To the Graduate Council:

I am submitting herewith a dissertation written by George Wesley Halsey entitled "Interpretation and Analysis of Perturbed Spectra of Axially Symmetric Molecules with Applications to $^{13}CD_3F$." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Physics.

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INTERPRETATION AND ANALYSIS OF PERTURBED SPECTRA OF AXIALLY SYMMETRIC MOLECULES WITH APPLICATIONS TO $^{13}CD_3F$

A Dissertation

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ABSTRACT

The main thrust of this study is the development and testing of an algorithm to fit perturbed vibration-rotation molecular spectra. The algorithm is first developed in a general form and then applied to the vibration-rotation spectra of axially symmetric molecules using simulated data.

The 5 μm absorption spectrum of $^{13}CD_3F$ is very complex. There are 24 vibrational levels in the region from 1800 cm^{-1} to 2250 cm^{-1}. There are many strong vibrational and rotational resonances linking these states. The states included in this analysis are $\nu_4(\ell_4=\pm1)$, $2\nu_2(\ell=0)$, $\nu_2+\nu_5(\ell_5=\pm1)$, $2\nu_5(\ell_5=0,\pm2)$, $\nu_2+\nu_3(\ell=0)$, $\nu_1(\ell=0)$ and $\nu_3+\nu_5(\ell_5=\pm1)$, all of which lie above 2050 cm^{-1}. The states omitted in this analysis are $\nu_2+\nu_6(\ell_6=\pm1)$, $\nu_5+\nu_6(\ell_5=\pm1,\nu_6=\pm1)$, $2\nu_3(\ell=0)$, $\nu_3+\nu_6(\ell_6=\pm1)$, and $2\nu_6(\ell_6=0,\pm2)$, all of which lie below 2025 cm^{-1}. These two groups of vibrational states are weakly linked by a higher order vibration-rotation resonance between ν_1 and $\nu_2+\nu_6(\ell_6=-1)$ and a weak vibrational resonance between ν_1 and $2\nu_3$.

The absorption spectrum of $^{13}CD_3F$ was recorded at a resolution of 0.018 cm^{-1} and deconvolved to an effective resolution of 0.006 cm^{-1}. The ν_1, $2\nu_5(\ell_5=0)$, $2\nu_2$ and $\nu_4(\ell_4=\pm1)$ bands were analyzed individually to obtain estimates of the molecular parameters of these states. The local and nonlocal resonances were characterized and interaction constants were estimated which gave a qualitative agreement with the observed spectrum.

The parameters were then refined using a Hamiltonian model which included all possible interactions from the vibration-rotation Hamiltonian through third order with the restriction that $\Delta K - \sum \Delta \ell = 0$.

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CHAPTER I

THE HAMILTONIAN FOR VIBRATION-ROTATION ENERGY

I-1. THE CLASSICAL PROBLEM

The total energy expression of a polyatomic molecule consisting of n nuclei and m electrons is very complicated. However, for the purpose of infrared molecular spectroscopy some simplifications can be made. The Born-Oppenheimer approximation (Born and Oppenheimer, 1927) allows one to neglect the motion of the m electrons. The motion of the electrons is so much faster than that of the nuclei that the electrons can be considered as a cloud about the whole molecule. Additionally, three degrees of freedom associated with the translational motion of the center of mass of the molecule can be neglected. The effect of this motion is to give an observed transition a Gaussian profile due to the statistical spread of the molecular velocities along the direction of a probing beam. Thus there are 3n-3 remaining degrees of freedom to describe the positions of the 3n nuclei. The 3n-3 degrees of freedom correspond to 3 rotational coordinates and 3n-6 vibrational coordinates. The vibrational and rotational energies cannot be completely separated however.

Most molecules can be considered as nearly rigid, the vibrational amplitudes of the individual nuclei being small compared to the average internuclear separation. For the purpose of analyzing the

rotational motion consider a reference frame set in the equilibrium configuration of the molecule. For convenience this system is oriented so that the inertia tensor is diagonal. There is no unique way of choosing the three angular coordinates needed to describe the position of the molecule-fixed reference frame with respect to a laboratory or space-fixed reference frame. In this development the angles chosen are rotations about the Cartesian axes of the space-fixed frame. The angular momentum $\underline{P}$ and the angular velocity $\underline{\omega}$ are related by:

$$\underline{P} = \underline{\underline{I}} \cdot \underline{\omega} \ , \tag{1-1}$$

where $\underline{\underline{I}}$ is the inertia tensor of the rigid body.

Assuming harmonic vibrations, a transformation can be made between the 3n Cartesian displacements of the nuclei and the 3n-6 normal coordinates of the form:

$$Q_{s\sigma} = \sum_{i=1}^{n} \sum_{\alpha=x,y,z} (\ell_{is\sigma}^{\alpha})^{-1} (\sqrt{m_i}\ \Delta\alpha_i) \tag{1-2}$$

or

$$(\sqrt{m_i}\ \Delta\alpha_i) = \sum_{s\sigma} \ell_{is\sigma} Q_{s\sigma} \tag{1-3}$$

where $\sqrt{m_i}\ \Delta\alpha_i$ are the mass adjusted Cartesian coordinates and $Q_{s\sigma}$ is the normal coordinate corresponding to the s-th vibrational mode with σ denoting the degeneracy of that mode. The mass of the i-th nucleus is m_i and $\Delta\alpha_i$ is the displacement from equilibrium for α = x, y, and z.

The conjugate momentum of the coordinate $Q_{s\sigma}$ is given by

$$p^*_{s\sigma} = -i\hbar \frac{\partial T}{\partial \dot{Q}_{s\sigma}} \tag{1-4}$$

where T is the total kinetic energy given by:

$$2T = \sum_{\alpha} P_{\alpha}\omega_{\alpha} + \sum_{s\sigma} p^*_{s\sigma}\dot{Q}_{s\sigma} \ . \tag{1-5}$$

With the additional definitions

$$P_{\alpha} = \sum_{s\sigma} A^{\alpha}_{s\sigma} p^*_{s\sigma} \tag{1-6}$$

and

$$A_{s\sigma} = \sum_{is'\sigma'} \{\ell^{\beta}_{is'\sigma'}\ell^{\gamma}_{is\sigma} - \ell^{\gamma}_{is'\sigma'}\ell^{\beta}_{is\sigma}\} \tag{1-7}$$

the total kinetic energy becomes

$$2T = \sum_{\alpha} (P_{\alpha} - p_{\alpha})\omega_{\alpha} + \sum_{s\sigma} (p^*_{s\sigma})^2 \ . \tag{1-8}$$

It is necessary to carefully distinguish between $\underline{P}$, the total angular momentum, and $\underline{p}$, the angular momentum due to vibration. The angular momentum due to rotation is thus $\underline{P} - \underline{p}$ and is related to the angular velocity $\underline{\omega}$ by:

$$\underline{\omega} = \underline{\underline{\mu}} (\underline{P} - \underline{p}) \ , \tag{1-9}$$

or

$$\omega_\alpha = \sum_\beta \mu_{\alpha\beta}(P_\alpha - p_\alpha) \ , \qquad (1\text{-}10)$$

where the elements of $\underline{\underline{\mu}}$ are functions of the inertia tensor elements and the $A_{s\sigma}$'s.

With the addition of the potential energy V, the vibration-rotation Hamiltonian can now be written:

$$H = 1/2 \sum_{\alpha\beta} \mu_{\alpha\beta}(P_\alpha - p_\alpha)(P_\beta - p_\beta) + 1/2 \sum_{s\sigma} (p^*_{s\sigma})^2 + V \ . \qquad (1\text{-}11)$$

It can be assumed that for small displacements from the equilibrium position the potential energy can be expanded in a Taylor series in the normal coordinates, $Q_{s\sigma}$:

$$V = 1/2 \sum_{s\sigma} \lambda_s Q^2_{s\sigma} + \sum_{s\sigma} \sum_{s'\sigma'} \sum_{s''\sigma''} K_{s\sigma s'\sigma' s''\sigma''} Q_{s\sigma} Q_{s'\sigma'} Q_{s''\sigma''} +$$

$$\text{higher order terms.} \qquad (1\text{-}12)$$

I-2. THE QUANTUM MECHANICAL PROBLEM

Direct substitution of quantum mechanical operators into Eq. (1-12) does not directly yield a Hamiltonian operator in Hermitian form. This problem has been studied by Wilson and Howard (1936), Darling and Dennison (1946), and by Watson (1968). The formalism of Watson yields the simplest form:

$$H_{op} = 1/2 \sum_{\alpha\beta} (P_\alpha - p_\alpha)\mu_{\alpha\beta}(P_\beta - p_\beta) + 1/2 \sum_{s\sigma} (p^*_{s\sigma})^2 + U + V \ , \qquad (1\text{-}13)$$

in which U is a function of coordinates but not momenta and is small

compared to V. The wave equation for this operator cannot be solved analytically due to the complicated form of H_{op} given in Eq. (1-13). A systematic method of finding approximate solutions to the wave equation, developed by Goldsmith (1956), Amat and Nielsen (1957,1958) and specialized by Tarrago (1965) is outlined here.

