simultaneous Fit of ν_4 and $2\nu_4$ of CD_3I (in cm^{-1}).

Constant	Value	95% s.c.i.[a]
$\nu_0(\nu_4)$	2298.526_5	0.003
$\nu_0(2\nu_4\perp)$	4580.494_8	0.005
$\nu_0(2\nu_4\parallel)$	4546.115_6	0.005
A_0	2.5788_2	0.0004
$A_e\zeta_4^z$	0.4467_6	0.0002
D_0^K	0.000035_8	0.000002
α_4^A	0.01290	0.00004
α_4^B	0.000083	0.000002

Standard Deviation of fit = 0.008 cm^{-1}

Input Microwave Values of Ground State Constants (37)

Constant	Value (cm^{-1})
B_0	0.2014822
D_0^J	1.197×10^{-7}
D_0^{JK}	1.612×10^{-6}

[a] Simultaneous confidence intervals (95%) for the eight constants determined. In this case ≃ 4 x standard error of the coefficient.

This approach has three obvious difficulties:

1. (1) The manner of combining these two constants is uniquely determined by their algebraic forms. Thus, as in the case above, if one constant comes from a rather incompletely assigned band, it is still not possible to give it a lower weight in combining it with the results from the better band.
2. (2) A final result of such an analysis is to find two values of each of the constants α_4^A, α_4^B, and D_0^K, even though there is certainly only one true value of each.
3. (3) While it is possible to calculate the standard error of the A_0 which results from combining the sets of constants, the calculation of any sort of a meaningful simultaneous confidence interval (s.c.i.) (see Appendix B) would be most difficult.

The first two of these difficulties can be overcome by performing a weighted average of the two sets of constants from ν_4 and $2\nu_4$. Weights should be given which are inversely proportional to the variance of the individual constants. The new averaged constants (usually $D_{0\ av}^K$, $\alpha_{4\ av}^A$, and $\alpha_{4\ av}^B$) must then be held constant in new fits of ν_4 and $2\nu_4$ in order to determine the best values of $A_0 - kA_e\zeta_4^z$ ($k = 1$ and $k = -2$).

For example, in the case of α_4^A from ν_4 and $2\nu_4$ of CD_3I,

$$\left[\frac{1}{(10)^2} + \frac{1}{(1)^2}\right]\alpha_{4\ av}^A = \frac{1}{(10)^2}\,\alpha_4^A(\nu_4) + \frac{1}{(1)^2}\,\alpha_4^A(2\nu_4)$$

Therefore in this case,

$$\alpha_{4\ av}^{A} \simeq \alpha_4^A(2\nu_4)$$

The situation is similar for α_4^B and D_0^K. If the average values $\alpha_{4\ av}^{A}$, $\alpha_{4\ av}^{B}$, and $D_{0\ av}^{K}$ are held constant in the ν_4 fit, the new value of $A_0 - A_e\zeta_4^z$ is 2.1321. If this is combined with the $A_0 + 2A_e\zeta_4^z$ from $2\nu_4$, one obtains

$$A_0 = 2.5789$$

This should be the most precise A_0 value which can be obtained by combining single-band fits. However, the difficulty of obtaining the correct s.c.i. still remains.

A simultaneous fit of ν_4 and $2\nu_4$ with the generalized frequency expression of Table 3.1 provides a more direct way to overcome the above difficulties. The results of such a fit for this case are given in Table 6.2 along with previous values of A_0 obtained by the method of zeta-sums. The standard deviation of this fit of 464 lines (0.008 cm^{-1}) is only slightly larger than that of the single-band fits (0.007 cm^{-1}). The final assignments, observed frequencies, and the line weights are given in Appendix C.

The sixteen apparently perturbed lines of ν_4 were given zero weights in the simultaneous fit, and their observed minus calculated frequencies are shown along with the other lines in Appendix C. The simultaneous fit indicated the lines were indeed perturbed since they clearly did not fit well with the other lines in either band. The observed minus calculated (OBS-CALC) values are almost independent of J, but increase rapidly with K. The ability of the simultaneous fit to help find perturbed subbands and the corresponding energy level shifts is more clearly illustrated in the case of the more extensive perturbation in ν_4 of CD_3Cl (see Chapter VII).

The A_0 resulting from the zeta-sum analysis of Morino and Nakamura (20), as shown in Table 6.2, was obtained from an analysis using the Q branches of ν_4, ν_5, and ν_6 by fitting the frequencies with Eq. (3.3a). By refitting their data, the standard error of the resultant A_0 has been calculated by SYMFIT to be approximately 0.001 cm^{-1}, which is an order of magnitude larger than the standard error resulting from a simultaneous fit of ν_4 and $2\nu_4$. This is the standard error of the constant due to random errors in observed frequencies and is theoretically quite independent of various approximations made in zeta-sum method (see Chapter III). The standard error of the zeta-sum A_0 could be considerably lowered in the case of a fairly complete set of ν_4, ν_5, and ν_6 bands. In practice, for CD_3X molecules it is found that the strongly absorbing ν_2 parallel band overlaps the low-frequency Q branches of ν_5 (20).

In summary, the determination of A_0 for CD_3I by a simultaneous fit has proven to be precise and direct. The advantages of this method over either determination by single-band fits or by the method of zeta-sums have been illustrated.

CHAPTER VII

ANALYSIS OF ν_4 AND $2\nu_4$ OF CD_3Cl

Survey spectra of the ν_4 and $2\nu_4$ bands of CD_3Cl are shown in Figure 7.1. Except for the ${}^RQ_{14}$ and ${}^RQ_{15}$ lines of ν_4, which seem rather perturbed, the general appearance of both bands is quite normal. The CO_2 lines which appeared strongly in CD_3I are much weaker in this case and do not show on the survey spectra of ν_4. The calibration fits of the averaged frequencies result in standard deviations of 0.002 cm^{-1} for ν_4 and 0.003 cm^{-1} for $2\nu_4$.

The analysis procedure started with the $2\nu_4$ band and proceeded in a manner similar to that used in the case of CD_3I. The first new problems which arose involved the $2\nu_4$ parallel component which could not be predicted with the constants obtained by fitting the ${}^RR_K(J)$ and ${}^PP_K(J)$ lines of the perpendicular component. The effect of a perturbation in the parallel component is very obvious in the ${}^QQ_K$ lines at its center. Identifications for $K \leq 6$ are uncertain for both the ${}^QQ_K$ lines and for the ${}^RQ_K$ and ${}^PQ_K$ lines, even though the ${}^QQ_K$ line positions are quite normal for $K > 6$. It is possible that a further study could result in a better understanding of this perturbation; however, since the perpendicular component did fit well, no more time was spent on the parallel component in this study. The results from the final single-band fit (201 lines) are given in Table 7.1. As in the case of CD_3I, only second-order terms were found to have statistically significant values.

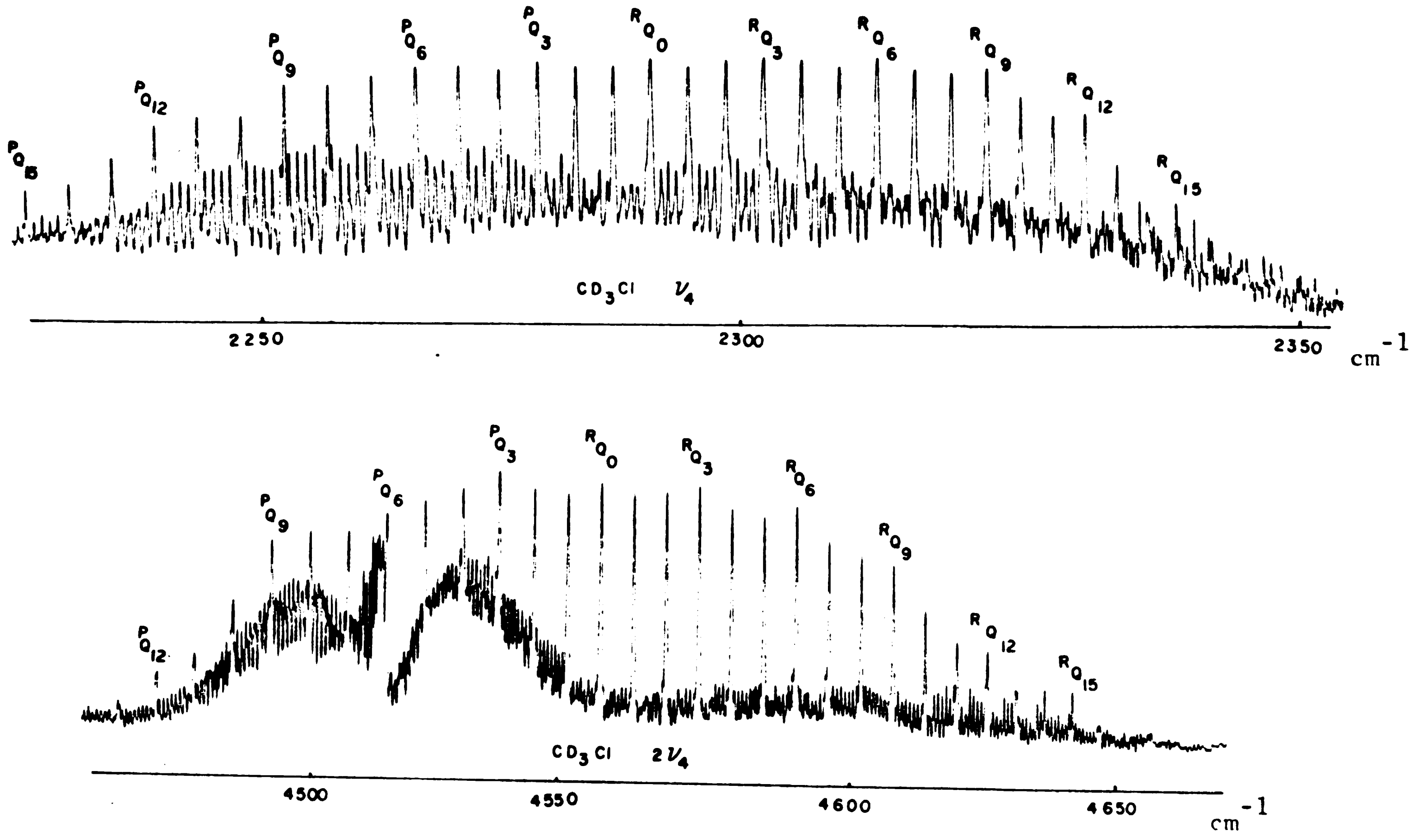


Figure 7.1 Survey Spectra of ν_4 and $2\nu_4$ of CD_3Cl

Table 7.1

Second Order Molecular Constants of CD_3Cl from Single Band Fits (in cm^{-1})

Constant	$\nu_4(k = 1)$	$2\nu_4(k = -2)$
$\nu_0 - k(\Delta K)^2(A_e\zeta_4^z)$	2283.001 ± 0.009	4552.175 ± 0.006
$A_0 - kA_e\zeta_4^z$	2.138 ± 0.002	3.5001 ± 0.0006
D_0^K	(from $2\nu_4$)	$(28 \pm 4) \times 10^{-6}$
α_4^A	$(12.1 \pm 0.2) \times 10^{-3}$	$(12.47 \pm 0.06) \times 10^{-3}$
α_4^B	$(101 \pm 17) \times 10^{-6}$	$(117 \pm 4) \times 10^{-6}$

Standard Deviations of Fits: $\nu_4 \sim 0.010\ cm^{-1}$
$2\nu_4 \sim 0.008\ cm^{-1}$

Average Microwave Values of Ground State Constants (37)

Constant	Value (cm^{-1})
B_0	0.360127
D_0^J	0.000000359
D_0^{JK}	0.00000339

In the ν_4 and $2\nu_4$ bands of CD_3Cl there is little evidence of the two naturally occurring chlorine isotopes (Cl^{35} and Cl^{37}). Because of this, the values of B_0, D_0^J, and D_0^{JK} which are available for both isotopes from microwave work (37) were averaged with weights given according to the natural abundance of Cl^{35} and Cl^{37} (approximately 3 to 1).

The ${}^PP_K(J)$ and ${}^RR_K(J)$ assignments were easily made in the ν_4 band. However, when these 250 lines were put into a single-band fit, the disappointing result was a standard deviation of over 0.02 cm^{-1}, even though no lines seemed to be obviously perturbed. In an effort to determine the cause of the problem, the ${}^RR_K(J)$ and ${}^PP_K(J)$ lines were separated. It was found that the two halves of the band fit well separately (to about 0.008 cm^{-1}) in each case. The major difference in the sets of constants determined by the two fits was in α_4^B, which was much larger in the case of the ${}^PP_K(J)$ lines. The α_4^B as determined by the ${}^RR_K(J)$ lines was approximately equal to that found in the case of $2\nu_4$, whereas that from the ${}^PP_K(J)$ lines was about twice as large. At this point one might guess that the ${}^PP_K(J)$ lines of ν_4 are subject to a J-dependent perturbation which shifts the upper states in such a way as to produce a new "effective α_4^B".

To further study this effect, the subbands of ν_4 and $2\nu_4$ were analyzed individually. In such fits, the single-band frequency expression (with K and ΔK constant) takes the form,

$$\begin{aligned} \nu = \nu_0 &\text{ (subband origin)} \\ &+ \text{(microwave determined terms)} \\ &- \alpha_4^B(\Delta v_4)(J + 1 + \Delta J)(J + \Delta J) \end{aligned}$$

when third and fourth-order terms are ignored. To determine a statistically significant α_4^B from a subband, approximately 10 to 20 lines of differing J values are required. All the subbands of ν_4 and $2\nu_4$ having a sufficient number of lines to individually determine α_4^B were fit with the above expression, and the results of these fits are shown on the graph of Figure 7.2. It will be noticed that α_4^B values determined by the ${}^{R}R_K(J)$ lines of ν_4 and those from $2\nu_4$ are compatible; however, the effective α_4^B values from the $K\Delta K \leq 0$ subbands of ν_4 are clearly quite different. The error bars given on the graph are ± (standard errors of α_4^B) and are therefore somewhat optimistic.

Another effective and perhaps more direct way to determine exactly which subbands are perturbed is to perform a simultaneous fit of all the identified lines of ν_4 and $2\nu_4$. When the perturbed lines of ν_4 are fit with the many unperturbed lines of both bands, they no longer have such a large effect on the constants from the fit. Therefore the perturbed lines no longer fit well, and the OBS-CALC values from the fit clearly indicate which subbands are perturbed. These lines are then given zero weights in the simultaneous fit, and their OBS-CALC values from the fit indicate the magnitude and direction of the shifts in the upper levels.

Figure 7.3 indicates the OBS-CALC values in the case of the four subbands on the far left of Figure 7.2. These deviations are seen to have a consistent J dependence, and also gradually become larger for higher K values. The ν_4 section of Appendix D includes the smaller deviations of the other perturbed subbands. In the case of the ${}^{P}P_3$ $(J \leq 12)$ and ${}^{P}P_1$ $(J \leq 12)$ subbands, the

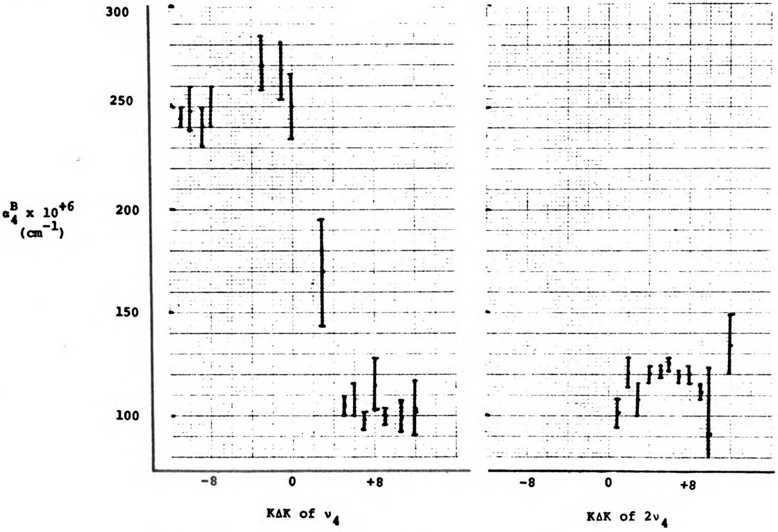


Figure 7.2 Effective α_4^B from Subbands of ν_4 and $2\nu_4$ of CD_3Cl

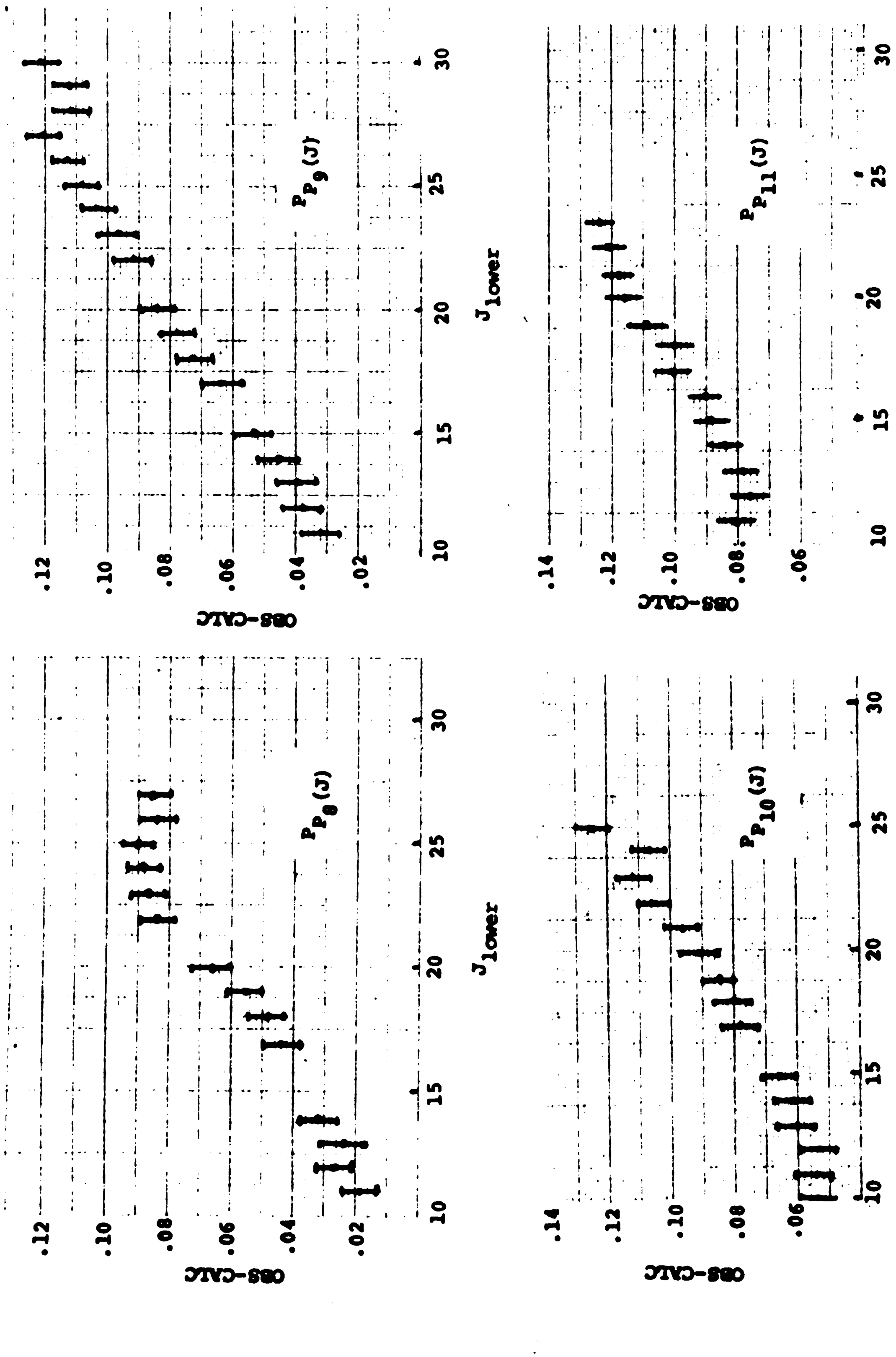


Figure 7.3 Deviations of Perturbed Subbands of ν_4 of CD_3Cl

deviations were sufficiently small so that these lines could be given some weight in the fit. This was advantageous since both ν_4 and $2\nu_4$ had very few usable negative ΔK lines, and thus these lines were very valuable in determining better values of α_4^A and D_0^K in the simultaneous fit.

The results of a single-band fit of the 130 largely unperturbed lines of ν_4 are given in Table 7.1. A fit of these lines was not able to determine a statistically significant D_0^K (i.e. the 95% s.c.i. was larger than the determined D_0^K), and thus this constant was taken from the fit of the $2\nu_4$ band and was held constant in the ν_4 fit.

The constants resulting from the simultaneous fit of ν_4 and $2\nu_4$ are given in Table 7.2. The resultant A_0 is seen to be less precise than that obtained for CD_3I, but still appears to be an order of magnitude more precise than the A_0 value from zeta-sums. The zeta-sum A_0 of CD_3Cl as determined by Morino and Nakamura is quite uncertain because the ν_2 band overlaps ν_5 to a larger extent in this case than for the other CD_3X molecules (20). This overlapping affects the A_0 determination in two ways:

(1) It limits the precision of A_0 by reducing the number of data points in ν_5; therefore $C_1(5)$, $C_2(5)$ and $C_3(5)$ are the major contributors to the variance of A_0. By use of SYMFIT, the resultant standard error in A_0 was determined to be 0.002 cm^{-1}.

(2) The large number of ${}^RQ_K$ lines compared to the small number of ${}^PQ_K$ lines lowers the accuracy of A_0 by increasing the effect of the systematic error resulting

Table 7.2

Molecular Constants Resulting from a Simultaneous Fit of ν_4 and $2\nu_4$ of CD_3Cl (in cm^{-1})

Constant	Value	95% s.c.i.
$\nu_0(\nu_4)$	2283.455	0.008
$\nu_0(2\nu_4)$	4551.273	0.006
A_0	2.5930	0.0006
$A_e\zeta_4^z$	0.4532	0.0002
D_0^K	23×10^{-6}	2×10^{-6}
α_4^A	12.53×10^{-3}	0.06×10^{-3}
α_4^B	114×10^{-6}	5×10^{-6}

Standard Deviation of Fit = 0.009 cm^{-1}

A_0 from ζ-Sum Approximation = 2.613 (20) from the assumption that the Q branch peaks all correspond to the same J value.