The elements of the Hamiltonian are expanded in the normal coordinates and the resulting terms are collected by order of magnitude to yield

$$H = H_0 + H_1 + H_2 + H_3 + H_4 + \ldots \tag{1-14}$$

The zero-th order term has the form

$$H_0 = 1/2 \sum_{\alpha\beta} \frac{P_\alpha^2}{I_{\alpha\beta}} + 1/2 \sum_{s\sigma} \{(p^*_{s\sigma})^2 + \lambda_s Q^2_{s\sigma}\} , \tag{1-15}$$

which is simply the rigid rotor-harmonic oscillator Hamiltonian. This Hamiltonian yields a solvable wave equation that describes the gross features of molecular vibration-rotation spectra. Specifically, for an axial molecule ($I_\alpha = I_\beta \neq I_\gamma$) the eigenfunctions may be written:

$$|\psi> = |\psi_r>|\psi_v> = |J,K>|v_{n_1}>|v_{n_2}> \ldots |v_{t_1},\ell_{t_1}>|v_{t_2},\ell_{t_2}> \ldots \tag{1-16}$$

where J and K are the angular momentum quantum numbers, the v_n are nondegenerate vibrational quantum numbers, and v_t, ℓ_t are the quantum numbers for the degenerate vibrations. These zero-th order eigenfunctions form a basis set in which wave functions for a model

Hamiltonian including higher order terms from the full Hamiltonian are expressible.

All matrix elements appearing in H of the form

$$\langle\psi|Op|\psi'\rangle = \langle\{v_n\},\{v_t,\ell_t\},J,K|Op|\{v_n'\},\{v_t',\ell_t'\},J',K'\rangle \qquad (1\text{-}17)$$

are tabulated by Amat (1957, 1958), where Op is p_x, p_y, p_z, $P^*_{s\sigma}$ or $Q_{s\sigma}$. Values of matrix elements from the Hamiltonian extended through fourth order are given by Goldsmith, Amat and Nielsen (1956) and Amat, Nielsen and Tarrago (1971).

The zero-th order Hamiltonian matrix is diagonal in all quantum numbers since its eigenfunctions form the basis set for the representation. Higher order terms in the expansion of the Hamiltonian are diagonal only in J. The off-diagonal elements of H_n will generally contribute to the energy as diagonal elements of H_{2n}. Thus the diagonal elements of $H_0 + H_1$ yield a good first order approximation. Amat and Nielsen (1957, 1958, 1962), Tarrago (1965), Goldsmith (1956), and Amat, Nielsen and Tarrago (1971) have shown that it is possible to recast H into a form which is diagonal in higher order terms. Their results are summarized here.

A contact transformation of the form:

$$h' = e^{i\lambda S} H\, e^{-i\lambda S} = H_0 + \lambda h_1' + \lambda^2 h_2' + \lambda^3 h_3' \ldots \qquad (1\text{-}18)$$

can be found with the proper choice of S such that H_0 and h_1' are diagonal in all quantum numbers. A second such transformation can be carried out resulting in

$$h'' = H_0 + h_1' + h_2'' + h_3'' + \ldots . \qquad (1\text{-}19)$$

Here h_2'' is made diagonal in v_s but not necessarily in K and ℓ_s. These off-diagonal elements generally do not contribute before fourth order. Thus the diagonal elements of H_0, h_1', h_2'' and h_3'' yield an energy expression good through third order. A partial fourth order correction can be made if necessary using the diagonal elements of h_4'' and a perturbation treatment of off-diagonal elements in h_2''. These energy expressions are valid only in the absence of accidental degeneracies. Table I-1, compiled by Blass (1963), gives the contribution to the energy for the diagonal elements of H through third order with some fourth order corrections for an axially symmetric molecule.

An estimate for the magnitude of the parameters used in the energy expression listed in Table I-1 can be obtained in the following way. If J and K are set to 30 and all the v_s, v_t and ℓ_t are set to one, then terms in H_0 contribute approximately 1000 cm^{-1}, terms in h_1' contribute about 30 cm^{-1}, terms in h_2'' contribute about 1 cm^{-1}, h_3'' about 1/30 cm^{-1}, etc. Thus $\omega_s \approx 1000$ cm^{-1}, $A_e \approx B_e \approx 1$ cm^{-1}, $\alpha^A \approx \alpha^B \approx 1/1000$ cm^{-1}, $D^J \approx D^{JK} \approx D^K \approx 10^{-6}$ cm^{-1}, etc. Here an order of magnitude constitutes a factor of 30, starting with zero-th order at 1000 cm^{-1}.

TABLE I-1

ENERGY FOR AXIALLY SYMMETRIC MOLECULES

Term	Energy
H_0	$B_e J(J+1)+(A_e-B_e)K^2 + \sum \omega_s \left(v_s + \frac{g_s}{2}\right)$
h_1'	$-2A_e \sum \zeta_t^z \ell_t K$
h_2''	$-D_e^J J^2(J+1)^2 - D_e^{JK} K^2 J(J+1) - D_e^K K^4$
	$-\sum \alpha_s^B \left(v_s + \frac{g_s}{2}\right) J(J+1) - \sum (\alpha_s^A - \alpha_s^B)\left(v_s + \frac{g_s}{2}\right) K^2$
	$+\sum x_{ss'} \left(v_s + \frac{g_s}{2}\right)\left(v_{s'} + \frac{g_{s'}}{2}\right) + \sum x_{\ell_t \ell_{t'}, \ell_t \ell_{t'}}$
h_3''	$+\sum \ell_t \eta_t^J J(J+1)K + \sum \ell_t \eta_t^K K^3 + \sum \ell_t \left[\eta_t + \sum \eta_{ts} \left(v_s + \frac{g_s}{2}\right)\right] K$
h_4''	$+\sum \beta_s^J \left[v_s + \frac{g_s}{2}\right] J^2[J+1]^2 + \sum \beta_s^{JK} \left[v_s + \frac{g_s}{2}\right] J[J+1] K^2 + \sum \beta_s^K K^4 \left[v_s + \frac{g_s}{2}\right]$
	$+ \left(\sum \gamma_{ss'}^A \left[v_s + \frac{g_s}{2}\right]\left[v_{s'} + \frac{g_{s'}}{2}\right] + \sum \gamma_{\ell_t \ell_{t'}, \ell_t \ell_{t'}}^B + \Delta B_e^{(a)} \right)$
	$\{J[J+1]-K^2\} + \left(\sum \gamma_{ss'}^A \left[v_s + \frac{g_s}{2}\right]\left[v_{s'} + \frac{g_{s'}}{2}\right] + \sum \gamma_{\ell_t \ell_{t'}, \ell_t \ell_{t'}}^A + \Delta A_e^{(a)} \right) K^2$
	$+ \sum Y_{ss's''} \left[v_s + \frac{g_s}{2}\right]\left[v_{s'} + \frac{g_{s'}}{2}\right]\left[v_{s''} + \frac{g_{s''}}{2}\right] + \sum Y_{s \ell_t \ell_{t'}, \ell_t \ell_{t'}} \left[v_s + \frac{g_s}{2}\right]$
	$+ \sum \Delta\omega_s \left[v_s + \frac{g_s}{2}\right] + H_0^J J^3(J+1)^3 + H_0^{JK} J^2(J+1)^2 K^2 + H_0^{KJ} J(J+1) K^4 + H_0^K K^6$

CHAPTER II

BAND STRUCTURE

The results of the theoretical development outlined in Chapter I can be used to predict the appearance of vibration-rotation absorption bands of axially symmetric molecules.

II-1. TRANSITION FREQUENCY

For an axially symmetric molecule the energy of any state is given through second order by:

$$\begin{aligned} &E(\{v_s\}, \{v_t,\ell_t\}, J, K) \\ &\quad = \nu_0 + B_0 J(J+1) + (A_0-B_0)K^2 - 2A_e \sum_t \zeta_t^Z \ell_t K \\ &\quad - D_0^J J^2(J+1)^2 - D_0^{JK} J(J+1)K^2 - D_0^K K^4 \\ &\quad - \sum_s \alpha_s^B v_s J(J+1) - \sum_s (\alpha_s^A-\alpha_s^B) v_s K^2 , \end{aligned} \tag{2-1}$$

where $\{v_s\}$ represents the set of nondegenerate vibration quantum numbers, $\{v_t,\ell_t\}$ the set of degenerate vibration quantum numbers and ν_0 is the vibrational energy and is a combination of first and second order terms. For the ground vibrational state Eq. (2-1) reduces to

$$\begin{aligned} &E(\{0\}, \{0,0\}, J, K) \\ &\quad = B_0 J(J+1) + (A_0-B_0)K^2 - D_0^J J^2(J+1)^2 - D_0^{JK} J(J+1)K^2 - D_0^K K^4 . \end{aligned} \tag{2-2}$$

It is usually the case in molecular absorption spectroscopy to observe transitions from the ground vibrational state to an excited vibrational state, with possibly different values for the rotational quantum numbers J and K. For such a transition:

$$\begin{aligned}\Delta E(\{\Delta v_s\}, \{\Delta v_t, \Delta \ell_t\}, J, K, \Delta J, \Delta K) &= {}^{\Delta K}\Delta J_K(J) \\ &= \nu_0 + B_0(J+\Delta J)(J+\Delta J+1) + (A_0-B_0)(K+\Delta K)^2 - 2A_e \sum_t \zeta_t^Z \Delta \ell_t (K+\Delta K) \\ &- D_0^J (J+\Delta J)^2 (J+\Delta J+1)^2 - D_0^{JK}(J+\Delta J)(J+\Delta J+1)(K+\Delta K)^2 - D_0^K (K+\Delta K)^4 \\ &- \sum_s \alpha_s^B \Delta v_s (J+\Delta J)(J+\Delta J+1) - \sum_s (\alpha_s^A - \alpha_s^B)\Delta v_s (K+\Delta K)^2 \\ &- (B_0 J(J+1) + (A_0-B_0)K^2 - D_0^J J^2(J+1)^2 - D_0^{JK} J(J+1)K^2 - D_0^K K^4) ,\end{aligned} \tag{2-3}$$

where $\Delta v_s = v_{s'} - v_s$, $\Delta v_t = v_{t'} - v_t$, $\Delta \ell_t = \ell_{t'} - \ell_t$, $\Delta J = J' - J$ and $\Delta K = K' - K$, where the primed quantum numbers refer to the upper state. This expression can be further simplified if the summations involving the α^A and α^B parameters are replaced by effective α^A and α^B parameters since normally only a few of the vibrational quanta are involved. Further, since the ground vibrational state has $\ell_t = 0$, a transition originating in the ground state must have $\Delta \ell_t = \ell_t$. Then

$$\begin{aligned}\Delta E &= \nu_0 + B_0(2J+\Delta J+1)\Delta J + (A_0-B_0)(2K+\Delta K)\Delta K \\ &- 2A_e \sum_t \zeta_t^Z \ell_t (K+\Delta K) - D_0^J[(J+\Delta J)^2(J+\Delta J+1)^2 - J^2(J+1)^2] \\ &- D_0^{JK}[(J+\Delta J)(J+\Delta J+1)(K+\Delta K^2) - J(J+1)K^2] - D_0^K[(K+\Delta K)^4 - K^4] \\ &- \alpha^B(J+\Delta J)(J+\Delta J+1) - \alpha^A(K+\Delta K)^2 .\end{aligned} \tag{2-4}$$

This expression is good through second order but terms of higher order, specifically the n_t^K and n_t^J terms of h_3'', are commonly used in the analysis of high resolution vibration-rotation absorption spectra. For $\Delta J=J=0$ Eq. (2-4) reduces to a subband origin expression,

$$\nu^0_{K\Delta K} = \nu_0 + (A_0-B_0)(2K+\Delta K)\Delta K - 2A_e \sum_t \zeta_t^Z \ell_t(K+\Delta K) - (\alpha^A-\alpha^B)(K+\Delta K)^2 - D_0^K[(K+\Delta K)^4-K^4] \quad (2\text{-}5)$$

In the transition frequency notation often used, the values of ΔK and ΔJ are written in a shorthand notation using letters of the alphabet. For ΔK or ΔJ = -1, P is used, for ΔK or ΔJ = 0, Q is used and for ΔK or ΔJ = +1, R is used, etc. Thus a transition from the state (K,J) = (6,10) to the state (K',J') = (5,11), would be labeled $^PR_6(10)$ or PR6,10.

II-2. SYMMETRY SELECTION RULES

In molecular absorption spectroscopy the observed transitions are almost always a result of the electric dipole moment interaction in the initial and final states with the electromagnetic field of a passing photon. For such a transition to occur

$$\langle \mu_{if} \rangle = \langle \psi_{initial} | \mu_{op} | \psi_{final} \rangle \quad (2\text{-}6)$$

must be nonzero, where $\psi_{initial}$ and ψ_{final} are the total eigenfunctions for the initial and final states, and μ_{op} is the electric dipole moment operator. Since we have used the solutions to the rigid

rotor-harmonic oscillator Hamiltonian to form a basis set, the selection rules are those of the rigid rotor-harmonic oscillator system. For transitions involving the dipole moment component parallel to molecule's symmetry axis:

$$\begin{aligned} &\Delta K = 0 \\ &\Delta J = 0, \pm 1 \qquad \text{if } K \neq 0 \\ &\Delta J = \pm 1 \qquad \text{if } K = 0 \end{aligned} \tag{2-7}$$

For transitions involving the dipole moment component perpendicular to the molecular symmetry axis:

$$\begin{aligned} &\Delta K = \pm 1 \\ &\Delta J = 0, \pm 1 \end{aligned} \tag{2-8}$$

The selection rules for the rigid rotor-harmonic oscillator system apply to all molecules. However, they do not reflect the full symmetry of the molecule. Additional selection rules are obtained when higher order terms in the Hamiltonian are considered. Molecules whose symmetry corresponds to the point group C_{3v} have been treated in detail by Tarrago (1965).

In order to determine a more complete set of selection rules, symmetry adapted wave functions must be used. These are given by

$$\begin{aligned} |+\rangle &= |\{v_s, \ell_s\}, K, J\rangle + |\{v_s, -\ell_s\}, -K, J\rangle \\ |-\rangle &= |\{v_s, \ell_s\}, K, J\rangle - |\{v_s, -\ell_s\}, -K, J\rangle \ . \end{aligned} \tag{2-9}$$

Under the operations of the point group C_{3v}, these new wave functions

have a definite symmetry as summarized in Table II-1 for the phase choice used throughout this development and corresponding to the convention of Tarrago (1965).

TABLE II-1

SYMMETRY PROPERTIES OF THE WAVE FUNCTIONS $|+\rangle$ AND $|-\rangle$

	$K - \sum_t \ell_t = 3p$		$K - \sum_t \ell_t = 3p \pm 1$
	$J + K + \sum_t \ell_t + \sum_{n(A_2)} v_n$		
	even	odd	
$\|+\rangle$	A_1	A_2	E
$\|-\rangle$	A_2	A_1	
	for p = 0, ±1, ±2, ...		

Using the symmetry rules defined in Table II-1, the symmetry selection rules listed in Table II-2 are obtained. One immediate result of this symmetry consideration is that $\Delta K = \Delta \ell$ for fundamentals. For combinations and overtones, $\Delta K - \Sigma \Delta \ell_t = 0, \pm 3, \pm 6 \ldots$ with the restriction that $|\Delta K| \leq 1$, since only one photon is being absorbed.

II-3. TRANSITION INTENSITIES

The intensities of allowed transitions can be calculated from Eq. (2-6). If $f(K,J,\Delta K,\Delta J)$ is the transition dipole moment, then the transition intensity is proportional to:

$$I \propto \nu g f(K,J,\Delta K,\Delta J) e^{-E_0(K,J)/kT} \qquad (2\text{-}10)$$

TABLE II-2

SYMMETRY SELECTION RULES FOR C_{3v} MOLECULES

		$\sum_t \Delta\ell_t + \sum_{n(A_2)} \Delta v_v$	
		even	odd
Parallel bands $\Delta K = 0$ $\sum_t \Delta\ell_t = 3p$	$\Delta J = 0$	$\|+\rangle\rightarrow\|-\rangle$ $\|-\rangle\rightarrow\|+\rangle$	$\|+\rangle\rightarrow\|+\rangle$ $\|-\rangle\rightarrow\|-\rangle$
	$\Delta J = \pm 1$	$\|+\rangle\rightarrow\|+\rangle$ $\|-\rangle\rightarrow\|-\rangle$	$\|+\rangle\rightarrow\|-\rangle$ $\|-\rangle\rightarrow\|+\rangle$
Perpendicular bands $\Delta K = \pm 1$ $\Delta K - \sum_t \Delta\ell_t = 3p$	$\Delta J = 0$	$\|+\rangle\rightarrow\|+\rangle$ $\|-\rangle\rightarrow\|-\rangle$	$\|+\rangle\rightarrow\|-\rangle$ $\|-\rangle\rightarrow\|+\rangle$
	$\Delta J = \pm 1$	$\|+\rangle\rightarrow\|-\rangle$ $\|-\rangle\rightarrow\|+\rangle$	$\|+\rangle\rightarrow\|+\rangle$ $\|-\rangle\rightarrow\|-\rangle$

$A_1 \rightarrow A_2 \qquad A_2 \rightarrow A_1 \qquad E \rightarrow E$

where ν is the transition frequency, g is the statistical weight of the ground state, $E_0(J,K)$ is the energy of the ground state, k is Boltzman's constant and T is the Kelvin temperature. The transition moments have been calculated by Herzberg (1945) and are given in Table II-3.

For molecules whose symmetry is that of the point group C_{3v} and having three identical nuclei, the statistical weights are tabulated by Herzberg (1945) and written by Blass and Nielsen (1974).

$$g = (2-\delta_{K,0})(2J+1)\left(1 + \frac{3}{4I(I+1)}\,\delta_{K,3n}\right) \qquad (2\text{-}11)$$

where δ_{ij} is the Kronecker delta function and I is the spin quantum number of the identical nuclei.

TABLE II-3

TRANSITION MOMENTS $f(K,J,\Delta K,\Delta J)$

	$\Delta K = -1$	$\Delta K = 0$	$\Delta K = +1$
$\Delta J = -1$	$\frac{(J-1+K)(J+K)}{J(2J+1)}$	$\frac{J^2-K^2}{J(2J+1)}$	$\frac{(J-1-K)(J-K)}{J(2J+1)}$
$\Delta J = 0$	$\frac{(J+1-K)(J+K)}{J(J+1)}$	$\frac{K^2}{J(J+1)}$	$\frac{(J+1+K)(J-K)}{J(J+1)}$
$\Delta J = +1$	$\frac{(J+2-K)(J+1-K)}{(J+1)(2J+1)}$	$\frac{(J+1)^2-K^2}{(J+1)(2J+1)}$	$\frac{(J+2+K)(J+1+K)}{(J+1)(2J+1)}$

This expression for the statistical weight g, causes an intensity alternation which is useful in assigning a spectrum. For a molecule such as $^{13}CD_3F$, I = 1. Thus for $K \neq 0$,

$$g = 2(2J+1)(1+3/8\delta_{K,3n}) \ . \qquad (2\text{-}12)$$

Thus for a given J, the transitions associated with consecutive values of K show an alternation of intensity of the form "strong-weak-weak-strong."