In summary, a simultaneous analysis of ν_4 and $2\nu_4$ of CD_3Cl has resulted in an accurate value of A_0 which is statistically different from and superior to that obtained by zeta-sum methods. The simultaneous fit was useful in determining the location and magnitude of a systematic perturbation in the low-frequency half of the ν_4 band. The perturbation is seen to increase the magnitude of the effective α_4^B in the perturbed region.

CHAPTER VIII

ANALYSIS OF ν_4 AND $2\nu_4$ OF CD_3Br

Survey spectra of these two bands are shown in Figure 8.1. Several irregular features occur in both ν_4 and $2\nu_4$ of CD_3Br, not all of which can be readily seen in the figure. The more obvious abnormalities in the ν_4 band are the perturbed Q branch on the low-frequency side $({}^PQ_8)$ and the strong fine structure between ${}^RQ_6$ and ${}^RQ_{12}$. In $2\nu_4$, perturbations are obvious in ${}^PQ_{12}$ and ${}^RQ_7$. The Q branches to the right of ${}^RQ_7$ are narrower and closer together (which hints of a shift in the effective values of α_4^B and $A_0 + 2A_e\zeta_4^z$). Another characteristic of $2\nu_4$ under higher resolution is a splitting of almost all lines, with the splittings differing in magnitude from one subband to another.

High resolution spectra were recorded under the experimental conditions given in Table 4.3. The measured spectra were calibrated and averaged with program SHAFT, with calibrations fitting to 0.002 cm^{-1} for ν_4 and to 0.003 cm^{-1} for $2\nu_4$.

Over 240 lines were assigned in ν_4 without undue difficulty. The only problem encountered in the ${}^RR_K$ lines (for $3 < K < 9$) was an overlapping of lines which results in the many strong absorptions which may be seen on the rapid survey of Figure 8.1. The previously mentioned perturbation in the $K\Delta K = -8$ subband made it impossible to assign any ${}^PP_8(J)$ lines. The same perturbation would also seem to be responsible for the smaller shifts (less than 0.05 cm^{-1}) in the line positions of the adjacent

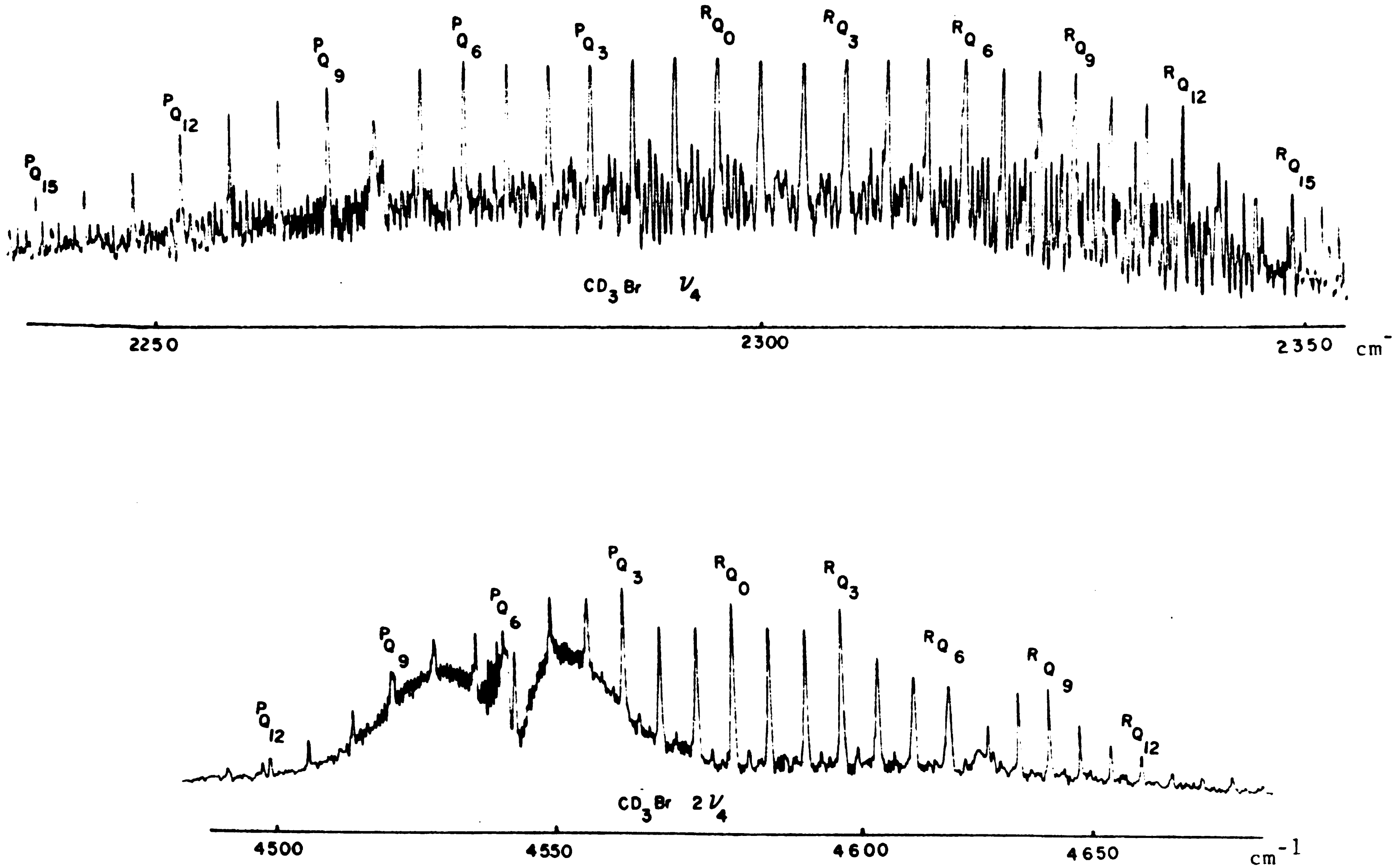


Figure 8.1 Survey Spectra of ν_4 and $2\nu_4$ of CD_3Br

subbands ($K\Delta K$ = -9 and -7).

When the ${}^{P}P_7$ and ${}^{P}P_9$ lines were given zero weights, the constants resulting from a single-band fit of the 209 unperturbed lines are given in Table 8.1. The OBS-CALC values for the perturbed subbands along with those of other lines are given in Appendix E.

Assuming that the splittings of lines due to the isotopes of bromine (Br^{79} and Br^{81}) would not be resolved, the microwave values of B_0, D_0^J, and D_0^{JK} for the two isotopes were averaged according to natural abundance. These average values were used in the ν_4 fit described above and are recorded in Table 8.1. We did, however, notice the effects of B_0^{79} and B_0^{81} for high values of J in series of ${}^{P}P_1$, ${}^{P}P_2$ and ${}^{P}P_3$ subbands. For $J > 20$ the lines are broad and in some cases are split. The calculated line splittings for these cases is approximately 0.04 cm^{-1}, and therefore this effect is barely resolved by the spectrometer. Because of this isotopic broadening, no lines of $J > 28$ were included in the ν_4 fit. The limited number of high J values reduces the precision of the α_4^B value determined by the fit.

Even before attempting to analyze the $2\nu_4$ band, the following characteristics were noted:

(1) Most of the lines of the $2\nu_4$ band are split into two components of nearly equal intensities.

(2) In the perpendicular component, the Q branch separations on the left side of ${}^{R}Q_7$ are different from those on the right.

(3) Because of the overlap of subbands in the parallel component, our resolution is too low to determine if the

Table 8.1

Molecular Constants from a Single Band

Fit of ν_4 CD_3Br

Constant	Value	95% s.c.i.
$\nu_0 - A_e\zeta_4^z$	2295.986	0.005
$A_0 - A_e\zeta_4^z$	2.1289	0.0005
D_0^K	10×10^{-6}	2×10^{-6}
α_4^A	13.19×10^{-3}	0.07×10^{-3}
α_4^B	129×10^{-6}	16×10^{-6}

Standard Deviation of Fit = 0.009 cm^{-1}

Average Microwave Values of Ground State Constants (37)

Constant	Value
B_0	0.256775
D_0^J	0.0000001945
D_0^{JK}	0.000002115

Previous Results (cm^{-1}):

(A) Morino and Nakamura (20)

$A_0 = 2.589$

$\nu_0(\nu_4) = 2296.3$

$\alpha_4^A = 0.013$

(B) Wiggins, Shull, and Rank (38)

$\nu_0(2\nu_4\|) = 4541.05$

$\nu_0(2\nu_4\perp) = 4579.9$

$\alpha_4^B - \alpha_4^A = -0.012$

$^{Q}P_K$ and $^{Q}R_K$ lines are split; consequently line identifications are uncertain. The $^{Q}Q_K$ lines are distinctly split for $K < 6$.

The combination of these unusual features has prevented a satisfactory analysis of $2\nu_4$. A description of the methodology used in trying to analyze the band follows.

The analysis started with an emphasis upon individual subbands of the parallel and perpendicular components. Subband fits were made in the perpendicular component using the lower frequency component of the double lines. α_4^B values resulting from the more completely assigned subbands are shown in Figure 8.2 with the "error bars" indicating standard errors. With the exception of the two subbands close to the $^{R}Q_7$ perturbation ($^{R}Q_5$ and $^{R}Q_6$), the α_4^B values are concentrated in the region between $(200 - 300) \times 10^{-6}$ cm^{-1}. If lines from these supposedly compatible subbands are then put into a single-band fit, the results (in cm^{-1}) are:

$$\nu_0 + 2A_e\zeta_4^z = 4577.8 \pm .4$$

$$A_0 + 2A_e\zeta_4^z = 3.5 \pm .1$$

$$D_0^K = (201 \pm 120) \times 10^{-6}$$

$$\alpha_4^A = (20 \pm 10) \times 10^{-3}$$

$$\alpha_4^B = (239 \pm 30) \times 10^{-6}$$

The poorly determined constants from this fit are the result of a shift in Q branch separations on different sides of the $^{R}Q_7$ perturbation. There appears to be no way to fit these lines (with our molecular model) without identification and inclusion of the effects of the perturbation. In this case the perturbation seems

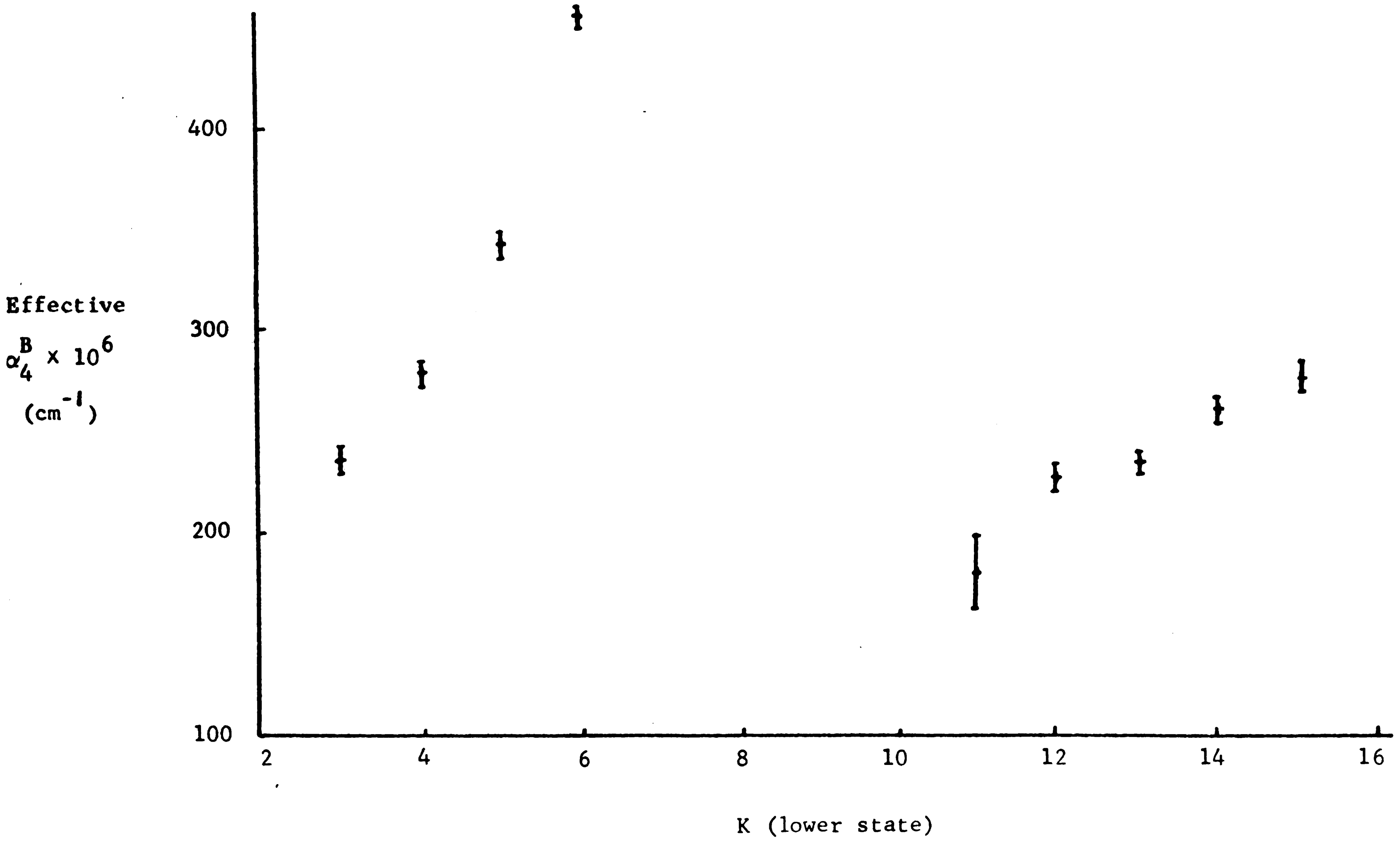


Figure 8.2 Effective α_4^B Values Determined from $2\nu_4(\perp)$ Subbands of CD_3Br

to be general enough to make it difficult to treat.

Analysis of the parallel band has depended on the rather uncertain assignments of ${}^{Q}R_K$ lines. Present assignments result in the following α_4^B determinations from the subbands indicated.

		$\alpha_4^B \times 10^6$ cm^{-1} (95% s.c.i.)
${}^{Q}R_2$	-	203 ± 10
${}^{Q}R_3$	-	235 ± 14
${}^{Q}R_6$	-	181 ± 20

These α_4^B values are not greatly different than those determined from ${}^{R}R_K$ subbands, but a single-band fit of all the parallel-component lines results in a large standard deviation and very poorly determined coefficients of K dependent terms. Similar single-band fits were attempted using various combinations of lines from the parallel and perpendicular components without much success.

The above analyses of the perpendicular and parallel components were repeated with the hypothesis that the lower frequency components of the double lines correspond to Br^{81} (using its associated microwave values). This lowers α_4^B for each subband by approximately 20×10^{-6} cm^{-1}, but does not help the basic fitting problem with K-dependent terms.

The following conclusions can be drawn from the above attempts to analyze $2\nu_4$:

(1) α_4^B values determined for major portions of the band vary smoothly in areas away from centers of perturbations

(see Figure 8.2). Except for subbands very close to strong perturbations, α_4^B values obtained from different parts of the band are not greatly different, but are considerably larger than those from the subbands of ν_4 of CD_3Br or those of any other CD_3X molecule in this study.

(2) Much higher resolution is needed to make assignments in the parallel component more certain.

(3) The perturbation (or perturbations) which affects the band has a strong K dependence which makes a fit of the $2\nu_4$ frequencies impossible with the usual frequency expression.

As a consequence of the perturbed nature of $2\nu_4$, an A_0 value cannot be obtained by a simultaneous fit. The results of the zeta-sum work of Morino and Nakamura on CD_3Br (20), as quoted in Table 8.1, include a value of $A_0 = 2.589$ which is currently the only value available in the literature. The value of α_4^A from our analysis of ν_4 is believed to be an order of magnitude more accurate than the values previously determined at lower resolution (20, 38). Even though the values of α_4^B and D_0^K from our analysis are somehwat lacking in precision, they do have some significance since to our knowledge they have never been previously obtained.

CHAPTER IX

CONCLUSION

Table 9.1 is a comparative summary of the best available values for the molecular constants which may be determined from ν_4 and $2\nu_4$ for the three molecules investigated. Except for the cases indicated by superscripts, they are the results of single or double-band fits with program SYMFIT (see Chapters VI, VII, and VIII). Uncertainties specified in the table correspond to 95% simultaneous confidence intervals.

For CD_3I, all the constants were well determined from a simultaneous fit of ν_4 and $2\nu_4$. In the case of CD_3Cl, the constants are somewhat less precise because of a perturbation affecting the low frequency half of ν_4. A second perturbation in the parallel component of CD_3Cl $2\nu_4$ prevents an accurate measurement of $\nu_0(\|)$. The least well determined parameters are those of CD_3Br. The band origins for both the perpendicular and parallel components of $2\nu_4$ could not be accurately determined because of the large effect of K-dependent perturbations. Because $2\nu_4$ is highly perturbed, A_0 of CD_3Br is limited in accuracy by the nature of the zeta-sum technique (see Chapter III).

A possible method of confirming the accuracy of the A_0 values would be to perform a simultaneous analysis of other ν_t and $2\nu_t$ bands of a symmetric top. Thus A_0 as obtained from ν_4 and $2\nu_4$ could be confirmed or disproved by a simultaneous analysis

Table 9.1

Summary of Constants for CD_3X Molecules (cm^{-1})

	CD_3Cl	CD_3Br	CD_3I
$\nu_0(\nu_4)$	2283.455 ± 0.008	2296.45^b	2298.526 ± 0.003
$\nu_0(2\nu_4 \perp)$	4551.273 ± 0.006	4576.9^d	4580.494 ± 0.005
$\nu_0(2\nu_4 \parallel)$	4516.4^a	4541.05^d	4546.115 ± 0.005
A_0	2.5930 ± 0.0006	2.589^c	2.5788 ± 0.0004
$A_e\zeta_4^z$	0.4532 ± 0.0002	0.46^c	0.4467 ± 0.0002
D_0^K	$(23 \pm 2) \times 10^{-6}$	$(10 \pm 2) \times 10^{-6}$	$(36 \pm 2) \times 10^{-6}$
α_4^A	$(12.53 \pm 0.06) \times 10^{-3}$	$(13.19 \pm 0.07) \times 10^{-3}$	$(12.90 \pm 0.04) \times 10^{-3}$
α_4^B	$(114 \pm 5) \times 10^{-6}$	$(129 \pm 16) \times 10^{-6}$	$(83 \pm 2) \times 10^{-6}$

[a] Approximated from our chart (± 0.2 cm^{-1} due to perturbation in ${}^{Q}Q_K$ lines)

[b] From our single band value of $\nu_0 - A_e\zeta_4^z$

[c] Morino and Nakamura (20)

[d] Wiggins, et al (38)

of high resolution spectra of ν_6 and $2\nu_6$. Such an approach has recently become feasible with the advent of Fourier transform spectrometers which can offer excellent resolution over wide spectral ranges (e.g. 2μ to 20μ).

A considerable amount of theoretical work has recently been done (33, 39, 40, 41) which may be applicable to the perturbations observed and recorded in this work. The perturbations found on the lower frequency sides of the ν_4 bands of each molecule appear to have very systematic deviations. The question as to whether these effects could be caused by the nearby fundamental ν_1 must be thoroughly investigated. Now that shifts in energy levels for all three ν_4 bands have been determined, such an investigation would be feasible.

Finally it should be possible to use the results of this work to determine certain of the anharmonic constants, and to improve the values of the structural parameters of these molecules.