II-4. GROUND STATE COMBINATION DIFFERENCES

To any upper state with rotational quantum numbers K' and J', there are in general three ground states from which transitions can occur, corresponding to the three possible values of $\Delta J(0, \pm 1)$. These transitions are:

$\Delta KPK,J'+1, \quad \Delta KQK,J', \quad \Delta KRK,J'-1.$

It is possible that one of these transitions would not exist because of the limitation that J be greater than K in both the upper and lower state. For such a group of transitions the transition frequencies differ only by the differences in their ground state energies. Thus the differences in the three possible transition frequencies are functions of the ground state energy coefficients and not the upper state energy coefficients and are also independent of most perturbations in the upper state. Thus the ground state energy coefficients can be determined if a sufficient number of transitions can be correctly assigned and their frequencies measured (Blass, 1963; Blass and Edwards, 1967). Ground state combination differences are also useful in verifying transition assignments.

It is possible to represent all the possible ground state combination differences in a single expression. This form is readily adapted to a least-squares fitting technique to determine the ground state energy coefficients and was developed by Blass and Edwards (1967).

$$\Delta K\Delta J_1 K(J-\Delta J) - \Delta K\Delta J_2 K(J-\Delta J_2) = B_0(\Delta_2-\Delta_1) - D_0^J(\Delta_2^2-\Delta_1^2) + H_0^J(\Delta_2^3-\Delta_1^3)$$
$$- D_0^{JK}(\Delta_2-\Delta_1)K^2 - H_0^{JK}(\Delta_2^2-\Delta_1^2)K^2 + \ldots \qquad (2\text{-}13)$$

where $\Delta_i = (J-\Delta J_i)(J+1-\Delta J_i)$, J is the J of the common upper state and K is the K of the lower state.

Note that some of the ground state energy coefficients such as A_0 and D_0^K are not included in this expression. These coefficients

cannot be directly determined by allowed electric dipole transitions. The constants can sometimes be determined from forbidden transitions as explained in Chapter III. Also it must be kept in mind that in some cases the degeneracy of the upper state of a perpendicular band may be lifted in such a way that the $\Delta J = 0$ upper state differs from the $\Delta J = \pm 1$ upper state. The validity of the $\Delta J_1 = +1$, $\Delta J_2 = -1$ (R-P) combination differences is not affected in this case.

II-5. EFFECTIVE Q-BRANCHES

Once the ground state constants have been determined they can be used to reduce the number of transition frequencies used in determining the upper state constants. This is done by converting the R-branch transitions ($\Delta J = +1$) and P-branch transitions ($\Delta J = -1$) into Q-branch transitions with the same upper state. This is done by adding or subtracting the ground state energy differences. These are termed effective Q-branch transition frequencies. If all the Q-branch and effective Q-branch transitions for a particular J, K, and ℓ are averaged the number of "observations" is reduced by nearly a factor of three and the uncertainty is reduced by a factor of $3^{1/2}$. For a degenerate band, the RR_0 and RP_0 transitions are used to produce effective Q-branches labeled "PQ_0" transitions.

II-6. LOOMIS-WOOD PLOTS

From Eq. (2-4), it is evident that for a fixed value of K and ΔK, transitions differing in $J\Delta J$ by one are separated by approximately

$2B_0$. A technique developed by Loomis and Wood (1928) makes use of this fact. In their formulation a marker is used to denote the intensity or peak height of a transition. The position of the marker is determined by dividing the frequency range into sections of width $2B_0$ in such a way that when adjacent frequency ranges are plotted side-by-side, transitions of the same KΔK form rows across the frequency ranges. If the transitions in a subband are separated by slightly less than $2B_0$ the markers will form a row which slants toward lower frequencies. For a subband with a separation slightly greater than $2B_0$ the row of markers will slant toward higher frequencies. By examining such a plot it is straightforward to assign many transitions even in the case of localized resonances.

The availability of video displays and on-line plotters makes it possible to use the Loomis-Wood technique to even greater advantage. The markers can now better represent the transition intensity by making the intensity of the dots on a video display or the size of a symbol produced by a digital plotter proportional to the peak height of the transitions. It is also possible to readily vary the effective B_0 until a satisfactory result is obtained. This technique was used extensively in the initial phases of the $^{13}CD_3F$ analysis.

CHAPTER III

ACCIDENTAL RESONANCES

The energy, transition frequency and transition intensity developed in Chapters I and II are valid only where resonances can be ignored. There are two kinds of resonances; essential resonances between states with the same v_t and ℓ_t, and accidental resonances between states with different vibrational quantum numbers. The accidental resonances have been classified by Tarrago (1965).

III-1. TYPES OF INTERACTIONS

Using the Hamiltonian outlined in Chapter I, Amat (1957, 1958) and Tarrago (1965) determined the possible coupling terms arising from elements in the Hamiltonian through third order. These results are summarized in Table III-1 for the six possible resonance terms. For two vibrational states the possible coupling terms are determined by considering the number of vibrational quanta involved in the coupling. For two such states $|\{v_n\}, \{v_t, \ell_t\}, K\rangle$ and $|\{v_n+\Delta v_n\}, \{v_t+\Delta v_t, \ell_t+\Delta\ell_t\}, K+\Delta K\rangle$ the quantities p and p_t are defined by:

$$p_t = \sum_t |\Delta v_t|$$
$$p = \sum_t |\Delta v_t| + \sum_n |\Delta v_n| \ . \qquad (3\text{-}1)$$

Thus p is just the total number of vibrational quanta involved in the interaction and p_t is the total number of degenerate vibrational

TABLE III-1

COUPLING TERMS

Type	Matrix Element
I	W_0
I'	$W_0 J(J+1)+W_0' K^2+W_0''$
II	$W_0 \sqrt{J(J+1)-K(K\pm1)}$
III	$W_0 K$
IV	$W_0 \sqrt{J(J+1)-K(K\pm1)}\ \sqrt{J(J+1)-(K\pm1)(K\pm2)}$
V	$W_0 \sqrt{J(J+1)-K(K\pm1)}\ \sqrt{J(J+1)-(K\pm1)(K\pm2)}\ \sqrt{J(J+1)-(K\pm2)(K\pm3)}$

quanta involved in the interaction. Considering elements from the Hamiltonian through third order, p and p_t can take on the following values:

$$2 \leq p \leq 5$$
$$0 \leq p_t \leq p \qquad (3\text{-}2)$$

These possibilities are grouped into four cases as follows:

(a) $p \geq 3$ $\qquad p_t \neq 1$

(b) $p \geq 2$ $\qquad p_t = 1$

(c) $p = 2$ $\qquad p_t = 2$

(d) $p = 2$ $\qquad p_t = 0$.

Up to this point we have considered only whether the Hamiltonian contains a term of the proper form to allow a particular interaction. The symmetry of the two states must also be considered. For molecules of c_{3v} symmetry, this consideration is summarized in Amat's rule (Amat, 1960) which can be stated as follows: The matrix element connecting two states is nonzero only if

$$\Delta K - \sum_t \Delta \ell_t = 3p = 0, \pm 3, \pm 6 \ldots \qquad (3\text{-}3)$$

Application of Amat's rule to the four cases leads directly to Tables III-2 through III-5 (Tarrago, 1965). These tables give all symmetry and Hamiltonian allowed interactions through third order. For these tables ΔK is the difference in K between the interacting states, $\sum_t \Delta \ell_t$ is the total change in ℓ_t for degenerate modes for which $\Delta v_t \neq 0$, $\sum_{t'} \Delta \ell_{t'}$ is the total change in ℓ_t for those degenerate

TABLE III-2

PERTURBATION COUPLING CASE a:
$p \geq 3$, $p_t \neq 1$

p_t	Matrix Elements	ΔK	$\sum_t \Delta\ell_t$	$\sum_{t'} \Delta\ell_{t'}$	Cplg. Type	Order of Magnitude		
						p=3	p=4	p=5
0	$W_{(1,2,3)}$	0	0	0	I	1	2	3
2	$W_{(1,2,3)}$	0	0*	0	I	1	2	3
	$W_{(3,4)}\ f_{\pm 1}$	± 1	∓ 2	0	II	2	3	
	$W_{(3)}$	0	± 2	∓ 2	I	3		
	$W_{(5)}\ f_{\pm 1}\ f_{\pm 2}$	± 2	± 2	0	IV	3		
	$W_{(1,2,3)}$	0	± 3	0	I	1	2	3
	$W_{(3,4)}\ f_{\pm 1}$	± 1	± 1	0	II	2,3	3	
	$W_{(3)}K$	0	± 3	0	III	2		
	$W_{(3)}$	0	± 1	± 2	I	3		
	$W_{(5)}\ f_{\pm 1}\ f_{\pm 2}$	± 2	∓ 1	0	IV	3		
4	$W_{(2,3)}$	0	0*	0	I		2	3
	$W_{(4)}\ f_{\pm 1}$	± 1	± 4	0	II		3	
5	$W_{(3)}$	0	± 3	0	I		3	

TABLE III-3

PERTURBATION COUPLING CASE b:
$p \geq 2$, $p_t = 1$

Matrix Elements	ΔK	$\sum_t \Delta \ell_t$	$\sum_{t'} \Delta \ell_{t'}$	Cplg. Type	Order of Magnitude		
					p=2	p=3	p=4
$W_{(2,3,4)}\ f_{\pm 1}$	± 1	± 1	0	II	1,2	2,3	3
$W_{(2,3)}$	$\begin{pmatrix} 0 \\ 0 \end{pmatrix}$	$\begin{matrix} \pm 3 \\ \pm 1 \end{matrix}$	$\begin{matrix} 0 \\ \pm 2 \end{matrix}$	I	2	3	
$W_{(4,5)}\ f_{\pm 1}\ f_{\pm 2}$	± 2	∓ 1	0	IV	2	3	

TABLE III-4

PERTURBATION COUPLING CASE c:
$p = 2,\ p_t = 2$

Matrix Elements	ΔK	$\sum_t \Delta\ell_t$	$\sum_{t'} \Delta\ell_{t'}$	Cplg. Type	Order of Magnitude p=2
$W_{(2)}\ f_{\pm 1}$	± 1	∓ 2	0	II	1,2
$W_{(2)}K$	0	0*	0	III	1,2
$W_{(2)}$	$\begin{matrix}0\\0\end{matrix}$	$\begin{matrix}0^*\\\pm 2\end{matrix}$	$\begin{matrix}0\\\mp 2\end{matrix}$	I	2
$W_{(4)}\ f_{\pm 1}\ f_{\pm 2}$	± 2	± 2	0	IV	2
$W_{(6)}\ f_{\pm 1}\ f_{\pm 2}\ f_{\pm 3}$	± 3	0	0	V	3

TABLE III-5

PERTURBATION COUPLING CASE d:
$p = 2,\ p_t = 0$

Matrix Elements	ΔK	$\sum_{t'} \Delta \ell_{t'}$	Cplg. Type	Order of Magnitude p=2
$W_{(2)} + W'_{(4)} J(J+1) + W''_{(4)} K^2$	0	0	I'	2
$W_{(4)}\ f_{\pm 1}$	± 1	∓ 2	II	3
$W_{(6)}\ f_{\pm 1}\ f_{\pm 2}\ f_{\pm 3}$	± 3	0	V	3

modes for which $\Delta v_t = 0$. If $\sum_t \Delta \ell_t$ (or $\sum_{t'} \ell_{t'}$) is zero but $\sum_t |\Delta \ell_t|$ (or $\sum_{t'} |\Delta \ell_{t'}|$) is not zero 0* appears under those headings. The numbers listed under order of magnitude give the approximate limits of the energy shift corresponding to J = K = 30, where order of magnitude is the same here as for terms in the energy expression of Chapter I. The subscripts on W in parentheses give the order of magnitude of the interaction parameter W or the order of magnitude of the energy shift for $J \approx K \approx 1$. Where multiple subscripts are present, they refer to the different possible values of p. The $f_{\pm n}$ coefficients of the interaction parameters are defined as:

$$f_{\pm 1} = \sqrt{J(J+1)-K(K\pm 1)}$$

$$f_{\pm 2} = \sqrt{J(J+1)-(K\pm 1)(K\pm 2)} \qquad (3\text{-}4)$$

$$f_{\pm 3} = \sqrt{J(J+1)-(K\pm 2)(K\pm 3)} \ .$$

In addition to the accidental resonances discussed above, essential resonances are also important in the interpretation of vibration-rotation spectra. Two common forms of essential resonance correspond to $(\Delta K, \Delta \ell_t) = (\pm 2, \pm 2)$ and $(\Delta K, \Delta \ell_t) = (\pm 1, \mp 2)$. For essential resonances Amat's rule still holds true and the formalisms of the preceding section need no modification. For almost all perpendicular bands the $(\pm 2, \pm 2)$ essential resonance produces observable effects. The $(\pm 1, \mp 2)$ essential resonance is less commonly observed, because potentially interacting states are not in close coincidence unless there is an accidental resonance which pushes the two states

closer together. The (±2, ±2) resonance effect is usually only of importance for transitions whose upper state is (K = +1, ℓ = +1) or RQ_0, RR_0 and RP_0 transitions. In this case the interaction is between the states (k=1, ℓ=1) and (k=-1, ℓ=-1). Since the energy is independent of the sign of kℓ, these states are always degenerate, hence the term essential resonance. It is also possible for an accidental resonance to push other (K,ℓ) states into a (±2, ±2) resonance. Both of these essential resonances are referred to as ℓ-resonance and ℓ-doubling and are considered in detail by Herzberg (1945).

III-2. PERTURBATION EFFECTS ON THE TRANSITION FREQUENCY

To calculate the upper state energy including perturbations it is necessary to diagonalize a Hamiltonian matrix where the unperturbed energies are the diagonal elements and the off-diagonal elements are taken from Tables III-2 through III-5. This is explained by the following example. Assume that in $^{13}CD_3F$, ν_1 is coupled to $\nu_3 + \nu_5$. Here p = 3, p_t = 1, p_n = 2 and from Table III-3 we see that a type II or a type IV coupling is possible. (The type I coupling is rejected because the values of $\sum \Delta\ell_t$ and $\sum \Delta\ell_{t'}$ cannot be attained in this case.) Depending on the molecular parameters for ν_1 and $\nu_3 + \nu_5$ for $^{13}CD_3F$, either the type II coupling, the type IV coupling or both will affect the appearance of the observed spectrum.

The matrix to be diagonalized for the type II coupling is generally written as

$$H = \begin{vmatrix} \nu_3 + \nu_5(K-1,\ \ell=-1) & W_1 f_- & 0 \\ W_1 f_- & \nu_1(K,0) & W_1 f_+ \\ 0 & W_1 f_+ & \nu_3 + \nu_5(K+1,\ \ell=+1) \end{vmatrix} \quad (3\text{-}5)$$

where

$$f_+ = \sqrt{J(J+1)-K(K+1)}$$
$$f_- = \sqrt{J(J+1)-K(K-1)}\ . \quad (3\text{-}6)$$

If an ℓ-doubling essential resonance in $\nu_3 + \nu_5$ is to be considered then the matrix of Eq. (3-5) must be modified by setting

$$H_{13} = H_{31} = 1/2\ q_5^+\ f_+ f_- \quad (3\text{-}7)$$

where q_5^+ is the ℓ-doubling parameter. To calculate a transition frequency it is necessary to generate and diagonalize the matrix in Eq. (3-5) for the upper state (K',J') and subtract the appropriate ground state energy calculated in Eq. (2-2).

This process is somewhat more complicated if the type II and type IV coupling must be considered simultaneously. Consider an upper state in ν_1 with rotational quantum numbers (K,J). The type II coupling with $\Delta K = \Delta \ell_t = +1$, will couple $\nu_1(K,J)$ to $\nu_3 + \nu_5(K+1,J,$ $\ell_5 = +1)$. The type IV coupling will couple this state back to $\nu_1(K+3,\ J)$. Thus it is now necessary to calculate all upper state energies in ν_1 and $\nu_3 + \nu_5$ for a given J and diagonalize a matrix of the form shown in Figure III-1. The coupling indicated in Figure III-1 continues to the left until the $K \geq 0$ limit is reached and to the

$$
\begin{array}{ccccccc}
\cdots & & & & & & \\
 & E_1(K-3) & F_2^{+}(K-3) & & & & \\
 & F_2^{+}(K-3) & E_{35}(K-2,+1) & & F_4^{-}(K) & & \\
 & & & E_{35}(K-1,-1) & F_2^{-}(K) & Q(K) & \\
 & & F_4^{-}(K) & F_2^{-}(K) & E_1(K) & F_2^{+}(K) & F_4^{+}(K) \\
 & & & Q(K) & F_2^{+}(K) & E_{35}(K+1,+1) & \\
 & & & & F_4^{+}(K) & E_{35}(K+2,-1) & F_2^{-}(K+3) \\
 & & & & & F_2^{-} & E_1(K+3) \quad \cdots
\end{array}
$$

where $F_4^{\pm}(K) = W_4\sqrt{J(J+1)-K(K\pm1)}\ \sqrt{J(J+1)-(K\pm1)(K\pm2)}$

$F_2^{\pm}(K) = W_2\sqrt{J(J+1)-K(K\pm1)}$

$Q(K) = 1/2\ q_t^{+}\sqrt{J(J+1)-K(K+1)}\ \sqrt{J(J+1)-K(K-1)}$

Figure III-1. Model Hamiltonian for simultaneous type II and type III coupling.

right until the $K \leq J$ limit is reached. Fortunately the expanded matrix can be factored into two matrices corresponding to $K = 3n$ and $K \neq 3n$ where n is a non-negative integer. This factorization case can be used to reduce computational time.

III-3. INTENSITY EFFECTS

Consider the matrix to be diagonalized in the example of the last section, Eq. (3-5). We have for the perturbed energies

$$E = U^{\dagger}HU \tag{3-8}$$

where E is the diagonal energy matrix and U is the product of a number of rotation matrices. The eigenvectors of the perturbed state are the columns of U. Thus the new eigenvectors are a linear combination of the old:

$$\psi' = a\psi_{3+5}^{-1} + b\psi_1 + c\psi_{3+5}^{+1} \tag{3-9}$$

where a, b and c are taken from the appropriate row or column of U, $\psi_{3+5}^{\pm 1}$ is the eigenvector corresponding to $\nu_3 + \nu_5$ ($\ell_5 = \pm 1$) and ψ_1 is the eigenvector corresponding to ν_1. If we call the unperturbed intensities I_{3+5}^{-1}, I_1 and I_{3+5}^{+1} for transitions from the ground state to $\nu_3 + \nu_5$ (K=1, ℓ= -1), ν_1(K), and $\nu_3 + \nu_5$(K+1, ℓ= +1), respectively, then the perturbation intensity for the state considered in Eq. (3-9) is

$$I' = \{a(I_{3+5}^{-1})^{1/2} + b(I_1)^{1/2} + c(I_{3+5}^{+1})^{1/2}\}^2 . \tag{3-10}$$

If more than one of the I's of Eq. (3-10) are nonzero, some care must be exercised in choosing the sign of $I^{1/2}$.

Typically the observed transition intensities are used primarily as an aid in assigning a spectrum using the intensity formalisms described in Chapter II. In the presence of perturbations however, there are two interesting exceptions to this. These cases will be referred to as resonance enhanced transitions and resonance allowed transitions.