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APPENDICES

APPENDIX A

PROGRAM SYMFIT

```
      PROGRAM SYMFIT (INPUT,OUTPUT)
      COMMON /12/ INFO1,INFO2,INFC3,NUMCON,JUMP,EFIN,EFOUT,T
     1OL,IDENT(2)
C
C     COMMON /123/ IMPLIES USE IN DRIVER, STEPFIT, AND
C     PRINTOUT,
C
      COMMON /123/ NK(30),NDELMAX,XDEVMAX,CCNST(30),ILEVEL
      COMMON /A/ NAME(30),INL(30),IBAND
      COMMON /100/ JJ(850),KK(850),JDEL(850),KDEL(850),NUDEL
     1(850)
      DIMENSION CON(18,850), FOBS(850), FCALC(850), WT(850),
     1 NUSE(850)
      DIMENSION IH(10)
C
C     NAME CORRESPONDES TO NAMES CF VARIARLES IN A SINGLE
C     BAND FIT, INL IS THE SAME FCR A DOURLEBAND FIT
C
      DATA (NAME=2HB0,3HD0J,4HD0JK,5HNUZRO,8HAZRO-AEZ,
     16H-DZROK,6H-ALFAA,6H-ALFAB,4HETAJ,5HBETAJ,6HBETAJK,
     25HBETAK,5HHZROJ,6HHZROJK,6HHZROKJ,5HHZROK,7HNUZROPL)
      DATA (INL=2HB0,3HD0J,4HD0JK,7HNUZONU4,8HNUZ02NU ,
     14HAZRO,7HAEZETA+,
     16H-DZROK,8H-ALPHA4A,8H-ALPHA4B;5HETA4K,6HBETA4K,
     25HHZROK,4HETAJ,5HBETAJ,6HBETAJK,7HNUZROPL)
      NUMCON=17
      NCONP1=NUMCON+1
C
C     OPTION LABEL IBAND IS LABELED COMMON
C
      READ 180, IBAND
      IF(IBAND.NE,8HQ BRANCH,AND.IBAND.NE.8HCORIOLIS)GO TO 5
      NUMCON=5
      NCONP1=18
      INL(1)=4HCON1
      NAME(1)=INL(1)
      INL(2)=4HCON2
      NAME(2)=INL(2)
      INL(3)=4HCON3
      NAME(3)=INL(3)
```

```
      INL(4)=4HCON4
      NAME(4)=INL(4)
      INL(5)=4HCON5
      NAME(5)=INL(5)
C
C     JUMP = 1 ONLY WHEN NEW CONSTANTS (TRIAL) ARE
C     BEING READ IN
C
    5 JUMP=0
      READ 200, IH
C
C     STATEMENTS 10, 15, AND 20 ARE THE MAIN DIVIDING
C     PTS, FOR THE DRIVER
C
   10 IF (IH(10).EQ.8HLAST FIT) GO TO 175
      GO TO 15
   15 IF (IH(10).EQ.8HCONSTANT) GO TO 25
      GO TO 20
   20 IF (IH(10).EQ.8HNEW DATA) GO TO 65
      GO TO 175
   25 JUMP=1
   30 READ 200, IH
      PRINT 200, (IH(I),I=1,9)
      IF (IH(10).EQ.8HEND HEAD) GO TO 35
      GO TO 30
   35 PRINT 205
      DO 60 J1=1,NUMCON
      IF (IH(10).EQ.8HENDCONST) GO TO 45
      GO TO 40
   40 READ 215, CONST(J1),IH(10)
      GO TO 50
   45 CONST(J1)=0.0
   50 IF (IBAND.EQ.8HSINGLEBD) GO TO 55
C
C     PRINTS READ IN CONSTS AND THEIR LABELS FOR SINGLE
C     OR DOUBLE BAND FITS, WILL SET ALL CONSTS,
C     ZERO AFTER AN ENDCONST IS FOUND IN COLS, 73-80
C
      PRINT 220, INL(J1),CONST(J1)
      GO TO 60
   55 PRINT 220, NAME(J1),CONST(J1)
   60 CONTINUE
      READ 200, IH
      GO TO 10
   65 M=1
C
C     HERE WE READ IN CHANGE IN  QUANTUM NUMBERS,
C     GROUND STATE QUANTUM NUMBERS, OBSERVED
C     FREQ, AND RELATIVE WEIGHT FOR EACH SPECTRAL LINE,
C     WILL KEEP READING UNTIL AN F IS FOUND IN COLUMN 10
C
```

```
   70 READ 185, NUDEL(M),KDEL(M),JDEL(M),KK(M),JJ(M),FOBS(M)
     1,WT(M)
      IF (NUDEL(M).EQ.0) NUDEL(M)=1
      IF (KDEL(M).EQ.1RF) GO TO 160
      INDATA=M
      IKDEL=KDEL(M)-1RQ
      IJDEL=JDEL(M)-1RQ
      DELTA1=KK(M)+IKDEL
      DELTA2=KK(M)
      DELTA3=JJ(M)+1+IJDEL
      DELTA4=JJ(M)+IJDEL
      DELTA5=JJ(M)+1
      DELTA6=JJ(M)
      IF(IBAND.NE.8HQ BRANCH.AND.IBAND.NE.8HCORIOLIS)GOTO100
      IF (IBAND.EQ.8HCORIOLIS) GO TO 75
C
C     THIS SECTION PROVIDES THE OPTION OF FITTING
C     Q BRANCHES TO THE THREE VARIABLES CON1, CON2, AND CON3,
C
      CON(1,M)=1.0
      CON(2,M)=KK(M)*IKDEL
      CON(3,M)=KK(M)**2
      GO TO 140
C
C     THIS SECTION PROVIDES A FIT OF THE DEVIATIONS SQUARED
C
   75 IF (KK(M)-8) 80,85,90
   80 CON(1,M)=FOBS(M)
      CON(2,M)=0.0
      CON(3,M)=0.0
      GO TO 95
   85 CON(2,M)=FOBS(M)
      CON(1,M)=0.0
      CON(3,M)=0.0
      GO TO 95
   90 CON(3,M)=FOBS(M)
      CON(1,M)=0.0
      CON(2,M)=0.0
   95 CON(4,M)=JJ(M)*(JJ(M)+1)*FOBS(M)
      CON(5,M)=JJ(M)*(JJ(M)+1)+KK(M)*(KK(M)-1)
      FOBS(M)=FOBS(M)**2
      GO TO 140
  100 IF (NUDEL(M)-1) 105,105,110
  105 LDEL=IKDEL
      GO TO 115
  110 LDEL=-2*IKDEL
  115 CON(1,M)=DELTA4*DELTA3-DELTA6*DELTA5-DELTA1**2+DELTA2*
     1*2
      CON(2,M)=-DELTA4**2*DELTA3**2+DELTA6**2*DELTA5**2
      CON(3,M)=-DELTA1**2*DELTA4*DELTA3+DELTA2**2*DELTA5*DEL
     1TA6
```

```
      IF (IBAND.EQ,8HDOUBLEBD) GO TC 120
      CON(4,M)=1,0
      CON(5,M)=DELTA1**2-DELTA2**2
      CON(6,M)=DELTA1**4-DELTA2**4
      CON(7,M)=NUDEL(M)*DELTA1**2
      CON(8,M)=NUDEL(M)*(DELTA4*DELTA3-DELTA1**2)
      CON(9,M)=LDEL*DELTA1*DELTA4*DELTA3
      CON(10,M)=NUDEL(M)*DELTA4**2*DELTA3**2
      CON(11,M)=NUDEL(M)*DELTA1**2*DELTA4*DELTA3
      CON(12,M)=NUDEL(M)*DELTA1**4
      CON(13,M)=DFLTA4**3*DELTA3**3-DELTA6**3*DELTA5**3
      CON(14,M)=DELTA1**2*DELTA4**2*DELTA3**2-DELTA2**2*DELT
     1A6*DELTA5
      CON(15,M)=DELTA1**4*DELTA4*DELTA3-DELTA2**4*DELTA6*DEL
     1TA5
      CON(16,M)=DELTA1**6-DELTA2**6
      GO TO 135
C
C     THE SECOND CON MATRIX IS FOR DOUBLE BAND FITS,
C
  120 IF (NUDEL(M),NE,1) GO TC 125
      CON(4,M)=1,0
C
C     PROVIDES FOR TWO PERPENDICULAR BAND CENTERS
C
      CON(5,M)=0,0
      GO TO 130
  125 CON(5,M)=1,0
      CON(4,M)=0,0
  130 CON(6,M)=DELTA1**2-DELTA2**2
      CON(7,M)=LDFL*DELTA1*(-2)
      CON(8,M)=DELTA1**4-DELTA2**4
      CON(9,M)=NUDEL(M)*DELTA1**2
      CON(10,M)=NUDEL(M)*(DELTA4*DELTA3-DFLTA1**2)
      CON(11,M)=LDEL*DELTA1**3
      CON(12,M)=NUDEL(M)*DELTA1**4
      CON(13,M)=DELTA1**6-DELTA2**6
      CON(14,M)=LDEL*DELTA1*DELTA4*DELTA3
      CON(15,M)=NUDEL(M)*DELTA4**2*DELTA3**2
      CON(16,M)=NUDEL(M)*DELTA1**2*DELTA4*DELTA3
C
C     PROVIDES FOR  PARALLEL BAND CENTER IF KDEL = 0
C     LINES ARE READ IN
C
      CON(17,M)=1,0
      IF (IKDEL.NE,0) CON(17,M)=0,0
      IF (IKDEL.EQ,0) CON(5,M)=0,0
      GO TO 140
  135 CON(17,M)=1,0
      IF (IKDEL.EQ,0) CON(4,M)=0,0
      IF (IKDEL.NE,0) CON(17,M)=0,0
```

```
  140 FCALC(M)=0.0
      IF (JUMP) 145,155,145
C
      HERE WE CALCULATE FREQS, FROM THE TRIAL CONSTS,
C     WHICH HAVE BEEN READ IN
C
  145 DO 150 N=1,NUMCON
  150 FCALC(M)=FCALC(M)+CONST(N)*CON(N,M)
  155 CONTINUE
      M=M+1
      GO TO 70
C
C     HERE WE READ IN INSTRUCTIONS FOR THE FORTHCOMING
C     FIT.  INFO1 INDICATES DESIRE RAW SUMS AND CROSS PRODUCTS,
C     INFO2-CORRELATION COEFFIENTS, INFO3 THE DIAGONAL
C     ELEMENTS,  SEE STEPFIT WRITEUP FOR REST
C     ILEVEL = 1 IMPLIES UPPER STATE ENERGY LEVELS ARE
C     DESIRED
  160 READ 190, INFO1,INFO2,INFO3,NDELMAX,XDEVMAX,TOL,EFIN,E
     1FOUT,ILEVEL
C
C     TELLS WHICH VARIABLES ARE TO BE USED,  USUALLY
C     5 VARIABLES FOR SINGLE BAND SECOND ORDER FIT,
C     7 FOR DOUBLE BAND FIT,  FIRST THREE ARE
C     MICROWAVE, THEREFORE ARE NOT VARIED,
C
  165 READ 195, (NK(I),I=1,17),IH(10)
C
C     WILL TAKE NEW SET OF FREQS IF A (NEW DATA) CARD IS
C     SEEN,  THEREFORE USABLE FOR SUBBAND FITTING
C
      IF (IH(10).NE.8H        ) GO TO 10
  170 READ 200, IH
      PRINT 200, (IH(M),M=1,9)
      IF (IH(10).NE.8HEND HEAD) GO TO 170
      CALL STEPFIT (CON,FOBS,FCALC,NUSE,WT,NCONP1,INDATA)
      GO TO 165
  175 CONTINUE
      PRINT 210
C
  180 FORMAT (72X,A8)
  185 FORMAT (4X,I1,4X,R1,R1,I2,1X,I2,3X,F13.4,7X,F4.2)
  190 FORMAT (4I5,4F10,10X,I3)
  195 FORMAT (17I1,55X,A8)
  200 FORMAT (10A8)
  205 FORMAT (///)
  210 FORMAT (  1H5)
  215 FORMAT (F20,52X,A8)
  220 FORMAT (A20,F30.10)
      END
```

SUBROUTINE STEPFIT

```
      SUBROUTINE STEPFIT (DATA,FOBS,FCALC,NUSE,WT,NCONP1,IND
     1ATA)
      COMMON /12/ INFO1,INFO2,INFO3,NUMCON,JUMP,EFIN,EFOUT,T
     1OL,IDENT(2)
      COMMON /23/ NODATA,NOVMI,AVEWHT,STDY,NOSTEP,N,WTN,FREQ
     1PRD,YPRED,DEV,XAZRO,XDZRO
      COMMON /A/ NAME(30),INL(30),IBAND
      COMMON /123/ NK(30),NDELMAX,XDEVMAX,CONST(30),ILEVEL
      DIMENSION N1(30), VECTOR(31,31), INDEX(30), IDEX(30),
     1SIGMA(30),C
     1OEN(30), SIGMCO(30), NOTIN(30); XCONST(30)
      DIMENSION DATA(NCONP1,INDATA), FOBS(INDATA), FCALC(IND
     1ATA),WT(IND
     1ATA), NUSE(INDATA) ,SVECTOR(31,31),SSIGMCO(30),SCOEN(3
     20)
      DIMENSION XNEWCON(30)
      TYPE DOUBLE     VECTOR,SIGMA,COEN,SIGMCO,SIGY,DEFR,VAR
      IF (IDENT(1)) 5,10,5
    5 IDENT(1)=8HINPUT DA
      IDENT(2)=2HTA
   10 CONTINUE
      IF(EFOUT.EQ.0.0)EFOUT=1.0E-8
      IF (EFIN.EQ.0.0) EFIN=EFOUT=1.0E-8
      IF (TOL.EQ.0.0) TOL=0.001
      NOVAR=1
      DO 30 I=1,NUMCON
C
C     REDEFINES NAME AND INI
C
      IF (NK(I)) 15,30,15
   15 N1(NOVAR)=NAME(I)
      IF (IBAND.EQ.8HDOUBLEBD) N1(NOVAR)=INL(I)
      IF (JUMP) 20,25,20
   20 XCONST(NOVAR)=CONST(I)
   25 NOVAR=NOVAR+1
   30 CONTINUE
      NODATA=0
      DO 45 N=1,INDATA
      IF (WT(N)) 40,35,40
C
C     NUSE (N) IS AN INDEX OF ALL  NON-ZERO WT, LINES
C     NODATA = TOTAL NUMBER OF NON-ZERO LINES
C
   35 NUSE(N)=0
      GO TO 45
   40 NUSE(N)=1
```

```
      NODATA=NODATA+1
   45 CONTINUE
      NDEL=0
   50 FLEVEL=0.0
      VAR=FLEVEL
      NOMAX=VAR
      NOMIN=NOMAX
      NOENT=NOMIN
      K=NOENT
      NOIN=K
      LOOP=0
      NOVMI=NOVAR-1
      NOVPL=NOVAR+1
      DO 55 I=1,NOVPL
      DO 55 J=1,NOVPL
   55 VECTOR(I,J)=0.0
      IF (NDEL) 80,60,80
   60 SUMWHT=0.0
      IDEX(NOVAR)=NCONP1
      DO 75 N=1,INDATA
      NUM=0
      DO 70 I=1,NUMCON
      IF (NK(I)) 65,70,65
   65 NUM=NUM+1
      IDEX(NUM)=I
   70 CONTINUE
      DATA (NCONP1,N)= FOBS(N)- FCALC(N)
   75 SUMWHT=SUMWHT+WT(N)
   80 AVEWHT=SUMWHT/NODATA
      DO 95 N=1,INDATA
      IF (NUSE(N)) 85,95,85
   85 WHT=WT(N)/AVEWHT
      DO 90 I=1,NOVAR
      VECTOR(I,NOVPL)=VECTOR(I,NOVPL)+DATA(IDEX(I),N)*WHT
      DO 90 J=I,NOVAR
C
C     AT THIS POINT, VECTOR (I,J) IS  A
C     GENERAL VARIABLE ( INDEPENDENT OR DEPENDENT)
C
   90 VECTOR(I,J)=VECTOR(I,J)+DATA(IDEX(I),N)*DATA(IDEX(J),N
     1)*WHT
      VECTOR(NOVPL,NOVPL)=VECTOR(NOVPL,NOVPL)+WHT
   95 CONTINUE
      IF (INFO1) 100,130,100
  100 PRINT 490
      NOMAX=NOVMI
      IF (NOVMI.GT,7) NOMAX=7
      PRINT 500, (I,I=1,NOMAX)
      SVECTOR(NOVAR,NOVPL)=VECTOR(NOVAR,NOVPL)
      DO 104 I=1,NOMAX
 104  SVECTOR(I,NOVPL)=VECTOR(I,NOVPL)
```

```
      PRINT 505,SVECTOR(NOVAR,NOVPL);(SVECTOR(I,NOVPL),I=1,N
     1OMAX)
  105 IF (NOVMI.EQ,NOMAX) GO TO 110
      MOMAX=NOMAX+1
      NOMAX=MOMAX+7
      IF (NOMAX.GT,NOVMI) NOMAX=NOVMI
      PRINT 510, (I,I=MOMAX,NOMAX)
      DO 109 I=MOMAX,NOMAX
109   SVECTOR(I,NOVPL)=VECTOR(I,NOVPL)
      PRINT 505, (SVECTOR(I,NOVPL),I=MOMAX,NOMAX)
      GO TO 105
  110 CONTINUE
      NOMIN=1
      NOMAX=NOVMI
      NGO=5
  115 IF (NOVMI.GT,NGO) NOMAX=NGO
      PRINT 520, (I,I=NOMIN,NOMAX)
      DO 120 J=NOMIN,NOVMI
      JJJ=J
      IF (JJJ,GT.NOMAX) JJJ=NOMAX
      DO 118 I=NOMIN,JJJ
118   SVECTOR(I,J)=VECTOR(I,J)
      DO 119 I=NOMIN,NOMAX
119   SVECTOR(I,NOVAR)=VECTOR(I,NOVAR)
  120 PRINT 525, J,(SVECTOR(I,J),I=NOMIN,JJJ)
      PRINT 530, (SVECTOR(I,NOVAR),I=NOMIN,NOMAX)
      IF (NOMAX.EQ,NOVMI) GO TO 125
      NOMIN=NOMAX+1
      NGO=NGO+5
      NOMAX=NOVMI
      GO TO 115
  125 CONTINUE
      SVECTOR(NOVAR,NOVAR)=VECTOR(NOVAR,NOVAR)
      PRINT 535,SVECTOR(NOVAR,NOVAR)
  130 NOSTEP=-1
      ASSIGN 310 TO NUMBER
      DEFR=VECTOR(NOVPL,NOVPL)-1.0
      DO 150 I=1,NOVAR
      IF (VECTOR(I,I)) 135,140,145
  135 PRINT 580, I
      GO TO 485
  140 PRINT 585, I
      SIGMA(I)=1.0
      GO TO 150
  145 SIGMA(I)=DSQRT(VECTOR(I,I))
  150 VECTOR(I,I)=1.0
      DO 155 I=1,NOVMI
      IP1=I+1
      DO 155 J=IP1,NOVAR
      VECTOR(I,J)=VECTOR(I,J)/(SIGMA(I)*SIGMA(J))
  155 VECTOR(J,I)=VECTOR(I,J)
```

```
      IF (INFO2) 160,175,160
  160 NOMIN=1
      NOMAX=NOVMI
      NGO=15
      NOMINP=2
  165 IF (NOVMI.GT,NGO) NOMAX=NGO
      PRINT 540, (I,I=NOMIN,NOMAX)
      DO 170 I=NOMINP,NOVMI
      III=I-1
      IF (III,GT.NOMAX) III=NOMAX
      DO 168 J=1,III
 168  SVECTOR(I,J)=VECTOR(I,J)
  170 PRINT 545, I,(SVECTOR(I,J),J=1,III)
      DO 169 I=NOMIN,NOMAX
 169  SVECTOR(I,NOVAR)=VECTOR(I,NOVAR)
      PRINT 550, (SVECTOR(I,NOVAR),I=NOMIN,NOMAX)
      IF (NOMAX.EQ,NOVMI) GO TO 175
      NOMIN=NOMAX+1
      NOMINP=NOMIN+1
      NGO=NGO+15
      NOMAX=NOVMI
      GO TO 165
  175 NOSTEP=NOSTEP+1
      IF (VECTOR(NOVAR,NOVAR)) 180,180,185
  180 NSTPM1=NOSTEP-1
      PRINT 600, NSTPM1
      GO TO 395
  185 SIGY=SIGMA(NOVAR)*DSQRT(VECTOR(NOVAR,NOVAR)/DEFR)
      DEFR=DEFR-1.0
      IF (DEFR) 190,190,195
  190 PRINT 605, NOSTEP
      GO TO 395
  195 NOIN=0
      VMAX=NOIN
      VMIN=VMAX
      DO 245 I=1,NOVMI
      IF (VECTOR(I,I)) 200,245,205
  200 PRINT 610, I,NOSTEP
      GO TO 395
  205 IF (VECTOR(I,I)-TOL) 245,210,210
  210 VAR=VECTOR(I,NOVAR)*VECTOR(NOVAR,I)/VECTOR(I,I)
      IF (VAR) 215,245,235
  215 NOIN=NOIN+1
      INDEX(NOIN)=I
      COEN(NOIN)=VECTOR(I,NOVAR)*SIGMA(NOVAR)/SIGMA(I)
      SIGMCO(NOIN)=(SIGY/SIGMA(I))*DSQRT(VECTOR(I,I))
      IF (VMIN) 230,225,220
  220 PRINT 590
      GO TO 485
  225 VMIN=VAR
      NOMIN=I
```

```
      GO TO 245
  230 IF (VAR-VMIN) 245,245,225
  235 IF (VAR-VMAX) 245,245,240
  240 VMAX=VAR
      NOMAX=I
  245 CONTINUE
      IF (NOIN) 250,255,260
  250 PRINT 595
      GO TO 485
  255 STDY=SIGY
      GO TO 320
  260 IF (INFO3) 265,310,265
  265 IF (NOENT) 270,270,275
  270 PRINT 570, NOSTEP,K
      GO TO 280
  275 PRINT 575, NOSTEP,K
  280 IF (LOOP.NE.0) FLEVEL=FL
      SSIGY=SIGY
      PRINT 555, K,FLEVEL,SSIGY
      DO 285 J=1,NOIN
      N=INDEX(J)
      SCOEN(J)=COEN(J)
      SSIGMCO(J)=SIGMCO(J)
  285 PRINT 560, N,N1(N),SCOEN(J),SSIGMCO(J)
      IF (JUMP) 290,305,290
  290 IF (LOOP) 295,305,295
  295 PRINT 495
      DO 300 J=1,NOIN
      N=INDEX(J)
      XNEWCON(N)=COEN(J)+XCONST(N)
      SSIGMCO(J)=SIGMCO(J)
  300 PRINT 560, N,N1(N),XNEWCON(N),SSIGMCO(J)
  305 GO TO NUMBER, (310,400)
  310 FL=FLEVEL
      FLEVEL=VMIN*DEFR/VECTOR(NOVAR,NOVAR)
      IF (EFOUT+FLEVEL) 320,320,315
  315 K=NOMIN
      NOENT=0
      GO TO 335
  320 FLEVEL=VMAX*DEFR/(VECTOR(NOVAR,NOVAR)-VMAX)
      IF (EFIN-FLEVEL) 330,325,390
  325 IF (EFIN) 390,390,330
  330 K=NOMAX
      NOENT=K
  335 IF (K) 340,340,345
  340 PRINT 615, NOSTEP
      GO TO 485
  345 DO 365 I=1,NOVAR
      IF (I-K) 350,365,350
  350 DO 360 J=1,NOVAR
      IF (J-K) 355,360,355
```

```
 355 VECTOR(I,J)=VECTOR(I,J)-VECTOR(I,K)*VECTOR(K,J)/VECTOR
    1(K,K)
 360 CONTINUE
 365 CONTINUE
     DO 375 I=1,NOVAR
     IF (I-K) 370,375,370
 370 VECTOR(I,K)=-VECTOR(I,K)/VECTOR(K,K)
 375 CONTINUE
     DO 385 J=1,NOVAR
     IF (J-K) 380,385,380
 380 VECTOR(K,J)=VECTOR(K,J)/VECTOR(K,K)
 385 CONTINUE
     VECTOR(K,K)=1.0/VECTOR(K,K)
     GO TO 175
 390 PRINT 565, IDENT(1),IDENT(2),NODATA,NCVMI,NDELMAX,XDEV
    1MAX,AVEWHT,STDY,NOSTEP
 395 CONTINUE
     ASSIGN 400 TO NUMBER
     LOOP=1
     GO TO 265
 400 CONTINUE
     DO 401 L=1,NOVMI
401  SVECTOR(L,L)=VECTOR(L,L)
     IF (INFO3.NE,0) PRINT 620, (L,SVECTOR(L,L),L=1,NOVMI)
     IF (IBAND.EQ,8HCORIOLIS) GO TO 410
     IF (ILEVEL,NE.0) GO TO 405
     CALL PRINT2
     GO TO 415
 405 CALL PRINT4 (DATA,FOBS,FCALC,WT,NUSE,NCONP1,INDATA)
     GO TO 415
 410 CALL PRINT6
 415 XIR=0,0
     SWT=XIR
     DEVMAX=SWT
     VFIT=DEVMAX
     NOLINE=0
     IF (IBAND.EQ,8HDOUBLEBD) GO TO 420
     XAZRO=CONST(5)
     XDZRO=-XNEWCON(3)
     GO TO 425
 420 XAZRO=XNEWCON(3)
     XDZRO=-XNEWCON(5)
 425 DO 470 N=1,INDATA
     WTN=NUSE(N)*WT(N)
     WHT=WTN/AVEWHT
     YPRED=0,0
     DO 430 I=1,NOIN
     LASSIE=IDEX(INDEX(I))
 430 YPRED=YPRED+COEN(I)*DATA(LASSIE,N)
     DEV=FOBS(N)-FCALC(N)-YPRED
     IF (10,-WT(N)) 450,450,435
```

```
435 VFIT=VFIT+WTN*DEV**2
    XIR=XIR+1.0
    SWT=SWT+WT(N)
    NOLINE=NOLINE+1
    IF (NOLINE.LE,50) GO TO 450
    NOLINE=0
    IF (IBAND.EQ,8HCORIOLIS) GO TC 445
    IF (ILEVEL.NE,0) GO TO 440
    CALL PRINT2 (DATA,FOBS,FCALC,WT,NUSF,NCONP1,INDATA)
    GO TO 450
440 CALL PRINT4 (DATA,FOBS,FCALC,WT,NUSE,NCONP1,INDATA)
    GO TO 450
445 CALL PRINT6
450 FREQPRD=FCALC(N)+YPRED
    WHT=WHT*AVEWHT
    IF (ILEVEL,NE,0) GO TO 455
    CALL PRINT3 (DATA,FOBS,FCALC,WT,NUSF,NCONP1,INDATA)
    GO TO 460
455 CALL PRINT5 (DATA,FOBS,FCALC,WT,NUSF,NCONP1,INDATA)
460 ADEV=ABS(DEV)*SQRT(WHT)*NUSE(N)
    IF (DEVMAX-ADEV) 465,465,470
465 NMAX=N
    DEVMAX=ADEV
470 CONTINUE
    VFIT=VFIT*XIR/((XIR-NOIN)*SWT)
    STDFIT=SQRT(VFIT)
    PRINT 515, VFIT,STDFIT
    IF (NDELMAX-NDEL) 485,485,475
475 IF (DEVMAX-XDEVMAX) 485,485,480
480 NUSE(NMAX)=0
    NDEL=NDEL+1
    NODATA=NODATA-1
    SUMWHT=SUMWHT-WT(NMAX)
    PRINT 625, NMAX
    GO TO 50
485 RETURN
490 FORMAT ( 11H1SUM OF VAR,/)
495 FORMAT ( *2FINAL CONSTANTS AFTER CORRECTIONS WERE *
   1*ADDED*/)
500 FORMAT (  9H        Y,7I17,/)
505 FORMAT (X1P7E17.6,E16,6,//)
510 FORMAT (I10,6I17,/)
515 FORMAT ( 29H0STAT FROM LINES WHTD LT 10,0,/, *0VAR, =*
   1,F10.6, *      STD, DEV =*,F7,4/,  1H7)
520 FORMAT ( 15HRAW SSCP MATRIX,/5I26)
525 FORMAT (XI2,1P5E26,10)
530 FORMAT (  3H  Y,1P5E26,10)
535 FORMAT (  8H  Y VS Y,F15,4)
540 FORMAT ( 21H-PARTIAL CORR, COEFF,,//16I8)
545 FORMAT (I3,16F8,4)
550 FORMAT (  3H  Y,16F8,4)
```

```
555 FORMAT ( 16H   F LEVEL OF X-,I1,E10.2,9X, *STD DEV OF*
   1* (O-P)*,F7.4
   1//10X, 41HVARIABLE     COEFFICIENT         STD ERROR,/)
560 FORMAT(I11,1X,A8,2F17.12)
565 FORMAT ( 22H1LEAST SQUARES FIT OF ,2A8/,  5H FIT ,I4,
   116H DATA POINTS TO ,I2,10H VARIABLES,/, * DELETES UP *
   2*TO *,I2,23H POINTS IF (O-P) IS GT ,F6.3/, * WHT NORM*
   31X,F6.2/,17H STD DEV OF (O-C),F8.4/, 11H COMPLETED ,I2
   4, 6H STEPS)
570 FORMAT (  8H0STEP NO,I3/, 15H   VAR. REMOVED,I3)
575 FORMAT (  8H0STEP NO,I3/, 15H   VAR. ENTERED,I3)
580 FORMAT ( 19H ERROR RESID SQ VAR,I3,  7H IS NEG)
585 FORMAT (  4H0VAR,I5,  9H IS CONST)
590 FORMAT ( 16H0ERROR, VMIN POS)
595 FORMAT ( 15H0ERROR NOIN NEG)
600 FORMAT ( 18H0Y SQUARE NEG STEP,I5)
605 FORMAT ( 22H0ZERO DEG FREEDOM STEP,I3)
610 FORMAT (  9HSQUARE X-,I2, 14H NEGATIVE STEP,I3)
615 FORMAT (  8HK=0 STEP,I3)
620 FORMAT ( 16H0  DIAG ELEMENTS,/, 16H VAR NO    VALUE,//
   1(I4,E14.4))
625 FORMAT(  8H1LINE NO,I4,23H BEING DELETED FROM FIT )
    END
```