As the energy separation of the perturbing states decreases, the resonance effects increase and the two states become more thoroughly mixed. Thus if one of the interacting levels has insufficient intensity to be otherwise observed, it may be observable in the region of close resonance. Consider the last example of a type II coupling between ν_1 and $\nu_3 + \nu_5$ with $\Delta K = \Delta \ell_t = 1$, where $\nu_3 + \nu_5(K=6, \ell=+1)$ crosses with $\nu_1(K=5)$ for the parameters listed in Table III-6. The intensity borrowed from ν_1 RQ5,5 would appear in $\nu_3 + \nu_5$ as RR5,J, which is normally allowed but may be too weak to be observed in the absence of the interaction. This is termed a resonance enhanced transition or RET. The intensity sharing for this example is detailed in Table III-7 for $\Delta J = +1$, $K = 5$ assuming that $\nu_3 + \nu_5$ has negligible unperturbed intensity. The intensities have been scaled so that QR5,5 has unit intensity.

For a type IV coupling with $\Delta K = -2$, $\Delta \ell_t = +1$, the interacting states will be $\nu_1(K)$ and $\nu_3 + \nu_5(K-2, \ell_t = +1)$. This the intensity borrowed from QR2,10 will appear in NR5,10. This transition is

TABLE III-6

PARAMETERS FOR A TYPE II COUPLING EXAMPLE, ALL VALUES EXCEPT ζ^Z_{3+5} IN CM^{-1}

ν_1	2086.0
α^A_1	0.020
α^B_1	0.005
$\nu_3 + \nu_5$	2079.0
α^A_{3+5}	0.010
α^B_{3+5}	0.030
ζ^Z_{3+5}	0.240
W_{135}	0.050
A_0	2.6033
B_0	0.670836
D^J_0	1.1004×10^{-6}
D^{JK}_0	7.292×10^{-6}
D^K_0	16.40×10^{-6}

TABLE III-7

INTENSITY BORROWING IN A TYPE II COUPLING FOR A LOCALIZED RESONANCE

J	ν_1 Shift (cm^{-1})	I_{35}^{-1}	I_1	I_{35}^{+1}
5	0.00129	0.000	1.000	0.000
6	-0.00163	0.000	2.130	0.001
7	-0.00560	0.001	3.342	0.005
8	-0.01101	0.001	4.590	0.013
9	-0.01840	0.002	5.827	0.028
10	-0.02860	0.003	1.010	0.054
11	-0.04296	0.005	8.093	0.099
12	-0.06375	0.006	9.029	0.178
13	-0.09511	0.008	9.760	0.326
14	-0.14533	0.009	10.189	0.618
15	-0.23270	0.010	10.105	1.253
16	-0.40027	0.011	9.033	2.699
17	-0.73509	0.012	6.473	5.457
18	0.60959	0.013	8.351	3.606
19	0.44242	0.013	9.913	1.911
20	0.35417	0.014	10.448	1.098
21	0.30311	0.013	10.451	0.688
22	0.27099	0.013	10.166	0.461
23	0.24947	0.013	9.704	0.324
24	0.23435	0.012	9.129	0.235
25	0.22338	0.011	8.481	0.174
26	0.21520	0.010	7.791	0.131
27	0.20899	0.009	7.083	0.100
28	0.20421	0.008	6.376	0.077
29	0.20049	0.007	5.684	0.059

normally forbidden and is labeled a resonance allowed transition or RAT. If it is assumed that $\nu_3 + \nu_5$ has sufficient intensity to be observed a second RAT may be located. Here it would be TR2,10. It is possible to use resonance allowed transitions to form other types of ground state combination differences from which the ground state parameters A_0 and D_0^K may be determined (Graner, 1976). For example,

$$\begin{aligned}\Delta &= RR2,10 - OR5,10 = TR2,10 - QR5,10 \\ &= (A_0-B_0)(5^2-2^2) - D_0^K(5^4-2^4) - D_0^{JK}(10)(11)(6^2-2^2) \\ &= 21(A_0-B_0) - 609\ D_0^K - 2310\ D_0^{JK}\ . \end{aligned} \tag{3-10}$$

This resonance scheme is depicted in Figure III-2.

III-4. EFFECTIVE PARAMETERS

Consider a matrix of the form

$$A = \begin{pmatrix} E_2 & \delta \\ \delta & E_1 \end{pmatrix} \tag{3-11}$$

where δ is much smaller than either E_1 or E_2, δ is positive and $E_2 > E_1$. If the matrix A is diagonalized the shift in E_1 or E_2 can be approximated for the two extreme cases. For $\delta << E_2 - E_1$,

$$\Delta E = E_2' - E_2 = E_1 - E_1' \approx \delta^2/(E_2 - E_1)\ . \tag{3-12}$$

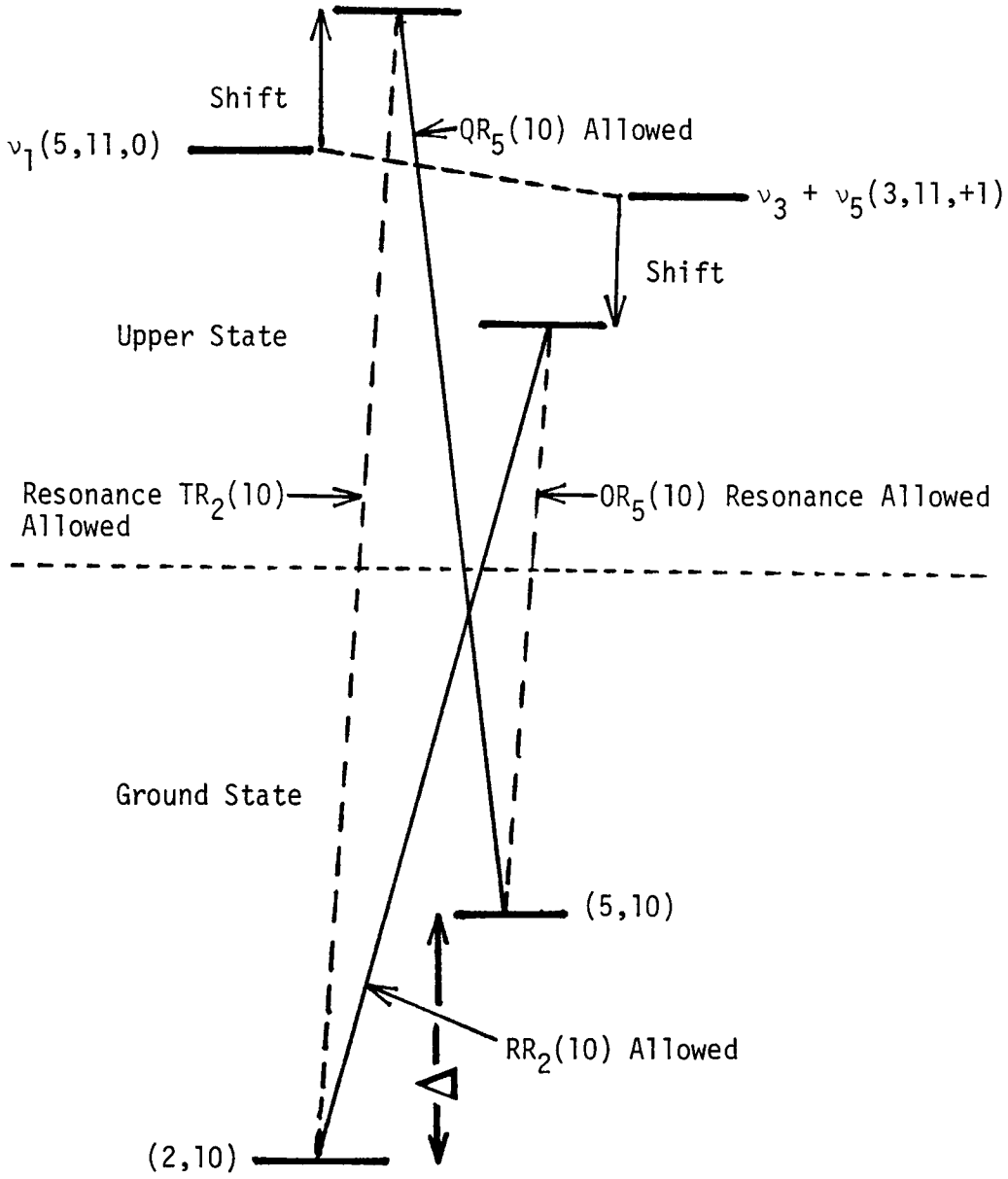


Figure III-2. Resonance allowed transitions for a $\Delta K = -2$, $\Delta \ell = +1$ interaction.

For $\delta \approx E_2 - E_1$

$$\Delta E \approx \delta \ . \tag{3-13}$$

This effect may be very subtle if ΔE for two interacting bands is large or the interaction constant is small. The effects of such interactions have been summarized by Sarka (1972).

For two nondegenerate fundamentals ν_n and $\nu_{n'}$ coupled through a type I interaction term this effect can be absorbed into the constants α^A and β^K for the two bands.

$$\Delta\alpha^A = \pm W^2/\Delta E = \alpha^A_{\text{true}} - \alpha^A_{\text{observed}} \tag{3-14}$$

$$\Delta\beta^K = (\Delta\alpha^A)^2/\Delta E = \beta^K_{\text{true}} - \beta^K_{\text{observed}} \tag{3-15}$$

where the subscripts "true" and "observed" refer to the values of the parameters in the absence and presence of the resonance, respectively. The effect on other parameters will be negligible if ΔE is relatively independent of J and K.

For a Coriolis resonance (type II coupling term) between a nondegenerate fundamental and a degenerate fundamental, the effect on the nondegenerate band parameters is given by

$$\Delta\alpha^B = \pm W^2/\Delta E = \alpha^B_{\text{true}} - \alpha^B_{\text{observed}} \tag{3-16}$$

$$\Delta D^J = (\alpha^B)^2/\Delta E \tag{3-17}$$

$$\Delta D^{JK} = -2\Delta D^J \tag{3-18}$$

$$\Delta D^K = \Delta D^J \qquad (3\text{-}19)$$

where W is the resonance parameter. The constants α_n^A and α_t^A are not affected if ΔE does not depend strongly on J and K.

If the interaction effects are explicitly taken into account, the rotational parameters determined from fitting observed frequencies are sometimes referred to as "de-perturbed" parameters. Consider one example: The ν_4 degenerate fundamental in $^{12}CD_3F$ lies above the three nondegenerate fundamentals ν_1, ν_2 and ν_3. The type II interaction terms have been estimated by Robiette (1982) from a force field calculation. The values of $\Delta\alpha_4^B$ for these interactions are listed in Table III-8. A preliminary analysis of the ν_4 band yielded $\alpha_4^B = 0.00038$ cm^{-1}. If the combined effects of the three interactions are taken into account, α_4^B would be estimated as $\alpha_{4\ \text{true}}^B = 0.00167$ cm^{-1}. Thus the combined effects make a contribution three times larger than α_4^B itself. However the ν_4 band can be analyzed without explicitly taking this effect into account since the total energy shift can be accommodated using effective parameters. Then the parameters can be corrected if necessary if the interaction constants can be estimated.

TABLE III-8

RESONANCE EFFECTS ON α_4^B OF $^{12}CD_3F$

n	W (cm^{-1})	$\nu_4-\nu_n$ (cm^{-1})	$\Delta\alpha_4^B$ (cm^{-1})
1	0.0748	155	-0.00039
2	-0.4883	1127	-0.00082
3	0.1582	1255	-0.00008
		Total $\Delta\alpha_4^B$ = -0.00129 cm^{-1}	
		α_4^B observed = 0.00038 cm^{-1}	

CHAPTER IV

FITTING PERTURBED SPECTRA

Until recently the only proven method of fitting a perturbed spectrum was to use trial and error to estimate the molecular parameters. There was no viable alternative for low resolution spectra, but as the resolving power of infrared spectrometers has increased, the complexity of the molecular interactions has made this approach unworkable. While it is not difficult to calculate a vibration-rotation spectrum given the Hamiltonian model, the molecular parameters and dipole moments of the bands involved in an analysis—the reverse is not true. The problem of finding the molecular parameters given a spectrum and a Hamiltonian model has recently come under closer consideration. This problem has been studied by Graner (1981), Champion (1982) and Betrencourt (1977) and is referred to as the inverse spectrometric problem or inverse eigenvalue problem.

IV-1. NON-PERTURBATION TREATMENT

The transition frequency expression given in Eq. (2-4) is in a form that is convenient for the least-squares determination of the molecular parameters. This expression is somewhat simpler if effective Q-branch frequencies are used because part of the ground state contribution is eliminated and ΔJ is zero. In either case any remaining ground state contribution can be eliminated once the ground state parameters are known. If there are any interactions

affecting the observed frequencies the parameters that are determined must be considered effective parameters even if the fit is considered good. If a weak localized resonance affects the observed transition frequencies, the effect on the parameters can be minimized by weighting the perturbed transitions less or removing these observations from consideration. A superior method of weighting the observed frequencies is described by Beaton and Tukey (1974). In this weighting scheme the data are fitted and reweighted iteratively according to the formula:

$$w_i(x_k) = \begin{cases} [1 - (\Delta^k_{o-c}/t\sigma_{i-1})^2]^2 & \text{for } |\Delta^k_{o-c}| \leq t\sigma_{i-1} \\ 0 & \text{for } |\Delta^k_{o-c}| \leq t\sigma_{i-1} \end{cases} \qquad (4\text{-}1)$$

where $\Delta^k_{o-c} = (x_k)_{obs} - (x_k)_{calc}$ and w_i is the weight at the current iteration, $(x_k)_{calc}$ is the calculated value for the k-th transition frequency based on the results of the last fit, $(x_k)_{obs}$ is the k-th observed transition frequency, σ_{i-1} is the weighted standard deviation of the last fit and t is a parameter which controls the rate at which observations are deweighted. The weights for the initial fit, $w_0(x_k)$, are generally taken to be one. After the weights have been recalculated the data are refitted resulting in a smaller value of σ^2. This process is terminated using a χ-squared test of the variance. This dynamic reweighting procedure is also helpful in removing misassigned, mis-measured or blended lines.

If nonlocal resonances affect the observed transition frequencies, their effect can often be absorbed. Often higher order terms in the

general transition frequency expression are included solely for this purpose. The values of such parameters will of course be considered as effective parameters, but the resonance effects on the lower order terms should be decreased.

IV-2. FITTING PERTURBED SPECTRA

The non-perturbation biweighting method is useful for determining "deperturbed" molecular parameters. However, in many instances it is desirable to include the resonance in the Hamiltonian model in order to determine the resonance parameters, the parameters of the perturbing state or both. It is not unlikely that in a spectrum with only a localized interaction that the few shifted transitions and resonance allowed or resonance enhanced transitions would carry more information than the many unperturbed transitions. The perturbation fitting method described here has proven to be effective in cases where the Hamiltonian model is well known. Let

$$H = H(\{a_k\}) \tag{4-2}$$

be the model Hamiltonian for a perturbed set of vibration-rotation states where $\{a_k\}$ represents the set of molecular parameters including interaction terms. Then the upper state energies are given by

$$\underline{\underline{E}} = \underline{\underline{U}}^{\dagger}\, \underline{\underline{H}}\, \underline{\underline{U}} \quad \text{or} \quad \underline{\underline{H}}\,\underline{x} = \underline{\underline{E}}\,\underline{x} \tag{4-3}$$

where $\underline{\underline{E}}$ is a diagonal matrix and $\underline{x}$ is a column of U and the eigenvector

for a particular state. Define $\underline{\underline{B}}$ and $\underline{\underline{\beta}}$ by

$$\underline{\underline{B}} = \partial H/\partial a_k \tag{4-4}$$

$$\underline{\underline{\beta}} = \underline{\underline{U}}^{\dagger}\ \underline{\underline{B}}\ \underline{\underline{U}} \tag{4-5}$$

where a_k is any one of the molecular parameters. Then the equation

$$(\underline{\underline{H}} + \varepsilon\underline{\underline{B}})\ \underline{x}(\varepsilon) = \underline{\underline{E}}(\varepsilon)\ \underline{x}(\varepsilon) \tag{4-6}$$

can be expanded in a Taylor series and like terms in the expansion parameter ε collected to yield (Wilkinson, 1965)

$$E_m = E_{m,0} + E_{m,1}(\varepsilon) + E_{m,2}(\varepsilon^2) + \ldots \tag{4-7}$$

where

$$E_{m,0} = E_m(0) = E_m \tag{4-8}$$

$$E_{m,1} = \beta_{mm} \tag{4-9}$$

$$E_{m,2} = \sum_{i\neq m} \frac{\beta_{mi}\beta_{im}}{(E_m - E_i)} \tag{4-10}$$

$$E_{m,3} = \sum_{i\neq m} \sum_{j\neq m} \frac{\beta_{mi}\beta_{ij}\beta_{ji}}{(E_m - E_i)(E_m - E_j)} \tag{4-11}$$

and

$$x_m(\varepsilon) = x_{m,0} + \sum_{i\neq m} \frac{\beta_{im}}{(E_m - E_i)} \tag{4-12}$$

where

$$x_{m,0} = x_m(0) = x_m \ . \tag{4-13}$$

Thus if only the linear terms are kept the energy expansion is

$$E_m = E_{m,0} + \beta_{mm} \tag{4-14}$$

where again

$$\underline{\underline{\beta}} = \underline{\underline{U}}^{\dagger} \frac{\partial \underline{\underline{H}}}{\partial a_k} \underline{\underline{U}} \ , \tag{4-15}$$

where U is the matrix which diagonalizes H. Fortunately the form of the model Hamiltonian makes it trivial to calculate $\partial H/\partial a_k$. This is because all terms in the model Hamiltonian, including resonance terms, can be written in the form

$$H_{ij} = \sum_k a_k \, F_k(K,J,\{v_n\}, \{v_t,\ell_t\}) \tag{4-16}$$

where the F_k are fairly simple expressions and depend only on the vibration-rotation quantum numbers. Thus

$$\frac{\partial H_{ij}}{\partial a_m} = F_m(K,J, \{v_n\}, \{v_t,\ell_t\}) \tag{4-17}$$

$$= H_{ij}(\{a_k\} = \{\delta_{k,m}\}) \ . \tag{4-18}$$

This is more simple expressed by noting that the partial derivative of H with respect to any parameter in the model Hamiltonian is found by evaluating H with that parameter set to one and all other

parameters to zero. It should be noted that since the ground state parameters are considered constants in most instances, the derivative of the transition frequency is just the derivative of the upper state energy.

$$\frac{\partial \nu_i}{\partial a_m} = \frac{\partial E_i}{\partial a_m} = U^{\dagger} H(\{a_k\} = \{\delta_{k,m}\}) U \ . \tag{4-19}$$

Since the partial derivatives can be readily calculated, it is in principle possible to fit a perturbed spectrum if the appropriate Hamiltonian is known. Assume a starting value for the parameter set $\{a_k\} = \{a_k^0\}$, where a_k^0 represents an approximate value of a_k from previous studies, force field calculations or perhaps a biweighted fit as described in Section IV-1. Define the residuals at the n-th iteration as

$$D_{i,n} = E_i^{obs} - E_{i,n}^{calc} \tag{4-20}$$

where $D_{i,n}$ is the residual of the i-th observed energy E_i^{obs} at the n-th iteration and $E_{i,n}^{calc}$ is the calculated energy corresponding to the i-th observation based on the previous values of the molecular parameters $\{a_k^{n-1}\}$.

$$E_{i,n}^{calc} = U_n^{\dagger} H(\{a_{n-1}\}) U_n \ . \tag{4-21}$$

We can now write

$$D_{i,n} \approx \sum_k \delta a_k \frac{\partial E_i}{\partial a_k} \tag{4-22}$$

where $\frac{\partial E_i}{\partial a_k}$ is found in Eq. (4-19). This equation is in a form which can be used to find the corrections to the parameters $\{\delta a_k\}$ by least-squares fitting. If the estimates to the parameters are reasonable and the Hamiltonian model is correct the updated parameter set $\{a_k^{n+1}\}$ defined by

$$a_k^n = a_k^{n-1} + \delta a_k \tag{4-23}$$

should yield a better fit to the observed frequencies. Often the corrections are damped and Eq. (4-23) becomes

$$a_k^n = a_k^{n-1} + \delta a_k \, p_k \tag{4-24}$$

where p_k is the damping factor for parameter a_k. The damping factors are usually equal and a value of 1/2 generally yields reasonable results. This process is repeated until the standard deviation of the fit or root-mean-square error is approximately equal to the uncertainty in the measured transition frequencies or until the process yields no further correction to the parameters.