SUBROUTINE PRINTOU

```
      SUBROUTINE PRINTOU (DATA,FOBS,FCALC,WT,NUSE,NCONP1,IND
     1ATA)
      COMMON /123/ NK(30),NDELMAX,XDEVMAX,CONST(30),ILEVEL
      COMMON /23/ NODATA,NOVMI,AVEWHT,STDY,NOSTEP,N,WTN,FREQ
     1PRD,YPRED,DEV,XAZRO,XDZRO
      COMMON /100/ JJ(850),KK(850),JDEL(850),KDEL(850),NUDEL
     1(850)
      DIMENSION DATA(NCONP1,INDATA), FOBS(INDATA), FCALC(IND
     1ATA), WT(INDATA), NUSE(INDATA)
      ENTRY PRINT2
      PRINT 20
      RETURN
      ENTRY PRINT3
      PRINT 25, N,KDEL(N),JDEL(N),KK(N),JJ(N),WTN,FOBS(N),FC
     1ALC(N),FREQPRD,DATA(NCONP1,N),YPRED,DEV
      RETURN
      ENTRY PRINT4
      PRINT 5
      RETURN
      ENTRY PRINT5
      XGRD=XAZRO*KK(N)**2+CONST(1)*(JJ(N)*(JJ(N)+1)-KK(N)**2
     1)-CONST(2)*J
     2J(N)**2*(JJ(N)+1)**2-CONST(3)*KK(N)**2*JJ(N)*(JJ(N)+1)
     3-XDZRO*KK(N)**4
      XUPPER=XGRD+FREQPRD
      PRINT 10, N,KDEL(N),JDEL(N),KK(N),JJ(N),WTN,FOBS(N),FC
     1ALC(N),FREQP
     1RD,DATA(NCONP1,N),YPRED,DEV,XGRD,XUPPER
      RETURN
      ENTRY PRINT6
      PRINT 15
      RETURN
    5 FORMAT (*1  NO,              WT     OBS FREQ   CALC FREQ*
     1*  PRED FREQ   OBS-CALC  PRED-CALC   OBS-PRED  GRD EN*
     2*ERGY UP ENERGY*)
   10 FORMAT (I5,X,2R1,I2,1H,,I2,3X,F6,2,8F11,4)
   15 FORMAT ( 33H1  NO,    K J UP   WT          (O-C),5H**2  ,
     1*     ZEROS  PRE*
     2*D(O-C)*,5H**2  ,*    IGNORE      IGNORE    FIT DEV*)
   20 FORMAT (*1  NO,              WT   OBS FREQ  CALC FREQ  *
     1*PRED FREQ     OBS-CALC  PRED-CALC   OBS-PRED*)
   25 FORMAT (I5,X,2R1,I2,1H,,I2,3X,F6,2,6F11,4)
      END
```

TYPICAL DATA SET

```
      SINGLEBD - IN COLUMNS 73-80
      CONSTANT - IN COLUMNS 73-80
THIS IS THE INITIAL FIT FOR NANCYS CD3CL
       1   35 TO 37
      END HEAD - IN COLUMNS 73-80
0,360127
0,000000359
0,000003599
4000.00
2,594
      ENDCONST - IN COLUMNS 73-80
      NEW DATA - IN COLUMNS 73-80
CD3C2NU4 PQ 8, 8          4503,8080         0,02
CD3C2NU4 PQ 7, 7          4510,4474         0.02
CD3C2NU4 PQ 6, 6          4516,9891         0,02
CD3C2NU4 PQ 3, 3          4536,3361         0,02
CD3C2NU4 RR 5,10          4593,6840         0,06
CD3C2NU4 RR 5,11          4594,3735         0,02
CD3C2NU4 RR 5,12          4595,1176         0,02
CD3C2NU4 RR 5,13          4595,8257         0,02
CD3C2NU4 RR 5,14          4596,5446         0,02
CD3C2NU4 RR 5,16          4597,9716         0,02
CD3C2NU4 RR 5,17          4598,6701         0,02
CD3C2NU4 RR 5,18          4599,3722         0,06
CD3C2NU4 RR 5,19          4600,0848         0,02
CD3C2NU4 RR 5,20          4600,7945         0,02
CD3C2NU4 RR 5,21          4601,4998         0,02
CD3C2NU4 RR 5,22          4602,1981         0,02
CD3C2NU4 RR 5,23          4602,9030         0,02
CD3C2NU4 RR 5,24          4603,5916         0,02
CD3C2NU4 RR 5,25          4604,2975         0,02
CD3C2NU4 RR 5,26          4605,0018         0,02
CD3C2NU4 RR 6, 6          4596,7789         0,25
CD3C2NU4 RR 6, 8          4598,2018         0,06
CD3C2NU4 RR 6, 9          4598,9217         0,06
CD3C2NU4 RR 6,10          4599,6380         0,06
CD3C2NU4 RR 6,11          4600,3502         0,06
CD3C2NU4 RR 6,12          4601,0661         0,02
CD3C2NU4 RR 6,13          4601,7755         0,06
CD3C2NU4 RR 6,14          4602,4878         0,06
CD3C2NU4 RR 6,16          4603,8980         0,06
CD3C2NU4 RR 6,17          4604,6061         0,06
CD3C2NU4 RR 6,18          4605,3074         0.06
CD3C2NU4 RR 6,19          4606,0332         0,02
CD3C2NU4 RR 6,20          4606,7386         0,02
CD3C2NU4 RR 6,21          4607,4502         0,06
```

```
CD3C2NU4 RR 6,22          4608,1430          0,02
CD3C2NU4 RR 6,24          4609,5419          0,06
CD3C2NU4 RR 6,25          4610,2426          0,02
CD3C2NU4 RR 6,26          4610,9551          0,02
CD3C2NU4 RR 6,27          4611,6539          0,02
CD3C2NU4 RR 6,28          4612,3554          0,02
CD3C2NU4 RR 6,29          4613,0409          0,02
CD3C2NU4 RR 6,30          4613,7456          0,02
CD3C2NU4 RR 6,32          4615,1388          0,02
CD3C2NU4 RR 6,33          4615,8386          0,02
CD3C2NU4 RR 6,34          4616,5065          0,02
CD3C2NU4 RR 7, 8          4604,1030          0,06
CD3C2NU4 RR 7, 9          4604,8143          0,06
CD3C2NU4 RR 7,10          4605,5258          0,06
CD3C2NU4 RR 7,11          4606,2395          0,06
CD3C2NU4 RR 7,12          4606,9482          0,02
CD3C2NU4 RR 7,13          4607,6561          0,02
CD3C2NU4 RR 7,14          4608,3772          0,02
CD3C2NU4 RR 7,16          4609,7893          0,02
CD3C2NU4 RR 7,17          4610,4974          0,02
CD3C2NU4 RR 7,18          4611,2196          0,02
CD3C2NU4 RR 7,19          4611,9236          0,02
CD3C2NU4 RR 7,20          4612,6311          0,02
CD3C2NU4 RR 7,21          4613,3320          0,02
CD3C2NU4 RR 7,22          4614,0381          0,02
CD3C2NU4 RR 7,24          4615,4505          0,02
CD3C2NU4 RR 7,25          4616,1430          0,06
CD3C2NU4 RR 7,26          4616,8358          0,02
CD3C2NU4 RR 7,27          4617,5633          0,02
CD3C2NU4 RR 7,28          4618,2382          0,02
CD3C2NU4 RR 7,29          4618,9471          0,06
CD3C2NU4 RR 7,30          4619,6269          0,02
CD3C2NU4 RR 7,31          4620,3413          0,02
CD3C2NU4 RR 7,32          4621,0296          0,02
CD3C2NU4 RR 7,33          4621,7314          0,02
CD3C2NU4 RR 7,34          4622,4122          0,02
CD3C2NU4 RR 7,35          4623,1026          0,02
CD3C2NU4 RR 7,36          4623,7890          0,02
CD3C2NU4 RR 7,37          4624,4706          0,02
CD3C2NU4 RR 7,38          4625,1693          0,02
CD3C2NU4 RR 7,39          4625,8468          0,02
CD3C2NU4 RR 8, 8          4609,8933          0,25
CD3C2NU4 RR 8, 9          4610,6864          0,02
CD3C2NU4 RR 8,10          4611,3611          0,06
CD3C2NU4 RR 8,11          4612,0740          0,06
CD3C2NU4 RR 8,12          4612,7757          0,06
CD3C2NU4 RR 8,13          4613,4896          0,06
CD3C2NU4 RR 8,14          4614,1926          0,06
CD3C2NU4 RR 8,16          4615,6419          0,06
CD3C2NU4 RR 8,17          4616,3578          0,02
CD3C2NU4 RR 8,18          4617,0569          0,02
```

CD3C2NU4	RR 8,19	4617,7591	0,02
CD3C2NU4	RR 8,20	4618,4612	0,02
CD3C2NU4	RR 8,21	4619,1712	0,02
CD3C2NU4	RR 8,22	4619,8733	0,02
CD3C2NU4	RR 8,24	4621,2750	0,06
CD3C2NU4	RR 8,25	4621,9649	0,02
CD3C2NU4	RR 8,26	4622,6736	0,02
CD3C2NU4	RR 8,27	4623,3726	0,06
CD3C2NU4	RR 8,28	4624,0716	0,06
CD3C2NU4	RR 8,29	4624,7559	0,02
CD3C2NU4	RR 8,30	4625,4673	0,02
CD3C2NU4	RR 8,32	4626,8525	0,02
CD3C2NU4	RR 8,33	4627,5446	0,02
CD3C2NU4	RR 8,34	4628,2278	0,02
CD3C2NU4	RR 8,35	4628,9217	0,02
CD3C2NU4	RR 8,36	4629,6255	0,02
CD3C2NU4	RR 9, 9	4616,4211	0,06
CD3C2NU4	RR 9,10	4617,1314	0,06
CD3C2NU4	RR 9,11	4617,8425	0,06
CD3C2NU4	RR 9,12	4618,5613	0,06
CD3C2NU4	RR 9,13	4619,2750	0,06
CD3C2NU4	RR 9,14	4619,9827	0,06
CD3C2NU4	RR 9,16	4621,4097	0,06
CD3C2NU4	RR 9,17	4622,1151	0,06
CD3C2NU4	RR 9,21	4624,9363	0,02
CD3C2NU4	RR 9,22	4625,6402	0,02
CD3C2NU4	RR 9,24	4627,0488	0,02
CD3C2NU4	RR 9,25	4627,7620	0,02
CD3C2NU4	RR 9,26	4628,4484	0,02
CD3C2NU4	RR 9,27	4629,1599	0,02
CD3C2NU4	RR 9,28	4629,8485	0,02
CD3C2NU4	RR 9,29	4630,5741	0,02
CD3C2NU4	RR 9,30	4631,2631	0,00
CD3C2NU4	RR 9,31	4631,9642	0,02
CD3C2NU4	RR 9,32	4632,6422	0,02
CD3C2NU4	RR 9,33	4633,3350	0,02
CD3C2NU4	RR10,10	4622,8531	0,02
CD3C2NU4	RR10,11	4623,5619	0,02
CD3C2NU4	RR10,12	4624,2472	0,02
CD3C2NU4	RR10,13	4625,0039	0,02
CD3C2NU4	RR10,14	4625,7264	0,02
CD3C2NU4	RR10,16	4627,1279	0,02
CD3C2NU4	RR10,17	4627,8380	0,02
CD3C2NU4	RR10,18	4628,5651	0,02
CD3C2NU4	RR11,11	4629,2432	0,06
CD3C2NU4	RR11,12	4629,9569	0,06
CD3C2NU4	RR11,13	4630,6602	0,06
CD3C2NU4	RR11,14	4631,3779	0,06
CD3C2NU4	RR11,15	4632,0803	0,06
CD3C2NU4	RR11,16	4632,7822	0,06
CD3C2NU4	RR11,17	4633,4894	0,06

```
CD3C2NU4 RR12,12        4635,5688        0,06
CD3C2NU4 RR12,13        4636,2751        0,06
CD3C2NU4 RR12,15        4637,7007        0,06
CD3C2NU4 RR12.16        4638.4088        0,06
CD3C2NU4 RR12,17        4639,1136        0,06
CD3C2NU4 RR12,18        4639,8145        0,06
CD3C2NU4 RR12,19        4640,5095        0,06
CD3C2NU4 RR12,20        4641,2024        0,06
         F
    1    1    1    4           0.00000001
     11111
THIS IS A FIT OF 2NU4 OF CD3CL       WITHOUT THE PARALLEL
      COMPONENT
      END HEAD - IN COLUMNS 73-80
   111111111
THIS IS A CHECK FOR THE SIGNIFICANCE OF MORE VARIABLES IN
      THE FIT
      END HEAD - IN COLUMNS 73-80
      LAST FIT - IN COLUMNS 73-80
```

APPENDIX B

LEAST SQUARES FITS
AND ASSOCIATED STATISTICS

The frequency expressions which concern us most (e.g. Table 2.5 or Table 3.1) are of the form,

$$y_i = x_{i1}\beta_1 + x_{i2}\beta_2 + \dots x_{ip}\beta_p + e_i$$

where y_i = ith observed frequency

$i = 1, 2, \dots n$

n = number of observations

p = number of parameters to be determined

x_{ij} = value of quantum coefficient of molecular parameter β_j for the ith observation

e_i = the random error associated with the ith measurement.

The resultant set of equations for the n observations can be summarized in the vector-matrix form,

$$\underline{y} = \underline{\underline{X}}\,\underline{\beta} + \underline{e}$$

which is shorthand notation for

$$\begin{bmatrix} y_1 \\ y_2 \\ \vdots \\ y_i \\ \vdots \\ y_n \end{bmatrix} = \begin{bmatrix} x_{11} & x_{12} \cdots x_{1j} \cdots x_{1p} \\ x_{21} & \\ \vdots & \\ & \\ x_{i1} & x_{i2} \cdots x_{ij} \cdots x_{ip} \\ x_{n1} & x_{n2} \cdots x_{nj} \cdots x_{np} \end{bmatrix} \begin{bmatrix} \beta_1 \\ \beta_2 \\ \vdots \\ \beta_j \\ \vdots \\ \beta_p \end{bmatrix} . + \begin{bmatrix} e_1 \\ e_2 \\ \vdots \\ e_i \\ \vdots \\ e_n \end{bmatrix}$$

In the thesis of J. W. Boyd (34), it is shown that the best estimate of the unknown parameter vector $\underline{\beta}$ is given by the least squares estimate $(\underline{b})$

$$\text{where} \quad \underline{b} = \underline{\underline{N}}^{-1}\underline{\underline{X}}^{T}\underline{y}$$

$$\text{with} \quad \underline{\underline{N}} = \underline{\underline{X}}^{T}\underline{\underline{X}}$$

$$\text{and} \quad \underline{\underline{X}}^{T} \equiv \underline{\underline{X}} \text{ transposed}$$

Thus the job of a least squares fitting program is to find a value of $\underline{\underline{N}}^{-1}$. This corresponds to solving the set of normal equations,

$$\underline{\underline{N}}\,\underline{b} = \underline{\underline{X}}^{T}\underline{y}$$

This is exactly what the subroutine STEPFIT does. It first calculates the matrix $\underline{\underline{N}}$ and proceeds to invert it by the process of Gaussian elimination as described by Orden in Chapter 2 of <u>Mathematical Methods for Digital Computers</u> (35). The actual regression program used in subroutine STEPFIT is that written by M. A. Efroymson and is described briefly in Chapter 15 of the same book. Once the vector of molecular parameters $(\underline{b})$ has been determined, it is important to determine the statistical significance of the vector $\underline{b}$. The standard error (s_{b_j}) of any component b_j of $\underline{b}$ is given by,

$$s_{b_j}^{2} = s^{2}\,N_{jj}^{-1}$$

$$\text{where} \quad s^{2} = \frac{1}{n-p}\sum_{i} w_i (y_i - \hat{y}_i)^{2} \qquad n-p \equiv \text{degrees of freedom}$$

$$\text{with} \quad \underline{\hat{y}} = \underline{\underline{X}}\,\underline{b}$$

$$\text{and} \quad w_i = \text{normalized weight of ith measurement such that}$$

$$\sum_{i} w_i = n$$

Boyd showed that a simultaneous confidence interval for all components of $\underline{b}$ is defined such that the probability is $1 - \alpha$ for all b_j in $\{b_j\}$ that,

$$|b_j - \beta_j| \leq S_\alpha s_{b_j}$$

where S_α is a function of the well-known F_α (p, n-p) distribution

$$S_\alpha = \sqrt{pF_\alpha(p, n-p)}$$

This simultaneous confidence interval $[\pm sS_\alpha]$ is the meaningful statistic to quote for the results of a least squares fit when variables are statistically dependent. The common test for the statistical dependence of two variables x_{ij} and x_{iq} is the correlation coefficient r_{jq},

$$r_{jq} = \frac{\sum_i (x_{ij}-\bar{x}_j)(x_{iq}-\bar{x}_q)}{\sqrt{\sum_i (x_{ij}-\bar{x}_j)\sum_i (x_{iq}-\bar{x}_q)}}$$

Subroutine STEPFIT prints out r_{jq} for all variables. The coefficients (b̲) of variables having non-zero r_{jq} are dependent upon one another. For example, A_0 is highly dependent on the value determined for α_4^A and D_0^K. In such a case it is important to know that the probability is $1-\alpha$ that all three parameters are simultaneously within a specified interval of their true values. In our work we have chosen $\alpha = 0.05$.

The manner in which standard errors of independent and dependent variables are calculated in STEPFIT is described on pages 193 and 195 of Efroymson's Chapter 17 (35). At first glance (or even many glances) it appears his definitions differ from those given above. However, when one carries through the normalization factors of the correlation coefficients (r_{ij}) to the very end, agreement is reached.

APPENDIX C

RESULTS OF A SIMULTANEOUS FIT FOR CD3I

```
NO.     IDENT             OBS, FREQ    OBS-CALC     WT
  1   NU4 PP12,14        2246.4937    -0,2074    0.00
  2   NU4 PP12,13        2246,9074    -0,1971    0,00
  3   NU4 PP12,12        2247,3034    -0,2044    0,00
  4   NU4 PP11,13        2251,0347    -0,1467    0,00
  5   NU4 PP11,12        2251.4425    -0,1424    0,00
  6   NU4 PP 9,19        2256.7635    -0,0969    0,00
  7   NU4 PP 9,18        2257.1704    -0,0942    0,00
  8   NU4 PP 9,17        2257.5683    -0,1004    0.00
  9   NU4 PP 9,16        2257.9765    -0,0963    0,00
 10   NU4 PP 9,15        2258,3804    -0,0964    0,00
 11   NU4 PP 9,14        2258.7847    -0,0961    0.00
 12   NU4 PP 9,13        2259,1862    -0,0984    0,00
 13   NU4 PP 9,12        2259.5872    -0,1013    0,00
 14   NU4 PP 9,11        2259,9934    -0,0988    0.00
 15   NU4 PP 9, 9        2260.8079    -0,0915    0.00
 16   NU4 PP 8,16        2262,0221    -0,0750    0,00
 17   NU4 PP 5,15        2274.4411    -0,0153    0,12
 18   NU4 PP 5,14        2274,8471    -0,0138    0.12
 19   NU4 PP 5,13        2275,2569    -0,0084    0,12
 20   NU4 PP 5,12        2275.6610    -0,0086    0,03
 21   NU4 PP 5,11        2276.0695    -0,0043    0,12
 22   NU4 PP 5, 9        2276,8709    -0,0110    0,03
 23   NU4 PP 5, 8        2277,2833    -0,0024    0,03
 24   NU4 PP 5, 7        2277,6790    -0,0105    0,03
 25   NU4 PP 5, 6        2278.0863    -0,0068    0,03
 26   NU4 PP 5, 5        2278,4992     0,0026    0,03
 27   NU4 PP 4,28        2273.1313    -0,0000    0,03
 28   NU4 PP 4,27        2273.5429     0,0059    0,03
 29   NU4 PP 4,26        2273.9424    -0,0002    0,03
 30   NU4 PP 4,25        2274.3437    -0,0045    0,03
 31   NU4 PP 4,24        2274.7482    -0,0055    0,03
 32   NU4 PP 4,23        2275,1507    -0,0084    0,03
 33   NU4 PP 4,22        2275.5608    -0,0036    0,03
 34   NU4 PP 4,21        2275,9573    -0,0123    0,03
 35   NU4 PP 4,19        2276.7785    -0,0014    0,03
 36   NU4 PP 4,18        2277,1749    -0,0100    0.03
 37   NU4 PP 4,16        2277.9867    -0,0079    0,03
```

```
NO.      IDENT           OBS, FREQ   OBS-CALC    WT
38   NU4 PP 4,15         2278,3888   -0,0105    0,03
39   NU4 PP 4,14         2278,7913   -0,0126    0,03
40   NU4 PP 4,13         2279,1925   -0,0159    0,03
41   NU4 PP 4,12         2279.5892   -0,0236    0,03
42   NU4 PP 4,11         2280.0017   -0,0154    0,03
43   NU4 PP 3,36         2273,8050    0,0047    0,03
44   NU4 PP 3,35         2274,2093    0,0026    0,03
45   NU4 PP 3,34         2274,6182    0,0052    0,03
46   NU4 PP 3,33         2275,0222    0,0030    0,12
47   NU4 PP 3,32         2275.4196   -0,0058    0,12
48   NU4 PP 3,31         2275,8377    0,0061    0,12
49   NU4 PP 3,29         2276,6493    0,0056    0,03
50   NU4 PP 3,28         2277,0584    0,0088    0,12
51   NU4 PP 3,26         2277,8648    0,0035    0,03
52   NU4 PP 3,25         2278,2714    0,0044    0,03
53   NU4 PP 3,24         2278,6885    0,0158    0,03
54   NU4 PP 3,23         2279,0789    0,0006    0,03
55   NU4 PP 3,22         2279,4877    0,0040    0,03
56   NU4 PP 3,21         2279,8791   -0,0101    0,12
57   NU4 PP 3,19         2280,6929   -0,0068    0,03
58   NU4 PP 3,18         2281,1037   -0,0011    0,03
59   NU4 PP 3,17         2281,5041   -0,0058    0,03
60   NU4 PP 3,16         2281,9118   -0,0030    0,12
61   NU4 PP 3,15         2282,3280    0,0084    0,03
62   NU4 PP 3,14         2282,7357    0,0114    0,03
63   NU4 PP 3,13         2283,1301    0,0012    0,03
64   NU4 PP 3,12         2283.5271   -0,0063    0,03
65   NU4 PP 3,11         2283,9316   -0,0062    0,03
66   NU4 PP 3, 9         2284,7417   -0,0045    0,03
67   NU4 PP 3, 8         2285,1639    0,0136    0,03
68   NU4 PP 2,25         2282,1609   -0,0016    0,12
69   NU4 PP 2,24         2282,5623   -0,0061    0,12
70   NU4 PP 2,23         2282,9702   -0,0039    0,12
71   NU4 PP 2,22         2283,3794   -0,0004    0,12
72   NU4 PP 2,21         2283,7853   -0,0000    0,03
73   NU4 PP 2,19         2284,6019    0,0058    0,03
74   NU4 PP 2,18         2285,0122    0,0108    0,12
75   NU4 PP 2,16         2285,8244    0,0128    0,12
76   NU4 PP 2,15         2286,2272    0,0107    0,03
77   NU4 PP 2,14         2286,6300    0,0086    0,12
78   NU4 PP 2,13         2287,0398    0,0137    0,12
79   NU4 PP 2,12         2287,4459    0,0152    0,12
80   NU4 PP 2,11         2287,8464    0,0113    0,03
81   NU4 PP 1,15         2290,0854   -0,0038    0,03
82   NU4 PP 1,14         2290,4830   -0,0111    0,12
83   NU4 PP 1,13         2290,8815   -0,0171    0,03
84   NU4 PP 1,12         2291,2858   -0,0178    0,03
85   NU4 RR 1, 1         2304,6125   -0,0124    0,03
86   NU4 RR 1, 2         2305,0275    0,0003    0,03
87   NU4 RR 1, 3         2305,4365    0,0070    0,03
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NO.	IDENT	OBS, FREQ	OBS-CALC	WT
88	NU4 RR 1, 4	2305,8387	0,0071	0,03
89	NU4 RR 1, 5	2306,2496	0,0161	0,12
90	NU4 RR 1, 6	2306,6543	0,0191	0,12
91	NU4 RR 1,12	2309,0478	0,0067	0,12
92	NU4 RR 1,13	2309,4350	-0,0063	0,03
93	NU4 RR 1,14	2309,8304	-0,0110	0,03
94	NU4 RR 1,15	2310,2350	-0,0062	0,03
95	NU4 RR 1,16	2310,6363	-0,0045	0,03
96	NU4 RR 2,19	2315,6368	0,0048	0,12
97	NU4 RR 2, 2	2308,8106	-0,0120	0,03
98	NU4 RR 2, 3	2309,2150	-0,0098	0,03
99	NU4 RR 2,20	2316,0421	0,0116	0,03
100	NU4 RR 2,21	2316,4492	0,0204	0,12
101	NU4 RR 2,22	2316,8395	0,0126	0,12
102	NU4 RR 2,23	2317,2358	0,0111	0,00
103	NU4 RR 2,24	2317,6306	0,0083	0,02
104	NU4 RR 2,25	2318,0135	-0,0061	0,12
105	NU4 RR 3, 3	2312,9852	-0,0070	0,03
106	NU4 RR 3, 4	2313,4001	0,0060	0,12
107	NU4 RR 3, 5	2313,8060	0,0101	0,12
108	NU4 RR 3, 6	2314,2038	0,0063	0,03
109	NU4 RR 3, 7	2314,6076	0,0088	0,06
110	NU4 RR 3, 9	2315,4188	0,0179	0,08
111	NU4 RR 3,10	2315,8030	0,0014	0,12
112	NU4 RR 3,12	2316,6101	0,0077	0,50
113	NU4 RR 3,13	2317,0044	0,0020	0,50
114	NU4 RR 3,14	2317,4006	-0,0016	0,50
115	NU4 RR 3,15	2317,8006	-0,0012	0,12
116	NU4 RR 3,16	2318,2028	0,0016	0,12
117	NU4 RR 3,18	2318,9815	-0,0177	0,12
118	NU4 RR 3,19	2319,3846	-0,0132	0,12
119	NU4 RR 3,20	2319,8115	0,0153	0,12
120	NU4 RR 3,21	2320,1908	-0,0035	0,50
121	NU4 RR 3,22	2320,5917	-0,0005	0,50
122	NU4 RR 3,23	2320,9926	0,0027	0,12
123	NU4 RR 3,24	2321,3856	-0,0017	0,12
124	NU4 RR 3,25	2321,7816	-0,0028	0,12
125	NU4 RR 3,28	2322,9836	0,0094	0,03
126	NU4 RR 3,30	2323,7695	0,0035	0,03
127	NU4 RR 3,31	2324,1556	-0,0059	0,03
128	NU4 RR 3,32	2324,5592	0,0024	0,03
129	NU4 RR 4, 4	2317,1452	0,0124	0,00
130	NU4 RR 4, 5	2317,5387	0,0042	0,12
131	NU4 RR 4, 6	2317,9355	-0,0005	0,03
132	NU4 RR 4, 7	2318,3417	0,0044	0,03
133	NU4 RR 4,10	2319,5398	0,0000	0,03
134	NU4 RR 4,12	2320,3326	-0,0077	0,12
135	NU4 RR 4,13	2320,7471	0,0068	0,50
136	NU4 RR 4,15	2321,5383	-0,0011	0,03
137	NU4 RR 4,16	2321,9445	0,0058	0,03

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 NO.      IDENT             OBS, FREQ    OBS-CALC     WT
138   NU4 RR  4,18          2322.7438      0.0074   0.12
139   NU4 RR  4,19          2323.1373      0.0024   0.03
140   NU4 RR  4,21          2323.9416      0.0105   0.12
141   NU4 RR  4,22          2324.3197     -0.0091   0.12
142   NU4 RR  4,23          2324.7312      0.0049   0.12
143   NU4 RR  4,24          2325.1256      0.0021   0.50
144   NU4 RR  4,25          2325.5308      0.0104   0.03
145   NU4 RR  4,27          2326.3136      0.0001   0.03
146   NU4 RR  4,28          2326.7147      0.0051   0.03
147   NU4 RR  4,29          2327.1142      0.0088   0.03
148   NU4 RR  4,31          2327.8816     -0.0147   0.12
149   NU4 RR  4,32          2328.2788     -0.0125   0.12
150   NU4 RR  4,34          2329.0703     -0.0101   0.03
151   NU4 RR  4,35          2329.4936      0.0191   0.03
152   NU4 RR  5,10          2323.2443     -0.0041   0.03
153   NU4 RR  5,12          2324.0364     -0.0123   0.12
154   NU4 RR  5,13          2324.4390     -0.0096   0.12
155   NU4 RR  5,14          2324.8421     -0.0060   0.12
156   NU4 RR  5,15          2325.2504      0.0029   0.03
157   NU4 RR  5,16          2325.6495      0.0030   0.03
158   NU4 RR  5,18          2326.4388     -0.0052   0.03
159   NU4 RR  6, 6          2325.3227     -0.0008   0.12
160   NU4 RR  6, 7          2325.7293      0.0047   0.12
161   NU4 RR  6, 9          2326.5224     -0.0038   0.12
162   NU4 RR  6,13          2328.1164     -0.0100   0.12
163   NU4 RR  6,14          2328.5188     -0.0070   0.50
164   NU4 RR  6,15          2328.9098     -0.0152   0.12
165   NU4 RR  6,16          2329.3159     -0.0081   0.00
166   NU4 RR  8, 9          2333.7780     -0.0100   0.12
167   NU4 RR  9, 9          2337.3626     -0.0073   0.12
168   NU4 RR  9,10          2337.7700      0.0000   0.03
169   NU4 RR  9,11          2338.1724      0.0026   0.50
170   NU4 RR  9,12          2338.5655     -0.0038   0.50
171   NU4 RR  9,13          2338.9576     -0.0110   0.00
172   NU4 RR10,14           2342.9304      0.0156   0.06
173   NU4 RR10,15           2343.3226      0.0092   0.02
174   NU4 RR10,17           2344.1098      0.0001   0.25
175   NU4 RR10,18           2344.5032     -0.0043   0.06


176  2NU4 QP  3,44          4527.8835      0.0009   0.50
177  2NU4 QP  3,43          4528.2985      0.0015   0.50
178  2NU4 QP  3,42          4528.7163      0.0051   0.50
179  2NU4 QP  3,41          4529.1306      0.0053   0.50
180  2NU4 QP  3,40          4529.5401      0.0010   0.50
181  2NU4 QP  3,39          4529.9517     -0.0010   0.50
182  2NU4 QP  3,38          4530.3546     -0.0114   0.50
183  2NU4 QP  3,37          4530.7753     -0.0039   0.12
184  2NU4 QP  3,36          4531.1819     -0.0102   0.03
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NO.	IDENT	OBS, FREQ	OBS-CALC	WT
185	2NU4 QP 3,35	4531.5996	-0,0052	0,50
186	2NU4 QP 3,34	4532,0100	-0,0072	0.12
187	2NU4 QP 3,33	4532.4274	-0,0021	0.12
188	2NU4 QP 3,32	4532.8407	-0,0008	0.12
189	2NU4 QP 3,31	4533.2594	0,0062	0,12
190	2NU4 QP 3,29	4534,0847	0,0087	0,02
191	2NU4 QP 3,28	4534.4991	0,0121	0,02
192	2NU4 QP 3,27	4534.8964	-0,0014	0.02
193	2NU4 QP 3,26	4535.2997	-0,0086	0,12
194	2NU4 QP 3,25	4535.7183	-0,0003	0,12
195	2NU4 QP 3,24	4536,1307	0,0021	0,12
196	2NU4 QP 3,23	4536,5459	0,0076	0.12
197	2NU4 QP 3,22	4536,9543	0,0065	0,12
198	2NU4 QP 3,21	4537.3666	0,0096	0,12
199	2NU4 QP 3,20	4537.7799	0,0139	0.03
200	2NU4 QP 3,19	4538.1800	0,0054	0.12
201	2NU4 QP 3,18	4538,5813	-0,0017	0,03
202	2NU4 QP 3,17	4539,0023	0,0112	0,12
203	2NU4 QP 3,16	4539,4044	0,0054	0.12
204	2NU4 QP 3,15	4539,8105	0,0040	0,12
205	2NU4 QP 3,13	4540,6255	0,0048	0,12
206	2NU4 QP 6,39	4529,2648	0,0010	0.03
207	2NU4 QP 6,38	4529,6798	0,0027	0,03
208	2NU4 QP 6,33	4531,7288	-0,0113	0,12
209	2NU4 QP 6,32	4532,1415	-0,0105	0,03
210	2NU4 QP 6,31	4532,5662	0,0025	0,03
211	2NU4 QP 6,30	4532.9783	0,0032	0.03
212	2NU4 QP 6,29	4533,3879	0,0016	0.03
213	2NU4 QP 6,28	4533.7953	-0,0020	0,03
214	2NU4 QP 6,27	4534.2093	0,0014	0,03
215	2NU4 QP 6,26	4534,6115	-0,0069	0.03
216	2NU4 QP 6,25	4535,0265	-0,0020	0.03
217	2NU4 QP 6,24	4535,4338	-0,0047	0.03
218	2NU4 QP 6,23	4535.8576	0,0095	0.03
219	2NU4 QP 6,21	4536,6783	0,0117	0,03
220	2NU4 QP 6,20	4537,0886	0,0131	0.03
221	2NU4 QP 6,16	4538.7200	0,0119	0.03
222	2NU4 QP 6,15	4539,1227	0,0071	0.03
223	2NU4 QP 6,14	4539,5342	0,0114	0.03
224	2NU4 QP 6,13	4539,9358	0,0062	0,03
225	2NU4 QP 6,10	4541.1618	0,0133	0,12
226	2NU4 QR 3,18	4553,4727	-0,0007	0.12
227	2NU4 QR 3,19	4553,8628	-0,0063	0,12
228	2NU4 QR 3,20	4554,2553	-0,0092	0.12
229	2NU4 QR 3,21	4554,6553	-0,0043	0,12
230	2NU4 QR 3,22	4555,0547	0,0005	0,12
231	2NU4 QR 3,23	4555,4483	-0,0001	0,12
232	2NU4 QR 3,24	4555.8528	0,0106	0,03
233	2NU4 QR 3,25	4556,2330	-0,0026	0.12
234	2NU4 QR 3,26	4556.6273	-0,0013	0.12

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NO.     IDENT           OBS. FREQ   OBS-CALC    WT
235 2NU4 QR 3,27        4557,0090   -0,0123   0,12
236 2NU4 QR 3,28        4557,4056   -0,0078   0,12
237 2NU4 QR 3,29        4557,7949   -0,0103   0,03
238 2NU4 PP11,15        4504,2280   -0,0103   0,02
239 2NU4 PP11,14        4504,6497    0,0054   0,03
240 2NU4 PP11,13        4505,0527    0,0027   0,03
241 2NU4 PP11,12        4505,4639    0,0084   0,03
242 2NU4 PP11,11        4505,8670    0,0062   0,03
243 2NU4 PP10,16        4510,7992   -0,0169   0,03
244 2NU4 PP10,15        4511,2185   -0,0038   0,03
245 2NU4 PP10,14        4511,6289    0,0003   0,03
246 2NU4 PP10,13        4512,0348    0,0004   0,03
247 2NU4 PP10,12        4512,4367   -0,0034   0,03
248 2NU4 PP10,11        4512,8363   -0,0092   0,03
249 2NU4 PP 9,13        4518,9842    0,0084   0,02
250 2NU4 PP 9,12        4519,3777   -0,0039   0,03
251 2NU4 PP 9,11        4519,7819   -0,0052   0,03
252 2NU4 PP 9,10        4520,2048    0,0124   0,03
253 2NU4 PP 9, 9        4520,6024    0,0049   0,12
254 2NU4 PP 2,10        4567,5155    0,0083   0,03
255 2NU4 PP 2, 9        4567,8967   -0,0163   0,03
256 2NU4 PP 2, 8        4568,3168   -0,0016   0,03
257 2NU4 PP 2, 7        4568,7171   -0,0064   0,03
258 2NU4 PP 1,19        4570,4055   -0,0031   0,03
259 2NU4 PP 1,15        4572,0233   -0,0171   0,12
260 2NU4 PP 1,14        4572,4315   -0,0160   0,03
261 2NU4 PP 1,13        4572,8452   -0,0094   0,03
262 2NU4 PP 1,12        4573,2570   -0,0042   0,12
263 2NU4 PP 1,11        4573,6752    0,0076   0,03
264 2NU4 PP 1,10        4574,0725   -0,0011   0,03
265 2NU4 PP 1, 9        4574,4934    0,0139   0,12
266 2NU4 PP 1, 8        4574,8849   -0,0000   0,12
267 2NU4 PP 1, 7        4575,2851   -0,0050   0,12
268 2NU4 PP 1, 6        4575,6946   -0,0004   0,12
269 2NU4 RR 0, 3        4586,2455    0,0035   0,12
270 2NU4 RR 0, 4        4586,6521    0,0088   0,03
271 2NU4 RR 0, 6        4587,4492    0,0044   0,03
272 2NU4 RR 0, 7        4587,8579    0,0129   0,03
273 2NU4 RR 0, 8        4588,2453    0,0005   0,03
274 2NU4 RR 0, 9        4588,6470    0,0027   0,03
275 2NU4 RR 0,10        4589,0383   -0,0052   0,03
276 2NU4 RR 0,11        4589,4426    0,0004   0,03
277 2NU4 RR 0,12        4589,8362   -0,0044   0,03
278 2NU4 RR 0,13        4590,2397    0,0010   0,03
279 2NU4 RR 0,16        4591,4300   -0,0005   0,12
280 2NU4 RR 0,17        4591,8305    0,0034   0,12
281 2NU4 RR 0,18        4592,2301    0,0069   0,12
282 2NU4 RR 0,19        4592,6253    0,0064   0,12
283 2NU4 RR 0,20        4593,0238    0,0095   0,03
284 2NU4 RR 0,21        4593,4126    0,0033   0,03
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NO.	IDENT	OBS, FREQ	OBS-CALC	WT
285	2NU4 RR 0,22	4593,8051	0,0013	0,12
286	2NU4 RR 0,23	4594.2056	0,0076	0,03
287	2NU4 RR 0,24	4594,5957	0,0039	0,03
288	2NU4 RR 0,25	4594,9858	0,0007	0,03
289	2NU4 RR 0,26	4595,3716	-0,0065	0,03
290	2NU4 RR 0,27	4595,7846	0,0139	0,03
291	2NU4 RR 0,28	4596,1703	0,0075	0,12
292	2NU4 RR 0,29	4596,5679	0,0134	0,12
293	2NU4 RR 0,30	4596,9640	0,0182	0,03
294	2NU4 RR 0,32	4597,7592	0,0321	0,03
295	2NU4 RR 0,33	4598,1467	0,0296	0,03
296	2NU4 RR 0,34	4598,5240	0,0173	0,03
297	2NU4 RR 0,35	4598,9164	0,0205	0,03
298	2NU4 RR 1, 7	4594,3069	-0,0021	0,03
299	2NU4 RR 1, 8	4594,7037	-0,0051	0,03
300	2NU4 RR 1, 9	4595,0924	-0,0158	0,03
301	2NU4 RR 1,11	4595,8950	-0,0110	0,03
302	2NU4 RR 1,12	4596,3007	-0,0036	0,12
303	2NU4 RR 2, 5	4599,9005	-0,0193	0,03
304	2NU4 RR 2, 6	4600,3110	-0,0093	0,03
305	2NU4 RR 2, 7	4600,7133	-0,0071	0,02
306	2NU4 RR 2, 8	4601,1074	-0,0127	0,03
307	2NU4 RR 2, 9	4601.5189	-0,0006	0,03
308	2NU4 RR 2,10	4601,9072	-0,0113	0,03
309	2NU4 RR 2,11	4602,3162	-0,0009	0,03
310	2NU4 RR 2,12	4602,7092	-0,0061	0,03
311	2NU4 RR 2,13	4603,1030	-0,0101	0,03
312	2NU4 RR 2,16	4604,3197	0,0154	0,03
313	2NU4 RR 2,17	4604,7080	0,0074	0,03
314	2NU4 RR 3, 4	4605,8710	-0,0061	0,12
315	2NU4 RR 3, 5	4606,2740	-0,0039	0,12
316	2NU4 RR 3, 6	4606,6694	-0,0089	0,12
317	2NU4 RR 3, 7	4607,0762	-0,0021	0,12
318	2NU4 RR 3, 8	4607,4707	-0,0073	0,12
319	2NU4 RR 3, 9	4607,8658	-0,0114	0,03
320	2NU4 RR 3,10	4608,2676	-0,0085	0,03
321	2NU4 RR 3,11	4608,6694	-0,0052	0,12
322	2NU4 RR 3,12	4609,0705	-0,0023	0,12
323	2NU4 RR 3,13	4609,4711	0,0006	0,12
324	2NU4 RR 3,15	4610,2503	-0,0145	0,03
325	2NU4 RR 3,16	4610,6536	-0,0077	0,03
326	2NU4 RR 3,17	4611,0559	-0,0016	0,03
327	2NU4 RR 3,18	4611,4446	-0,0086	0,12
328	2NU4 RR 3,19	4611,8369	-0,0117	0,12
329	2NU4 RR 4, 8	4613,7937	0,0122	0,12
330	2NU4 RR 4, 9	4614,1659	-0,0148	0,03
331	2NU4 RR 4,11	4614,9908	0,0129	0,03
332	2NU4 RR 4,12	4615,3824	0,0065	0,12
333	2NU4 RR 4,13	4615,7770	0,0035	0,12
334	2NU4 RR 4,14	4616,1725	0,0018	0,02

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NO.      IDENT          OBS, FREQ   OBS-CALC    WT
335  2NU4  RR  4,15     4616,5560   -0,0116   0,12
336  2NU4  RR  4,16     4616,9551   -0,0089   0,12
337  2NU4  RR  4,17     4617,3482   -0,0118   0,12
338  2NU4  RR  4,18     4617,7471   -0,0085   0,12
339  2NU4  RR  4,19     4618,1391   -0,0117   0,03
340  2NU4  RR  4,20     4618,5384   -0,0071   0,03
341  2NU4  RR  5,16     4623,2279    0,0165   0,03
342  2NU4  RR  5,17     4623,6151    0,0079   0,03
343  2NU4  RR  5,18     4624,0147    0,0120   0,03
344  2NU4  RR  5,19     4624,4016    0,0039   0,12
345  2NU4  RR  5,20     4624,7930    0,0007   0,03
346  2NU4  RR  5,21     4625,1734   -0,0131   0,03
347  2NU4  RR  5,22     4625,5731   -0,0071   0,12
348  2NU4  RR  5,23     4625,9681   -0,0054   0,12
349  2NU4  RR  5,24     4626,3620   -0,0044   0,12
350  2NU4  RR  5,25     4626,7550   -0,0039   0,03
351  2NU4  RR  5,26     4627,1346   -0,0163   0,03
352  2NU4  RR  5,27     4627,5309   -0,0115   0,03
353  2NU4  RR  5,28     4627,9338    0,0003   0,12
354  2NU4  RR  6, 6     4625,4211   -0,0017   0,12
355  2NU4  RR  6, 7     4625,8159   -0,0067   0,12
356  2NU4  RR  6, 8     4626,2275    0,0058   0,12
357  2NU4  RR  6, 9     4626,6252    0,0042   0,12
358  2NU4  RR  6,10     4627,0244    0,0048   0,12
359  2NU4  RR  6,11     4627,4245    0,0067   0,12
360  2NU4  RR  6,12     4627,8172    0,0016   0,12
361  2NU4  RR  6,13     4628,2194    0,0064   0,12
362  2NU4  RR  6,15     4629,0170    0,0105   0,12
363  2NU4  RR  6,16     4629,4076    0,0050   0,12
364  2NU4  RR  6,17     4629,7969   -0,0014   0,12
365  2NU4  RR  6,18     4630,1991    0,0055   0,12
366  2NU4  RR  6,21     4631,3880    0,0111   0,03
367  2NU4  RR  6,22     4631,7774    0,0069   0,03
368  2NU4  RR  6,23     4632,1738    0,0102   0,12
369  2NU4  RR  6,24     4632,5626    0,0063   0,12
370  2NU4  RR  6,25     4632,9544    0,0059   0,12
371  2NU4  RR  6,26     4633,3431    0,0028   0,12
372  2NU4  RR  6,27     4633,7348    0,0031   0,12
373  2NU4  RR  6,28     4634,1228    0,0002   0,12
374  2NU4  RR  6,29     4634,5152    0,0022   0,03
375  2NU4  RR  6,30     4634,8907   -0,0123   0,03
376  2NU4  RR  6,31     4635,2957    0,0032   0,12
377  2NU4  RR  6,32     4635,6860    0,0044   0,12
378  2NU4  RR  6,33     4636,0698   -0,0004   0,03
379  2NU4  RR  6,34     4636,4557   -0,0026   0,03
380  2NU4  RR  6,35     4636,8506    0,0047   0,03
381  2NU4  RR  6,36     4637,2349    0,0018   0,03
382  2NU4  RR  6,37     4637,6121   -0,0077   0,03
383  2NU4  RR  6,38     4637,9931   -0,0129   0,03
384  2NU4  RR  6,40     4638,7839    0,0069   0,03
```

NO.	IDENT	OBS. FREQ	OBS-CALC	WT
385	2NU4 RR 6,41	4639.1702	0.0084	0.03
386	2NU4 RR 6,42	4639.5516	0.0056	0.03
387	2NU4 RR 6,43	4639.9241	-0.0057	0.03
388	2NU4 RR 7, 7	4631.9520	-0.0061	0.12
389	2NU4 RR 7, 8	4632.3565	-0.0009	0.12
390	2NU4 RR 7, 9	4632.7599	0.0036	0.12
391	2NU4 RR 7,10	4633.1584	0.0037	0.12
392	2NU4 RR 7,11	4633.5531	0.0003	0.12
393	2NU4 RR 7,12	4633.9482	-0.0023	0.12
394	2NU4 RR 7,13	4634.3466	-0.0011	0.03
395	2NU4 RR 7,15	4635.1312	-0.0097	0.12
396	2NU4 RR 7,16	4635.5426	0.0057	0.12
397	2NU4 RR 7,17	4635.9357	0.0032	0.12
398	2NU4 RR 7,18	4636.3342	0.0066	0.03
399	2NU4 RR 7,19	4636.7214	-0.0009	0.03
400	2NU4 RR 7,20	4637.1257	0.0092	0.03
401	2NU4 RR 7,21	4637.5149	0.0045	0.03
402	2NU4 RR 7,22	4637.9021	-0.0016	0.03
403	2NU4 RR 7,23	4638.2990	0.0023	0.03
404	2NU4 RR 7,24	4638.6854	-0.0038	0.12
405	2NU4 RR 7,25	4639.0750	-0.0062	0.12
406	2NU4 RR 7,26	4639.4689	-0.0039	0.03
407	2NU4 RR 7,27	4639.8573	-0.0066	0.03
408	2NU4 RR 8, 9	4638.8261	-0.0076	0.12
409	2NU4 RR 8,10	4639.2300	-0.0021	0.12
410	2NU4 RR 8,11	4639.6290	-0.0010	0.12
411	2NU4 RR 8,12	4640.0291	0.0016	0.12
412	2NU4 RR 8,13	4640.4297	0.0051	0.03
413	2NU4 RR 8,15	4641.2185	0.0009	0.12
414	2NU4 RR 8,16	4641.6154	0.0020	0.12
415	2NU4 RR 8,17	4642.0096	0.0008	0.12
416	2NU4 RR 8,18	4642.4109	0.0072	0.12
417	2NU4 RR 8,19	4642.7871	-0.0112	0.03
418	2NU4 RR 8,20	4643.1923	-0.0000	0.03
419	2NU4 RR 8,21	4643.5807	-0.0053	0.03
420	2NU4 RR 8,22	4643.9714	-0.0077	0.03
421	2NU4 RR 8,23	4644.3732	0.0013	0.03
422	2NU4 RR 8,24	4644.7637	-0.0004	0.03
423	2NU4 RR 8,25	4645.1613	0.0054	0.03
424	2NU4 RR 8,26	4645.5441	-0.0032	0.03
425	2NU4 RR 8,28	4646.3339	0.0053	0.03
426	2NU4 RR 8,30	4647.0914	-0.0167	0.03
427	2NU4 RR 8,31	4647.4839	-0.0132	0.03
428	2NU4 RR 8,32	4647.8700	-0.0156	0.03
429	2NU4 RR 8,33	4648.2544	-0.0193	0.03
430	2NU4 RR 9, 9	4644.8629	0.0104	0.12
431	2NU4 RR 9,10	4645.2568	0.0061	0.12
432	2NU4 RR 9,11	4645.6501	0.0015	0.03
433	2NU4 RR 9,12	4646.0566	0.0106	0.03
434	2NU4 RR 9,13	4646.4455	0.0026	0.03

NO.	IDENT	OBS, FREQ	OBS-CALC	WT
435	2NU4 RR 9,15	4647,2276	-0,0079	0,12
436	2NU4 RR 9,16	4647,6261	-0,0051	0,03
437	2NU4 RR 9,17	4648,0173	-0,0091	0,03
438	2NU4 RR 9,18	4648,4101	-0,0111	0,12
439	2NU4 RR 9,19	4648,7989	-0,0166	0,12
440	2NU4 RR 9,20	4649,2113	0,0019	0,03
441	2NU4 RR 9,21	4649,6110	0,0082	0,12
442	2NU4 RR 9,22	4650,0045	0,0087	0,12
443	2NU4 RR 9,23	4650,3968	0,0085	0,12
444	2NU4 RR 9,24	4650,7837	0,0033	0,03
445	2NU4 RR 9,27	4651,9631	0,0093	0,03
446	2NU4 RR 9,28	4652,3468	0,0029	0,03
447	2NU4 RR 9,30	4653,1123	-0,0106	0,03
448	2NU4 RR 9,31	4653,5081	-0,0036	0,03
449	2NU4 RR 9,32	4653,8939	-0,0060	0,03
450	2NU4 RR 9,33	4654,2728	-0,0149	0,03
451	2NU4 RR 9,34	4654,6748	-0,0002	0,03
452	2NU4 RR 9,35	4655,0602	-0,0016	0,03
453	2NU4 RR 9,36	4655,4557	0,0076	0,03
454	2NU4 RR 9,37	4655,8379	0,0039	0,03
455	2NU4 RR 9,38	4656,2224	0,0031	0,03
456	2NU4 RR 9,39	4656,6053	0,0012	0,03
457	2NU4 RR10,11	4651,6152	0,0076	0,03
458	2NU4 RR10,12	4652,0099	0,0051	0,03
459	2NU4 RR10,14	4652,7916	-0,0064	0,03
460	2NU4 RR10,15	4653,1885	-0,0055	0,03
461	2NU4 RR10,16	4653,5954	0,0060	0,03
462	2NU4 RR10,17	4653,9858	0,0013	0,03
463	2NU4 RR10,18	4654,3788	-0,0003	0,03
464	2NU4 RR10,19	4654,7848	0,0116	0,03
465	2NU4 RR10,20	4655,1716	0,0047	0,03
466	2NU4 RR10,21	4655,5584	-0,0017	0,03
467	2NU4 RR10,22	4655,9492	-0,0037	0,03
468	2NU4 RR10,23	4656,3438	-0,0014	0,03
469	2NU4 RR10,24	4656,7391	0,0021	0,03
470	2NU4 RR10,25	4657,1293	0,0009	0,03
471	2NU4 RR11,12	4657,9076	0,0042	0,03
472	2NU4 RR11,13	4658,3005	0,0005	0,03
473	2NU4 RR11,14	4658,6873	-0,0089	0,12
474	2NU4 RR11,15	4659,0910	-0,0010	0,03
475	2NU4 RR11,16	4659,4878	0,0005	0,12
476	2NU4 RR11,17	4659,8777	-0,0044	0,03
477	2NU4 RR11,18	4660,2766	0,0001	0,03
478	2NU4 RR11,19	4660,6692	-0,0013	0,02
479	2NU4 RR12,12	4663,7373	-0,0033	0,12
480	2NU4 RR12,14	4664,5512	0,0180	0,03
481	2NU4 RR12,15	4664,9396	0,0109	0,03
482	2NU4 RR12,16	4665,3448	0,0209	0,03
483	2NU4 RR12,17	4665,7356	0,0171	0,03
484	2NU4 RR12,18	4666,1172	0,0045	0,03

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 NO.      IDENT          OBS. FREQ    OBS-CALC    WT
485 2NU4 RR12,19         4666,5143     0,0078   0,03
486 2NU4 RR12,20         4666,9085     0,0088   0,12
487 2NU4 RR12,21         4667,2821    -0,0105   0,12
488 2NU4 RR12,22         4667,6781    -0,0068   0,03
489 2NU4 RR12,23         4668,0715    -0,0052   0,03
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APPENDIX D

RESULTS OF A SIMULTANEOUS FIT

FOR CD3CL

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NO.      IDENT           OBS, FREQ   OBS-CALC    WT
 1   NU4 PP12,14        2230,5253    -0,1182   0,00
 2   NU4 PP12,13        2231,2480    -0,1149   0,00
 3   NU4 PP12,12        2231,9618    -0,1206   0,00
 4   NU4 PP11,23        2227,8271    -0,1227   0,00
 5   NU4 PP11,22        2228,5498    -0,1191   0,00
 6   NU4 PP11,21        2229,2721    -0,1161   0,00
 7   NU4 PP11,20        2229,9916    -0,1159   0,00
 8   NU4 PP11,19        2230,7186    -0,1083   0,00
 9   NU4 PP11,18        2231,4485    -0,0979   0,00
10   NU4 PP11,17        2232,1656    -0,1004   0,00
11   NU4 PP11,15        2233,6179    -0,0874   0,00
12   NU4 PP11,14        2234,3433    -0,0818   0,00
13   NU4 PP11,13        2235,0669    -0,0779   0,00
14   NU4 PP11,12        2235,7901    -0,0745   0,00
15   NU4 PP11,11        2236,5020    -0,0824   0,00
16   NU4 PP10,28        2227,9706    -0,1424   0,00
17   NU4 PP10,27        2228,6992    -0,1328   0,00
18   NU4 PP10,26        2229,4226    -0,1285   0,00
19   NU4 PP10,25        2230,1444    -0,1260   0,00
20   NU4 PP10,24        2230,8860    -0,1038   0,00
21   NU4 PP10,23        2231,5985    -0,1108   0,00
22   NU4 PP10,22        2232,3225    -0,1063   0,00
23   NU4 PP10,21        2233,0511    -0,0974   0,00
24   NU4 PP10,20        2233,7759    -0,0924   0,00
25   NU4 PP10,19        2234,5034    -0,0847   0,00
26   NU4 PP10,18        2235,2278    -0,0802   0,00
27   NU4 PP10,17        2235,9490    -0,0790   0,00
28   NU4 PP10,16        2236,6637    -0,0842   0,00
29   NU4 PP10,15        2237,4011    -0,0669   0,00
30   NU4 PP10,14        2238,1252    -0,0628   0,00
31   NU4 PP10,13        2238,8467    -0,0614   0,00
32   NU4 PP10,12        2239,5738    -0,0544   0,00
33   NU4 PP10,11        2240,2920    -0,0563   0,00
34   NU4 PP10,10        2241,0136    -0,0548   0,00
35   NU4 PP 9,31        2229,5606    -0,1327   0,00
36   NU4 PP 9,30        2230,2844    -0,1280   0,00
37   NU4 PP 9,29        2231,0178    -0,1139   0,00
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NO,     IDENT            OBS, FREQ     OBS-CALC    WT
38   NU4 PP 9,28        2231,7392     -0,1119   0,00
39   NU4 PP 9,27        2232,4486     -0,1220   0,00
40   NU4 PP 9,26        2233,1767     -0,1135   0,00
41   NU4 PP 9,25        2233,9007     -0,1092   0,00
42   NU4 PP 9,24        2234,6251     -0,1047   0,00
43   NU4 PP 9,23        2235,3534     -0,0963   0,00
44   NU4 PP 9,22        2236,0787     -0,0910   0,00
45   NU4 PP 9,20        2237,5256     -0,0844   0,00
46   NU4 PP 9,19        2238,2515     -0,0787   0,00
47   NU4 PP 9,18        2238,9772     -0,0732   0,00
48   NU4 PP 9,17        2239,7076     -0,0631   0,00
49   NU4 PP 9,16        2240,4442     -0,0469   0,00
50   NU4 PP 9,15        2241,1583     -0,0532   0,00
51   NU4 PP 9,14        2241,8862     -0,0456   0,00
52   NU4 PP 9,13        2242,6123     -0,0399   0,00
53   NU4 PP 9,12        2243,3342     -0,0384   0,00
54   NU4 PP 9,11        2244,0610     -0,0320   0,00
55   NU4 PP 9,10        2244,7748     -0,0386   0,00
56   NU4 PP 9, 9        2245,4983     -0,0354   0,00
57   NU4 PP 8,28        2235,5280     -0,0416   0,00
58   NU4 PP 8,27        2236,2055     -0,0841   0,00
59   NU4 PP 8,26        2236,9259     -0,0838   0,00
60   NU4 PP 8,25        2237,6393     -0,0906   0,00
61   NU4 PP 8,24        2238,3620     -0,0881   0,00
62   NU4 PP 8,23        2239,0835     -0,0870   0,00
63   NU4 PP 8,22        2239,8059     -0,0850   0,00
64   NU4 PP 8,20        2241,2647     -0,0673   0,00
65   NU4 PP 8,19        2241,9965     -0,0560   0,00
66   NU4 PP 8,18        2242,7244     -0,0488   0,00
67   NU4 PP 8,17        2243,4509     -0,0429   0,00
68   NU4 PP 8,15        2244,8896     -0,0456   0,00
69   NU4 PP 8,14        2245,6223     -0,0336   0,00
70   NU4 PP 8,13        2246,3538     -0,0228   0,00
71   NU4 PP 8,12        2247,0696     -0,0276   0,00
72   NU4 PP 8,11        2247,7983     -0,0196   0,00
73   NU4 PP 8,10        2248,5135     -0,0250   0,00
74   NU4 PP 8, 9        2249,2309     -0,0282   0,00
75   NU4 PP 8, 8        2249,9560     -0,0236   0,00
76   NU4 PP 7,11        2251,5033     -0,0191   0,00
77   NU4 PP 7,10        2252,2431     -0,0002   0,00
78   NU4 PP 7, 9        2252,9578     -0,0062   0,00
79   NU4 PP 7, 8        2253,6841     -0,0007   0,00
80   NU4 PP 3,20        2259,5787     -0,0481   0,00
81   NU4 PP 3,19        2260,3035     -0,0456   0,00
82   NU4 PP 3,18        2261,0304     -0,0409   0,00
83   NU4 PP 3,17        2261,7508     -0,0427   0,00
84   NU4 PP 3,16        2262,4768     -0,0388   0,00
85   NU4 PP 3,14        2263,9328     -0,0269   0,00
86   NU4 PP 3,13        2264,6567     -0,0250   0,00
87   NU4 PP 3,12        2265,3797     -0,0238   0,00
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 NO.     IDENT           OBS, FREQ   OBS-CALC    WT
  88   NU4 PP 3,11      2266,1055    -0,0198   0,03
  89   NU4 PP 3,10      2266,8419    -0,0050   0,03
  90   NU4 PP 3, 9      2267,5602    -0,0083   0,03
  91   NU4 PP 3, 8      2268,2871    -0,0028   0,03
  92   NU4 PP 3, 7      2269.0043    -0,0070   0,03
  93   NU4 PP 3, 6      2269,7428     0,0104   0,03
  94   NU4 PP 3, 4      2271.1857     0,0113   0,03
  95   NU4 PP 3, 3      2271,9029     0,0078   0,03
  96   NU4 PP 1,12      2272,5482    -0,0192   0,03
  97   NU4 PP 1, 6      2276,9011     0,0030   0,03
  98   NU4 PP 1, 4      2278,3278    -0,0126   0,03
  99   NU4 PP 1, 3      2279.0523    -0,0089   0,03
 100   NU4 RP 0,31      2262,2811    -0,0935   0,00
 101   NU4 RP 0,29      2263,7356    -0,0856   0,00
 102   NU4 RP 0,28      2264,4675    -0,0771   0,00
 103   NU4 RP 0,27      2265,1934    -0,0745   0,00
 104   NU4 RP 0,26      2265,9132    -0,0781   0,00
 105   NU4 RP 0,24      2267,3679    -0,0701   0,00
 106   NU4 RP 0,23      2268,0972    -0,0641   0,00
 107   NU4 RP 0,22      2268,8178    -0,0667   0,00
 108   NU4 RP 0,21      2269,5499    -0,0578   0,00
 109   NU4 RP 0,19      2271,0067    -0,0473   0,00
 110   NU4 RP 0,18      2271,7360    -0,0410   0,00
 111   NU4 RP 0,17      2272,4559    -0,0440   0,00
 112   NU4 RP 0,16      2273,1833    -0,0395   0,00
 113   NU4 RP 0,14      2274,6486    -0,0196   0,00
 114   NU4 RP 0,13      2275,3783    -0,0124   0,03
 115   NU4 RP 0,12      2276,0970    -0,0161   0,03
 116   NU4 RP 0,11      2276,8292    -0,0062   0,03
 117   NU4 RP 0, 9      2278,2813     0,0018   0,03
 118   NU4 RP 0, 7      2279,7223    -0,0007   0,03
 119   NU4 RP 0, 6      2280,4419    -0,0026   0,03
 120   NU4 RP 0, 4      2281,8765    -0,0104   0,03
 121   NU4 RP 0, 2      2283,3277    -0,0008   0,03
 122   NU4 RR 2, 2      2293,9625     0,0168   0,03
 123   NU4 RR 2, 3      2294,6755     0,0106   0.12
 124   NU4 RR 2, 4      2295,3784    -0,0053   0.12
 125   NU4 RR 2, 5      2296,0868    -0,0154   0,03
 126   NU4 RR 2, 6      2296,8321     0,0117   0,03
 127   NU4 RR 2, 7      2297,5648     0,0265   0,00
 128   NU4 RR 2, 8      2298,2868     0,0310   0,00
 129   NU4 RR 2, 9      2299,0001     0,0271   0,00
 130   NU4 RR 2,10      2299,7132     0,0233   0,00
 131   NU4 RR 2,11      2300,4418     0,0354   0,00
 132   NU4 RR 2,12      2301,1468     0,0243   0,00
 133   NU4 RR 2,14      2302,5955     0,0418   0,00
 134   NU4 RR 2,15      2303,2944     0,0257   0,00
 135   NU4 RR 2,16      2304,0138     0,0305   0,00
 136   NU4 RR 2,17      2304,7348     0,0374   0,00
 137   NU4 RR 2,19      2306,1620     0,0375   0,00
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NO.	IDENT	OBS, FREQ	OBS-CALC	WT
138	NU4 RR 2,20	2306,8718	0,0344	0,00
139	NU4 RR 2,21	2307,5908	0,0409	0,00
140	NU4 RR 3, 3	2298,1453	0,0111	0,12
141	NU4 RR 3, 4	2298,8638	0,0109	0,12
142	NU4 RR 3, 5	2299,5843	0,0130	0,12
143	NU4 RR 3, 6	2300,2992	0,0098	0,12
144	NU4 RR 3, 7	2301,0099	0,0028	0,12
145	NU4 RR 3, 9	2302,4393	-0,0023	0,12
146	NU4 RR 3,10	2303,1541	-0,0041	0,12
147	NU4 RR 3,11	2303,8818	0,0073	0,12
148	NU4 RR 3,12	2304,6077	0,0172	0,12
149	NU4 RR 3,14	2306,0276	0,0065	0,12
150	NU4 RR 3,15	2306,7300	-0,0059	0,12
151	NU4 RR 3,16	2307,4343	-0,0159	0,12
152	NU4 RR 5, 9	2309,3015	0,0044	0,12
153	NU4 RR 5,10	2310,0153	0,0020	0,12
154	NU4 RR 5,11	2310,7342	0,0050	0,00
155	NU4 RR 5,14	2312,8809	0,0066	0,12
156	NU4 RR 5,15	2313,5913	0,0028	0,12
157	NU4 RR 5,16	2314,3023	0,0000	0,12
158	NU4 RR 5,18	2315,7332	0,0048	0,03
159	NU4 RR 5,19	2316,4496	0,0088	0,12
160	NU4 RR 5,21	2317,8863	0,0222	0,03
161	NU4 RR 5,26	2321,4334	0,0198	0,03
162	NU4 RR 5,27	2322,1387	0,0168	0,12
163	NU4 RR 5,28	2322,8415	0,0118	0,03
164	NU4 RR 5,29	2323,5401	0,0032	0,12
165	NU4 RR 5,30	2324,2586	0,0150	0,12
166	NU4 RR 5,32	2325,6562	0,0010	0,03
167	NU4 RR 6, 7	2311,2250	-0,0246	0,03
168	NU4 RR 6, 9	2312,6814	-0,0015	0,12
169	NU4 RR 6,10	2313,4030	0,0040	0,12
170	NU4 RR 6,11	2314,1201	0,0055	0,12
171	NU4 RR 6,12	2314,8336	0,0038	0,12
172	NU4 RR 6,14	2316,2534	-0,0055	0,12
173	NU4 RR 6,15	2316,9835	0,0107	0,12
174	NU4 RR 6,16	2317,6930	0,0067	0,03
175	NU4 RR 6,19	2319,8257	0,0019	0,50
176	NU4 RR 6,20	2320,5397	0,0044	0,12
177	NU4 RR 6,21	2321,2457	-0,0007	0,12
178	NU4 RR 7, 9	2316,0348	-0,0053	0,12
179	NU4 RR 7,10	2316,7496	-0,0063	0,12
180	NU4 RR 7,11	2317,4589	-0,0124	0,12
181	NU4 RR 7,12	2318,1785	-0,0077	0,03
182	NU4 RR 7,14	2319,6148	0,0000	0,12
183	NU4 RR 7,15	2320,3188	-0,0096	0,50
184	NU4 RR 7,16	2321,0314	-0,0101	0,12
185	NU4 RR 7,18	2322,4604	-0,0059	0,03
186	NU4 RR 7,19	2323,1805	0,0025	0,03
187	NU4 RR 7,20	2323,8929	0,0038	0,03

NO.	IDENT	OBS, FREQ	OBS-CALC	WT
188	NU4 RR 7,21	2324,6060	0,0062	0,03
189	NU4 RR 7,22	2325.3123	0,0024	0.12
190	NU4 RR 7,23	2326.0143	-0,0052	0.03
191	NU4 RR 7,24	2326,7239	-0,0047	0.03
192	NU4 RR 7,25	2327,4320	-0,0051	0,03
193	NU4 RR 8,10	2320.0683	-0,0152	0,03
194	NU4 RR 8,11	2320,7808	-0,0178	0,03
195	NU4 RR 8,13	2322,2317	0,0042	0.03
196	NU4 RR 8,14	2322,9488	0,0075	0,12
197	NU4 RR 8,15	2323,6633	0,0088	0,03
198	NU4 RR 8,16	2324,3679	0,0006	0,12
199	NU4 RR 8,18	2325,7921	0,0007	0,12
200	NU4 RR 8,19	2326,4970	-0,0057	0,12
201	NU4 RR 8,20	2327,2015	-0,0120	0,03
202	NU4 RR 8,21	2327,9211	-0,0026	0,03
203	NU4 RR 9, 9	2322,6566	-0,0094	0,12
204	NU4 RR 9,10	2323,3769	-0,0044	0,50
205	NU4 RR 9,11	2324,0893	-0,0068	0,12
206	NU4 RR 9,12	2324,8019	-0,0086	0,12
207	NU4 RR 9,13	2325,5163	-0,0081	0,50
208	NU4 RR 9,14	2326,2244	-0,0134	0,50
209	NU4 RR 9,15	2326,9312	-0,0196	0.03
210	NU4 RR 9,16	2327,6577	-0,0055	0,03
211	NU4 RR 9,17	2328,3516	-0,0236	0,03
212	NU4 RR 9,18	2329,0830	-0,0036	0,12
213	NU4 RR 9,19	2329,7897	-0,0078	0,03
214	NU4 RR 9,21	2331,2222	0,0045	0,03
215	NU4 RR 9,22	2331,9255	-0,0015	0,03
216	NU4 RR 9,23	2332,6522	0,0165	0,12
217	NU4 RR 9,24	2333,3479	0,0040	0,12
218	NU4 RR 9,26	2334,7535	-0,0050	0,03
219	NU4 RR 9,27	2335,4637	-0,0012	0,03
220	NU4 RR 9,28	2336,1627	-0,0080	0,03
221	NU4 RR 9,29	2336,8596	-0,0163	0,03
222	NU4 RR10,11	2327,3515	-0,0117	0,03
223	NU4 RR10,12	2328,0773	0,0001	0,03
224	NU4 RR10,14	2329,4980	-0,0059	0,03
225	NU4 RR10,15	2330,2135	-0,0030	0,03
226	NU4 RR10,16	2330,9432	0,0146	0,03
227	NU4 RR10,19	2333,0780	0,0163	0.03
228	NU4 RR10,20	2333,7864	0,0147	0,03
229	NU4 RR10,17	2331,6488	0,0086	0,03
230	NU4 RR11,12	2331,3144	0,0015	0.03
231	NU4 RR11,13	2332,0213	-0,0049	0,03
232	NU4 RR11,14	2332,7416	0,0027	0.03
233	NU4 RR11,15	2333,4550	0,0038	0,12
234	NU4 RR11,17	2334,8748	0,0007	0,03
235	NU4 RR11,18	2335,5884	0,0037	0,03
236	NU4 RR11,19	2336,2920	-0,0028	0,03
237	NU4 RR11,20	2337,0143	0,0100	0,03

NO.	IDENT	OBS, FREQ	OBS-CALC	WT
238	NU4 RR12,15	2336,6614	0,0072	0,03
239	NU4 RR12,16	2337,3899	0,0244	0,03
240	NU4 RR12,17	2338,0937	0,0174	0,12
241	NU4 RR12,18	2338,7999	0,0134	0,12
242	NU4 RR12,19	2339,4982	0,0020	0,03
243	NU4 RR12,20	2340,2185	0,0133	0,03
244	NU4 RR12,21	2340,9297	0,0159	0,12
245	NU4 RR12,22	2341,6410	0,0193	0,12
246	2NU4 PP 9,17	4484,9809	-0,0248	0,03
247	2NU4 PP 9,16	4485,7244	-0,0053	0,12
248	2NU4 PP 9,15	4486,4538	0,0003	0,12
249	2NU4 PP 9,14	4487,1775	0,0004	0,03
250	2NU4 PP 9,13	4487,8975	-0,0029	0,03
251	2NU4 PP 9,12	4488,6233	-0,0003	0,03
252	2NU4 PP 9,11	4489,3547	0,0082	0,03
253	2NU4 PP 9,10	4490,0885	0,0195	0,12
254	2NU4 RR 0, 9	4562,4747	0,0047	0,03
255	2NU4 RR 0,10	4563,1895	0,0049	0,03
256	2NU4 RR 0,11	4563,9002	0,0014	0,03
257	2NU4 RR 0,12	4564,6199	0,0075	0,03
258	2NU4 RR 0,13	4565,3270	0,0017	0,03
259	2NU4 RR 0,14	4566,0513	0,0136	0,12
260	2NU4 RR 0,15	4566,7699	0,0204	0,03
261	2NU4 RR 1, 5	4565,8097	0,0001	0,12
262	2NU4 RR 1, 6	4566,5215	-0,0048	0,12
263	2NU4 RR 1, 8	4567,9420	-0,0161	0,12
264	2NU4 RR 1, 9	4568,6645	-0,0087	0,12
265	2NU4 RR 1,10	4569,3793	-0,0084	0,12
266	2NU4 RR 1,11	4570,1010	-0,0007	0,12
267	2NU4 RR 1,12	4570,8164	0,0014	0,03
268	2NU4 RR 1,13	4571.5252	-0,0026	0,12
269	2NU4 RR 1,14	4572,2372	-0,0028	0,12
270	2NU4 RR 2, 5	4571,9608	-0,0019	0,03
271	2NU4 RR 2, 6	4572,6896	0,0103	0,03
272	2NU4 RR 2, 8	4574,1170	0,0062	0,03
273	2NU4 RR 2, 9	4574,8353	0,0096	0,03
274	2NU4 RR 2,10	4575,5387	-0,0014	0,03
275	2NU4 RR 2,11	4576,2553	0,0015	0,12
276	2NU4 RR 2,12	4576,9579	-0,0091	0,03
277	2NU4 RR 2,13	4577,6685	-0,0110	0,03
278	2NU4 RR 2,14	4578,3829	-0,0086	0,03
279	2NU4 RR 2,15	4579,1013	-0,0015	0,03
280	2NU4 RR 2,17	4580,5310	0,0074	0,03
281	2NU4 RR 2,18	4581,2310	-0,0020	0,03
282	2NU4 RR 2,19	4581,9358	-0,0059	0,12
283	2NU4 RR 2,20	4582,6496	-0,0002	0,03
284	2NU4 RR 3, 3	4576,6255	-0,0045	0,50

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 NO.      IDENT             OBS. FREQ   OBS-CALC    WT
285 2NU4 RR 3, 4            4577.3433   -0.0042   0.12
286 2NU4 RR 3, 5            4578.0579   -0.0067   0.50
287 2NU4 RR 3, 6            4578.7714   -0.0096   0.12
288 2NU4 RR 3, 8            4580.2016   -0.0107   0.12
289 2NU4 RR 3, 9            4580.9248   -0.0022   0.12
290 2NU4 RR 3,10            4581.6371   -0.0041   0.12
291 2NU4 RR 3,11            4582.3548    0.0001   0.12
292 2NU4 RR 3,12            4583.0684    0.0007   0.12
293 2NU4 RR 3,13            4583.7833    0.0033   0.12
294 2NU4 RR 3,14            4584.4892   -0.0025   0.12
295 2NU4 RR 3,15            4585.2070    0.0042   0.03
296 2NU4 RR 3,16            4585.9162    0.0030   0.03
297 2NU4 RR 3,17            4586.6264    0.0034   0.03
298 2NU4 RR 3,18            4587.3246   -0.0075   0.03
299 2NU4 RR 3,19            4588.0407    0.0001   0.12
300 2NU4 RR 3,20            4588.7469   -0.0014   0.12
301 2NU4 RR 3,21            4589.4586    0.0032   0.12
302 2NU4 RR 4, 4            4583.3854   -0.0124   0.03
303 2NU4 RR 4, 5            4584.0991   -0.0156   0.03
304 2NU4 RR 4, 6            4584.8264   -0.0046   0.03
305 2NU4 RR 4, 8            4586.2600   -0.0019   0.12
306 2NU4 RR 4, 9            4586.9730   -0.0035   0.12
307 2NU4 RR 4,10            4587.7021    0.0116   0.12
308 2NU4 RR 4,11            4588.4057    0.0019   0.12
309 2NU4 RR 4,12            4589.1240    0.0075   0.03
310 2NU4 RR 4,13            4589.8452    0.0166   0.12
311 2NU4 RR 4,14            4590.5452    0.0051   0.12
312 2NU4 RR 4,16            4591.9598   -0.0012   0.12
313 2NU4 RR 4,17            4592.6623   -0.0082   0.03
314 2NU4 RR 4,18            4593.3679   -0.0114   0.12
315 2NU4 RR 4,19            4594.0921    0.0046   0.03
316 2NU4 RR 4,20            4594.7833   -0.0116   0.03
317 2NU4 RR 4,21            4595.5045    0.0029   0.03
318 2NU4 RR 4,22            4596.1957   -0.0120   0.03
319 2NU4 RR 4,23            4596.9218    0.0088   0.03
320 2NU4 RR 4,26            4599.0083   -0.0162   0.03
321 2NU4 RR 5, 5            4590.1197    0.0072   0.12
322 2NU4 RR 5, 6            4590.8389    0.0102   0.12
323 2NU4 RR 5, 8            4592.2640    0.0048   0.12
324 2NU4 RR 5, 9            4592.9683   -0.0053   0.12
325 2NU4 RR 5,10            4593.6840   -0.0034   0.12
326 2NU4 RR 5,12            4595.1176    0.0046   0.03
327 2NU4 RR 5,13            4595.8257    0.0009   0.03
328 2NU4 RR 5,14            4596.5446    0.0086   0.03
329 2NU4 RR 5,16            4597.9716    0.0152   0.03
330 2NU4 RR 5,17            4598.6701    0.0045   0.03
331 2NU4 RR 5,18            4599.3722   -0.0019   0.12
332 2NU4 RR 5,19            4600.0848    0.0029   0.03
333 2NU4 RR 5,20            4600.7945    0.0056   0.03
334 2NU4 RR 5,21            4601.4998    0.0045   0.03
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 NO.      IDENT               OBS, FREQ     OBS-CALC     WT
335 2NU4 RR 5,22             4602,1981     -0,0029    0,03
336 2NU4 RR 5,23             4602,9030     -0,0029    0,03
337 2NU4 RR 5,24             4603,5916     -0,0185    0,03
338 2NU4 RR 5,25             4604,2975     -0,0160    0,03
339 2NU4 RR 5,26             4605,0018     -0,0144    0,03
340 2NU4 RR 6, 6             4596,7789      0,0055    0,50
341 2NU4 RR 6, 8             4598,2018     -0,0018    0,12
342 2NU4 RR 6, 9             4598,9217      0,0039    0,12
343 2NU4 RR 6,10             4599,6380      0,0067    0,12
344 2NU4 RR 6,11             4600,3502      0,0060    0,12
345 2NU4 RR 6,12             4601,0661      0,0097    0,03
346 2NU4 RR 6,13             4601,7755      0,0075    0,12
347 2NU4 RR 6,14             4602,4878      0,0089    0,12
348 2NU4 RR 6,16             4603,8980     -0,0007    0,12
349 2NU4 RR 6,17             4604,6061     -0,0015    0,12
350 2NU4 RR 6,18             4605,3074     -0,0083    0,12
351 2NU4 RR 6,19             4606,0332      0,0100    0,03
352 2NU4 RR 6,20             4606,7385      0,0087    0,03
353 2NU4 RR 6,21             4607,4502      0,0143    0,12
354 2NU4 RR 6,22             4608,1430      0,0018    0,03
355 2NU4 RR 6,24             4609,5419     -0,0075    0,12
356 2NU4 RR 6,25             4610,2426     -0,0098    0,03
357 2NU4 RR 6,26             4610,9551      0,0004    0,03
358 2NU4 RR 6,27             4611,6539     -0,0022    0,03
359 2NU4 RR 6,28             4612,3554     -0,0014    0,03
360 2NU4 RR 6,29             4613,0409     -0,0158    0,03
361 2NU4 RR 6,30             4613,7456     -0,0102    0,03
362 2NU4 RR 6,32             4615,1388     -0,0127    0,03
363 2NU4 RR 6,33             4615,8386     -0,0095    0,03
364 2NU4 RR 7, 8             4604,1030      0,0085    0,12
365 2NU4 RR 7, 9             4604,8143      0,0059    0,12
366 2NU4 RR 7,10             4605,5258      0,0041    0,12
367 2NU4 RR 7,11             4606,2395      0,0052    0,12
368 2NU4 RR 7,12             4606,9482      0,0019    0,03
369 2NU4 RR 7,13             4607,6561     -0,0015    0,03
370 2NU4 RR 7,14             4608,3772      0,0090    0,03
371 2NU4 RR 7,16             4609,7893      0,0019    0,03
372 2NU4 RR 7,17             4610,4974      0,0015    0,03
373 2NU4 RR 7,18             4611,2196      0,0159    0,03
374 2NU4 RR 7,19             4611,9236      0,0128    0,03
375 2NU4 RR 7,20             4612,6311      0,0140    0,03
376 2NU4 RR 7,21             4613,3320      0,0092    0,03
377 2NU4 RR 7,22             4614,0381      0,0105    0,03
378 2NU4 RR 7,24             4615,4505      0,0154    0,03
379 2NU4 RR 7,25             4616,1430      0,0054    0,12
380 2NU4 RR 7,26             4616,8358     -0,0036    0,03
381 2NU4 RR 7,27             4617,5633      0,0229    0,03
382 2NU4 RR 7,28             4618,2382     -0,0024    0,03
383 2NU4 RR 7,29             4618,9471      0,0071    0,12
384 2NU4 RR 7,30             4619,6269     -0,0116    0,03
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NO.	IDENT	OBS, FREQ	OBS-CALC	WT
385	2NU4 RR 7,31	4620,3413	0,0050	0,03
386	2NU4 RR 7,32	4621,0295	-0,0036	0,03
387	2NU4 RR 7,33	4621,7314	0,0022	0,03
388	2NU4 RR 7,34	4622,4122	-0,0122	0,03
389	2NU4 RR 7,35	4623,1026	-0,0162	0,03
390	2NU4 RR 8,10	4611,3611	0,0031	0,12
391	2NU4 RR 8,11	4612,0740	0,0037	0,12
392	2NU4 RR 8,12	4612,7757	-0,0063	0,12
393	2NU4 RR 8,13	4613,4896	-0,0034	0,12
394	2NU4 RR 8,14	4614,1926	-0,0107	0,12
395	2NU4 RR 8,16	4615,6419	0,0201	0,12
396	2NU4 RR 8,17	4616,3578	0,0278	0,03
397	2NU4 RR 8,18	4617,0569	0,0194	0,03
398	2NU4 RR 8,19	4617,7591	0,0149	0,03
399	2NU4 RR 8,20	4618,4612	0,0110	0,03
400	2NU4 RR 8,21	4619,1712	0,0158	0,03
401	2NU4 RR 8,22	4619,8733	0,0135	0,03
402	2NU4 RR 8,24	4621,2750	0,0086	0,12
403	2NU4 RR 8,25	4621,9649	-0,0036	0,03
404	2NU4 RR 8,26	4622,6735	0,0038	0,03
405	2NU4 RR 8,27	4623,3726	0,0023	0,12
406	2NU4 RR 8,28	4624,0716	0,0016	0,12
407	2NU4 RR 8,29	4624,7559	-0,0130	0,03
408	2NU4 RR 8,30	4625,4673	0,0004	0,03
409	2NU4 RR 8,32	4626,8525	-0,0080	0,03
410	2NU4 RR 8,33	4627,5446	-0,0114	0,03
411	2NU4 RR 8,34	4628,2278	-0,0228	0,03
412	2NU4 RR 8,35	4628,9217	-0,0226	0,03
413	2NU4 RR 8,36	4629,6255	-0,0117	0,03
414	2NU4 RR 9, 9	4616,4211	-0,0057	0,12
415	2NU4 RR 9,10	4617,1314	-0,0081	0,12
416	2NU4 RR 9,11	4617,8425	-0,0091	0,12
417	2NU4 RR 9,12	4618,5613	-0,0017	0,12
418	2NU4 RR 9,13	4619,2750	0,0013	0,12
419	2NU4 RR 9,14	4619,9827	-0,0010	0,12
420	2NU4 RR 9,16	4621,4097	0,0081	0,12
421	2NU4 RR 9,17	4622,1151	0,0057	0,12
422	2NU4 RR 9,21	4624,9363	0,0032	0,03
423	2NU4 RR 9,22	4625,6402	0,0030	0,03
424	2NU4 RR 9,24	4627,0488	0,0060	0,03
425	2NU4 RR 9,25	4627,7620	0,0175	0,03
426	2NU4 RR 9,26	4628,4484	0,0031	0,03
427	2NU4 RR 9,27	4629,1599	0,0146	0,03
428	2NU4 RR 9,28	4629,8485	0,0040	0,03
429	2NU4 RR10,13	4625,0039	0,0048	0,03
430	2NU4 RR10,14	4625,7264	0,0176	0,03
431	2NU4 RR10,16	4627,1279	0,0020	0,03
432	2NU4 RR10,17	4627,8380	0,0046	0,03
433	2NU4 RR10,18	4628,5651	0,0251	0,03
434	2NU4 RR11,11	4629,2432	-0,0046	0,12

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 NO.      IDENT         OBS. FREQ    OBS-CALC    WT
435 2NU4 RR11,12       4629,9569    -0,0017   0,12
436 2NU4 RR11,13       4630,6602    -0,0084   0,12
437 2NU4 RR11,14       4631,3779    -0,0001   0,12
438 2NU4 RR11,15       4632,0803    -0,0062   0,12
439 2NU4 RR11,16       4632,7822    -0,0121   0,12
440 2NU4 RR11,17       4633,4894    -0,0120   0,12
441 2NU4 RR12,12       4635,5688    -0,0032   0,12
442 2NU4 RR12,13       4636,2751    -0,0066   0,12
443 2NU4 RR12,15       4637,7007     0,0018   0,12
444 2NU4 RR12,16       4638,4088     0,0025   0,12
445 2NU4 RR12,17       4639,1136     0,0007   0,12
446 2NU4 RR12,18       4639,8145    -0,0043   0,12
447 2NU4 RR12,19       4640,5095    -0,0144   0,12
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APPENDIX E

RESULTS OF A SINGLE BAND FIT

OF NU4 OF CD3BR

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NO,     IDENT         OBS, FREQ   OBS-CALC    WT
 1   NU4 PP13,18     2238,1461     0,0108   0,03
 2   NU4 PP13,17     2238,6520     0,0020   0,03
 3   NU4 PP13,14     2240,2005     0,0068   0,03
 4   NU4 PP13,13     2240,7118     0,0037   0,03
 5   NU4 PP12,27     2237,5328     0,0125   0,03
 6   NU4 PP12,26     2238,0451     0,0093   0,03
 7   NU4 PP12,25     2238,5516     0,0003   0,03
 8   NU4 PP12,22     2240,1022     0,0047   0,03
 9   NU4 PP12,21     2240,6178     0,0051   0,12
10   NU4 PP12,19     2241,6404    -0,0027   0,03
11   NU4 PP12,18     2242,1611     0,0030   0,03
12   NU4 PP12,17     2242,6710    -0,0021   0,03
13   NU4 PP12,15     2243,7338     0,0310   0,03
14   NU4 PP12,14     2244,2154    -0,0022   0,03
15   NU4 PP12,13     2244,7375     0,0054   0,03
16   NU4 PP12,12     2245,2479     0,0012   0,03
17   NU4 PP11,26     2242,0391     0,0056   0,03
18   NU4 PP11,25     2242,5653     0,0160   0,03
19   NU4 PP11,23     2243,5893     0,0086   0,03
20   NU4 PP11,22     2244,0991     0,0028   0,03
21   NU4 PP11,21     2244,6169     0,0050   0,03
22   NU4 PP11,20     2245,1193    -0,0080   0,03
23   NU4 PP11,18     2246,1568    -0,0012   0,03
24   NU4 PP11,17     2246,6706    -0,0027   0,03
25   NU4 PP11,15     2247,6988    -0,0046   0,03
26   NU4 PP11,14     2248,2099    -0,0085   0,12
27   NU4 PP11,13     2248,7185    -0,0147   0,12
28   NU4 PP11,12     2249,2431    -0,0048   0,03
29   NU4 PP11,11     2249,7539    -0,0086   0,03
30   NU4 PP10,27     2245,5153     0,0234   0,03
31   NU4 PP10,26     2246,0379     0,0299   0,03
32   NU4 PP10,25     2246,5417     0,0176   0,03
33   NU4 PP10,24     2247,0601     0,0200   0,03
34   NU4 PP10,23     2247,5686     0,0125   0,03
35   NU4 PP10,21     2248,6023     0,0145   0,03
36   NU4 PP10,20     2249,1150     0,0115   0,12
37   NU4 PP10,19     2249,6311     0,0119   0,03
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NO,      IDENT           OBS, FREQ   OBS=CALC    WT
38   NU4 PP10,18         2250,1420     0,0073   0,03
39   NU4 PP10,17         2250,6466    =0,0036   0,03
40   NU4 PP10,15         2251,6756    =0,0052   0,03
41   NU4 PP10,14         2252,1893    =0,0066   0,03
42   NU4 PP10,13         2252,6970    =0,0140   0,12
43   NU4 PP10,12         2253,2170    =0,0089   0,12
44   NU4 PP10,11         2253,7386    =0,0021   0,12
45   NU4 PP10,10         2254,2544    =0,0009   0,12
46   NU4 PP 9,35         2245,3752     0,0659   0,00
47   NU4 PP 9,34         2245,8885     0,0624   0,00
48   NU4 PP 9,33         2246,4041     0,0612   0,00
49   NU4 PP 9,32         2246,9183     0,0587   0,00
50   NU4 PP 9,30         2247,9425     0,0495   0,00
51   NU4 PP 9,29         2248,4630     0,0534   0,00
52   NU4 PP 9,28         2248,9582     0,0320   0,00
53   NU4 PP 9,27         2249,4815     0,0388   0,00
54   NU4 PP 9,25         2250,5143     0,0388   0,00
55   NU4 PP 9,26         2250,0025     0,0434   0,00
56   NU4 PP 9,24         2251,0254     0,0336   0,00
57   NU4 PP 9,23         2251,5490     0,0410   0,00
58   NU4 PP 9,22         2252,0538     0,0296   0,00
59   NU4 PP 9,21         2252,5654     0,0251   0,00
60   NU4 PP 9,20         2253,0802     0,0240   0,00
61   NU4 PP 9,19         2253,6034     0,0313   0,00
62   NU4 PP 9,18         2254,1055     0,0176   0,00
63   NU4 PP 9,17         2254,6158     0,0122   0,00
64   NU4 PP 9,16         2255,1324     0,0132   0,00
65   NU4 PP 9,14         2256,1673     0,0173   0,00
66   NU4 PP 9,13         2256,6824     0,0172   0,00
67   NU4 PP 9,12         2257,1961     0,0158   0,00
68   NU4 PP 9,11         2257,7060     0,0108   0,00
69   NU4 PP 9,10         2258,2212     0,0111   0,00
70   NU4 PP 9, 9         2258,7339     0,0091   0,00
71   NU4 PP 7,24         2258,7936    =0,0301   0,00
72   NU4 PP 7,22         2259,8332    =0,0240   0,00
73   NU4 PP 7,21         2260,3463    =0,0274   0,00
74   NU4 PP 7,20         2260,8664    =0,0238   0,00
75   NU4 PP 7,19         2261,3862    =0,0203   0,00
76   NU4 PP 7,18         2261,9002    =0,0225   0,00
77   NU4 PP 7,17         2262,4218    =0,0170   0,00
78   NU4 PP 7,16         2262,9418    =0,0130   0,00
79   NU4 PP 7,14         2263,9658    =0,0206   0,00
80   NU4 PP 7,15         2263,4564    =0,0143   0,00
81   NU4 PP 7,13         2264,4881    =0,0139   0,12
82   NU4 PP 7,12         2265,0032    =0,0142   0,12
83   NU4 PP 7,11         2265,5199    =0,0128   0,12
84   NU4 PP 7,10         2266,0381    =0,0097   0,12
85   NU4 PP 7, 9         2266,5597    =0,0031   0,12
86   NU4 PQ 7, 7         2271,1906     0,0067   0,03
87   NU4 PP 6,21         2264,2332    =0,0210   0,03
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NO,	IDENT	OBS, FREQ	OBS-CALC	WT
88	NU4 PP 6,20	2264,7451	-0,0258	0,03
89	NU4 PP 6,19	2265,2741	-0,0133	0,03
90	NU4 PP 6,18	2265,7814	-0,0225	0,03
91	NU4 PP 6,17	2266,3114	-0,0088	0,03
92	NU4 PP 6,14	2267,8472	-0,0211	0,03
93	NU4 PP 6,13	2268,3711	-0,0129	0,03
94	NU4 PP 6,12	2268,8852	-0,0144	0,03
95	NU4 PP 6,11	2269,4048	-0,0102	0,03
96	NU4 PP 6,10	2269,9172	-0,0131	0,03
97	NU4 PP 6, 9	2270,4325	-0,0129	0,03
98	NU4 PP 6, 7	2271,4642	-0,0109	0,03
99	NU4 PP 6, 6	2271,9765	-0,0132	0,03
100	NU4 PP 5,21	2268,0980	-0,0122	0,03
101	NU4 PP 5,20	2268,6136	-0,0135	0,03
102	NU4 PP 5,19	2269,1332	-0,0106	0,03
103	NU4 PP 5,18	2269,6517	-0,0088	0,12
104	NU4 PP 5,17	2270,1750	-0,0020	0,12
105	NU4 PP 5,16	2270,6936	0,0003	0,12
106	NU4 PP 5,14	2271,7162	-0,0094	0,12
107	NU4 PP 5,13	2272,2382	-0,0033	0,12
108	NU4 PP 5,12	2272,7600	0,0028	0,03
109	NU4 PP 5,11	2273,2782	0,0054	0,12
110	NU4 PP 5,10	2273,7970	0,0088	0,03
111	NU4 PP 5, 9	2274,3083	0,0049	0,12
112	NU4 PP 5, 7	2275,3454	0,0121	0,03
113	NU4 PP 5, 6	2275,8630	0,0150	0,12
114	NU4 PP 5, 5	2276,3786	0,0161	0,12
115	NU4 PP 4,20	2272,4563	-0,0022	0,12
116	NU4 PP 4,19	2272,9743	-0,0011	0,12
117	NU4 PP 4,18	2273,4914	-0,0009	0,12
118	NU4 PP 4,17	2274,0123	0,0034	0,12
119	NU4 PP 4,16	2274,5326	0,0071	0,12
120	NU4 PP 4,14	2275,5690	0,0110	0,12
121	NU4 PP 4,13	2276,0865	0,0124	0,12
122	NU4 PP 4,12	2276,5923	0,0023	0,03
123	NU4 PP 4,11	2277,1044	-0,0013	0,12
124	NU4 PP 4, 9	2278,1417	0,0052	0,03
125	NU4 PP 4, 7	2279,1680	0,0013	0,12
126	NU4 PP 4, 6	2279,6894	0,0080	0,12
127	NU4 PP 4, 5	2280,2060	0,0100	0,03
128	NU4 PP 4, 4	2280,7105	0,0002	0,12
129	NU4 PP 3,28	2272,1140	-0,0088	0,03
130	NU4 PP 3,27	2272,6342	-0,0068	0,03
131	NU4 PP 3,26	2273,1543	-0,0047	0,12
132	NU4 PP 3,25	2273,6712	-0,0058	0,03
133	NU4 PP 3,24	2274,1894	-0,0054	0,12
134	NU4 PP 3,22	2275,2239	-0,0062	0,12
135	NU4 PP 3,21	2275,7379	-0,0096	0,12
136	NU4 PP 3,20	2276,2683	0,0035	0,12
137	NU4 PP 3,19	2276,7840	0,0020	0,03

NO,	IDENT	OBS, FREQ	OBS-CALC	WT
138	NU4 PP 3,18	2277,2938	-0,0052	0,12
139	NU4 PP 3,17	2277,8149	-0,0010	0,12
140	NU4 PP 3,16	2278,3258	-0,0067	0,12
141	NU4 PP 3,14	2279,3682	0,0028	0,12
142	NU4 PP 3,13	2279,8759	-0,0057	0,12
143	NU4 PP 3,12	2280,3995	0,0019	0,12
144	NU4 PP 3,11	2280,9130	-0,0004	0,03
145	NU4 PP 3,10	2281,4261	-0,0030	0,12
146	NU4 PP 3, 9	2281,9391	-0,0054	0,03
147	NU4 PP 3, 7	2282,9787	0,0039	0,03
148	NU4 PP 3, 6	2283,4894	-0,0003	0,03
149	NU4 PP 3, 5	2284,0116	0,0073	0,03
150	NU4 PP 3, 4	2284,5000	-0,0187	0,03
151	NU4 PP 2,26	2276,9509	0,0121	0,03
152	NU4 PP 2,25	2277,4610	0,0040	0,12
153	NU4 PP 2,24	2277,9812	0,0061	0,03
154	NU4 PP 2,23	2278,5071	0,0141	0,03
155	NU4 PP 2,21	2279,5345	0,0061	0,03
156	NU4 PP 2,20	2280,0495	0,0036	0,03
157	NU4 PP 2,19	2280,5578	-0,0054	0,03
158	NU4 PP 2,18	2281,0867	0,0063	0,03
159	NU4 PP 2,17	2281,5968	-0,0006	0,12
160	NU4 PP 2,16	2282,1255	0,0112	0,12
161	NU4 PP 2,14	2283,1556	0,0081	0,03
162	NU4 PP 2,13	2283,6737	0,0099	0,12
163	NU4 PP 2,12	2284,1815	0,0016	0,03
164	NU4 PP 2,11	2284,7007	0,0049	0,12
165	NU4 PP 2,10	2285,2247	0,0131	0,12
166	NU4 PP 2, 9	2285,7294	0,0023	0,12
167	NU4 PP 2, 7	2286,7684	0,0108	0,12
168	NU4 PP 2, 6	2287,2826	0,0101	0,12
169	NU4 PP 2, 5	2287,8034	0,0162	0,03
170	NU4 PP 1,24	2281,7436	0,0138	0,03
171	NU4 PP 1,23	2282,2605	0,0126	0,03
172	NU4 PP 1,21	2283,2810	-0,0027	0,12
173	NU4 PP 1,20	2283,8120	0,0106	0,03
174	NU4 PP 1,19	2284,3277	0,0088	0,03
175	NU4 PP 1,18	2284,8275	-0,0088	0,12
176	NU4 PP 1,17	2285,3656	0,0122	0,03
177	NU4 PP 1,16	2285,8789	0,0085	0,12
178	NU4 PP 1,14	2286,9124	0,0085	0,03
179	NU4 PP 1,13	2287,4272	0,0069	0,12
180	NU4 PP 1,12	2287,9286	-0,0079	0,03
181	NU4 PP 1,10	2288,9817	0,0133	0,03
182	NU4 PP 1, 9	2289,4866	0,0025	0,03
183	NU4 PP 1, 7	2290,5250	0,0103	0,03
184	NU4 PP 1, 6	2291,0302	0,0005	0,03
185	NU4 PP 1, 5	2291,5511	0,0067	0,03
186	NU4 RR 1,11	2307,6975	0,0065	0,03
187	NU4 RR 2, 3	2307,3015	0,0206	0,03

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NO,      IDENT          OBS, FREQ   OBS-CALC     WT
188   NU4 RR 2, 4      2307,7993     0,0063   0,12
189   NU4 RR 2, 5      2308,3107     0,0059   0,03
190   NU4 RR 2, 7      2309,3233    -0,0041   0,12
191   NU4 RR 2, 8      2309,8464     0,0081   0,12
192   NU4 RR 2, 9      2310,3478    -0,0010   0,12
193   NU4 RR 2,10      2310,8660     0,0070   0,12
194   NU4 RR 2,11      2311,3728     0,0040   0,00
195   NU4 RR 2,15      2313,4089     0,0041   0,03
196   NU4 RR 2,16      2313,9141     0,0011   0,03
197   NU4 RR 3, 4      2311,4467     0,0021   0,03
198   NU4 RR 3, 5      2311,9493    -0,0070   0,03
199   NU4 RR 3, 7      2312,9699    -0,0089   0,03
200   NU4 RR 3, 8      2313,4775    -0,0120   0,03
201   NU4 RR 3, 9      2313,9926    -0,0073   0,03
202   NU4 RR 6,17      2328,8390    -0,0175   0,12
203   NU4 RR 6,16      2328,3370    -0,0124   0,12
204   NU4 RR 6,15      2327,8278    -0,0142   0,12
205   NU4 RR 6,14      2327,3165    -0,0177   0,12
206   NU4 RR 6,13      2326,8269     0,0009   0,12
207   NU4 RR 6,12      2326,3069    -0,0106   0,12
208   NU4 RR 6,11      2325,7889    -0,0196   0,12
209   NU4 RR 6,10      2325,2724    -0,0268   0,03
210   NU4 RR 6, 9      2324,7824    -0,0071   0,12
211   NU4 RR 6, 8      2324,2723    -0,0072   0,50
212   NU4 RR 6, 7      2323,7660    -0,0031   0,50
213   NU4 RR 8, 8      2331,3546     0,0209   0,12
214   NU4 RR 8, 9      2331,8566     0,0131   0,12
215   NU4 RR 8,11      2332,8803     0,0184   0,12
216   NU4 RR 8,13      2333,8937     0,0150   0,12
217   NU4 RR 8,14      2334,4027     0,0162   0,03
218   NU4 RR 8,15      2334,9003     0,0064   0,12
221   NU4 RR 9, 9      2335,3456     0,0176   0,00
222   NU4 RR 9,11      2336,3765     0,0309   0,00
223   NU4 RR 9,13      2337,3790     0,0166   0,00
224   NU4 RR 9,14      2337,8857     0,0156   0,00
225   NU4 RR 9,15      2338,4011     0,0238   0,00
226   NU4 RR 9,16      2338,9160     0,0319   0,00
244   NU4 RR 9,18      2339,9188     0,0224   0,03
227   NU4 RR 9,20      2340,9374     0,0304   0,00
228   NU4 RR 9,21      2341,4396     0,0279   0,00
229   NU4 RR 9,22      2341,9348     0,0189   0,00
230   NU4 RR 9,23      2342,4344     0,0148   0,00
231   NU4 RR 9,24      2342,9363     0,0134   0,00
232   NU4 RR 9,26      2343,9399     0,0117   0,00
233   NU4 RR 9,28      2344,9120    -0,0195   0,00
234   NU4 RR 9,29      2345,4149    -0,0176   0,00
235   NU4 RR 9,31      2346,4055    -0,0275   0,00
236   NU4 RR 9,32      2346,9146    -0,0180   0,00
237   NU4 RR 9,33      2347,4038    -0,0278   0,00
238   NU4 RR 9,34      2347,9114    -0,0187   0,00
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 NO,     IDENT          OBS, FREQ   ORS-CALC    WT
239   NU4 RR 9,35       2348,3876   -0,0406   0,00
219   NU4 RR10,11       2339,8142    0,0128   0,03
220   NU4 RR10,13       2340,8403    0,0228   0,03
240   NU4 RR10,14       2341,3327    0,0078   0,03
241   NU4 RR10,15       2341,8417    0,0098   0,03
242   NU4 RR10,16       2342,3458    0,0073   0,03
243   NU4 RR10,17       2342,8533    0,0087   0,03
245   NU4 RR11,11       2343,2354    0,0075   0,03
246   NU4 RR11,13       2344,2572    0,0137   0,03
247   NU4 RR11,14       2344,7590    0,0083   0,03
248   NU4 RR11,15       2345,2595    0,0020   0,03
249   NU4 RR11,16       2345,7679    0,0041   0,03
250   NU4 RR11,19       2347,2805    0,0003   0,03
251   NU4 RR11,21       2348,2927    0,0038   0,03
252   NU4 RR12,12       2347,1066   -0,0264   0,03
253   NU4 RR12,14       2348,1422   -0,0051   0,03
254   NU4 RR12,15       2348,6535   -0,0004   0,12
255   NU4 RR12,16       2349,1612    0,0012   0,03
256   NU4 RR12,17       2349,6548   -0,0108   0,12
257   NU4 RR12,18       2350,1752    0,0044   0,03
258   NU4 RR12,19       2350,6686   -0,0070   0,03
259   NU4 RR12,20       2351,1791   -0,0007   0,03
260   NU4 RR12,23       2352,6971    0,0072   0,03
261   NU4 RR12,24       2353,1904   -0,0019   0,00
262   NU4 RR13,15       2352,0231    0,0024   0,03
263   NU4 RR13,16       2352,5269    0,0004   0,03
264   NU4 RR13,18       2353,5385    0,0016   0,03
265   NU4 RR13,22       2355,5457   -0,0062   0,03
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