One problem in least-square fitting the residuals in this manner is the correlation between parameters. Table IV-1 gives some of the derivatives of the ν_1 frequencies for K=5 using the parameters of Table III-7 (p. 33). There is a localized crossing in this subband occurring between J=17 and J=18. Below this point the derivative with respect to the resonance parameter W and the derivative with respect to α^B of the perturbing band $\nu_3+\nu_5$ are highly correlated. Also if the parameters are such that no other crossings occur, then

TABLE IV-1

DERIVATIVES OF THE ν_1 FREQUENCY FOR THE PARAMETER SET GIVEN IN TABLE III-7 FOR K=5

J	ν_1 Shift	$\frac{\partial \nu_1}{\partial W}$	$\partial^2 \nu_1 / \partial W^2$	$\partial \nu_1 / \partial (\alpha^B_{35})$	$\partial^2 \nu_1 / \partial (\alpha^B_{35})^2$
5	0.00129	0.05143	1.02836	-0.00003	0.00000
6	-0.00163	-0.06517	-1.29926	-0.00062	-0.00010
7	-0.00560	-0.22377	-4.44352	-0.00214	-0.00066
8	-0.01101	-0.43900	-8.66878	-0.00532	-0.00256
9	-0.01840	-0.73207	-14.34078	-0.01143	-0.00808
10	-0.02860	-1.13482	-21.96722	-0.02277	-0.02286
11	-0.04296	-1.69686	-32.24208	-0.04348	-0.06142
12	-0.06375	-2.49903	-46.04234	-0.08400	-0.16306
13	-0.09511	-3.67892	-64.12250	-0.16437	-0.44216
14	-0.14533	-5.47623	-85.37576	-0.33752	-1.26122
15	-0.23270	-8.27406	-99.28212	-0.74653	-3.82302
16	-0.40027	-12.31503	-67.93658	-1.77284	11.28762
17	-0.73509	-15.93788	8.21708	-3.98428	22.49420
18	0.60959	17.01210	58.77130	-2.95664	20.90860
19	0.44242	14.81993	137.03028	-1.77515	12.70294
20	0.35417	12.80469	167.86830	-1.16519	7.50672
21	0.30311	11.36162	173.99418	-0.84189	4.81406
22	0.27099	10.35657	172.02960	-0.65521	3.36070
23	0.24947	9.64442	168.01624	-0.53853	2.51344
24	0.23435	9.12754	163.91096	-0.46085	1.98306
25	0.22338	8.74409	160.28982	-0.40654	1.63088
26	0.21520	8.45444	157.26714	-0.36709	1.38566
27	0.20899	8.23254	154.80768	-0.33756	1.20826
28	0.20421	8.06068	152.83429	-0.31494	1.07590
29	0.20049	7.92654	151.26862	-0.29727	0.97460

α^{A}_{3+5}, ζ^{Z}_{3+5} and ν_{3+5} cannot be independently determined. In these cases it is necessary to fix one or more of the parameters.

A recurring problem in the assignment and analysis of perturbed spectra is the labeling of transitions in a region of strong mixing. For example, in the region of a local resonance between $\nu_1(K)$ and $\nu_3+\nu_5(K+1,\ell=1)$ a transition is labeled as ν_1 but is a linear combination of ν_1, $\nu_3+\nu_5$ and possibly other states. The upper state of this transition may be only 51% of ν_1 and 49% of $\nu_3+\nu_5$. For a very small change in the parameter set, causing negligible frequency shifts, the percentages can be reversed making it necessary to reverse the assignments also. In an interaction scheme involving many interacting levels the calculated value of a specified transition frequency can be shifted over 10 cm^{-1} for an otherwise negligible change in the parameter set.

Computer algorithms used to diagonalize matrices generally reduce the off-diagonal elements through a series of rotations. This produces a reasonably correct set of eigenvalues, but the ordering does not necessarily correspond to the original ordering particularly where there are nearly exact degeneracies. One way to overcome this is to reassign a transition to the closest calculated state based on the current estimate of the molecular parameters. This approach has been successful in fitting simulated and real data but can lead to problems if the parameter estimates are not sufficiently accurate to characterize the spectrum.

IV-3. MULTIPLE RESONANCES

The perturbation analysis scheme outlined in Section IV-2 can be applied to a wide variety of resonance schemes if the model Hamiltonian is known. However, there are cases where it may be practical to limit the Hamiltonian in order to limit computational time. A weak local resonance can be omitted from the model Hamiltonian if the transitions which are affected are omitted in the analysis. If this resonance can be adequately treated with second order perturbation theory computation cost can be reduced. This is particularly true for local resonances with $\Delta K - \sum \Delta \ell \neq 0$ which cause all upper states of the same J to be coupled.

Consider a weak localized resonance between one state of a complex interaction system and a state not considered in the model Hamiltonian. Second order perturbation theory is simple to apply here because the states involved have very nearly the same eigenvectors for several consecutive values of J and a fixed value of K. Assume the weak interaction is a Coriolis (type II) coupling and analysis of the local resonance yields an interaction parameter C_{nt} = 0.0025 cm^{-1}. Here ν_t is a degenerate band considered in the model Hamiltonian and ν_n is a nondegenerate band which interacts with the ν_t band but no other band in the model Hamiltonian. If in the region of the local resonance ν_t is a mixture of several states it cannot automatically be assumed that ν_n is interacting directly with ν_t. It is possible that one of the other states in the system, say $\nu_{t'}$, is actually responsible for the resonance and ν_t is participating because of its interaction with $\nu_{t'}$. If it is assumed that the

interaction is with $\nu_{t'}$ and not ν_t the interaction parameter $C_{nt'}$ can be calculated once the eigenvalues of the complex system are known.

If a $\Delta K - \sum \Delta \ell_t \neq 0$ interaction affects the observed spectrum, it is necessary to diagonalize matrices of the size nxn, where $n = 3(2J+1)$. If this resonance is strong this cannot be avoided. If the resonance is weak a second order perturbation approach can be used to avoid this problem. The effects of second order interactions for such a coupling would be difficult to predict and some care should be exercised in using the second order perturbation approach.

CHAPTER V

RESONANCE FITTING EXAMPLES

The algorithm developed in Chapter IV is tested for a wide variety of cases using simulated and real data.

V-1. SIMULATED CORIOLIS RESONANCE CASE: BOTH STATES OBSERVED

The transition frequencies for a nondegenerate (parallel) band and a degenerate (perpendicular) band with a Coriolis (type II) coupling are generated with K_{max}=12 and J_{max}=30. The parameters used in the simulation are listed in the first column of Table V-1. The parameters are defined in Table V-2. These bands exhibit a (+1,+1) crossing in the K=5 and K=6 subbands with some weak effects in nearby subbands. For this test case it is assumed that both bands have sufficient intensity to be observed for all K and J values.

The second column of Table V-1 contains the starting value for all the parameters. Note that the resonance parameter cannot be initialized to zero because the first derivative of the eigenvalues with respect to the resonance is zero for a zero resonance parameter. The third, fourth, and fifth columns of Table V-1 give the value of the parameters after five, ten and fifteen iterations, respectively. The damping factors were all set to one-half for this fit. The standard deviation at each iteration is listed in Table V-3. The columns headed σ_P, σ_Q and σ_R give the standard deviation for the P,

TABLE V-1

PARAMETER VALUES FOR CORIOLIS RESONANCE FITTING, CASE 1

Parameter Number	Simulation Value	Start Value	Five Iterations	Ten Iterations	Fifteen Iterations
1	2059.70000	2057.70000	2059.64350	2059.69870	2059.70000
2	2086.00000	2085.92000	2088.43160	2086.85470	2086.03620
3	-0.28000	-0.30000	-0.27913	-0.27981	-0.27999
4	10.00000	12.00000	8.50355	9.78408	9.99387
5	20.00000	18.80000	184.42892	78.88354	22.51480
6	18.00000	20.00000	18.07670	18.00323	18.00015
7	5.00000	4.50000	3.90378	4.80337	4.99201
8	0.00000	0.00000	1.43208	-0.13133	-0.00241
9	0.00000	0.00000	-80.23112	-10.40528	-0.27410
10	0.00000	0.00000	-0.01120	-0.00315	-0.00007
11	0.00000	0.00000	3.75660	0.27485	0.01274
12	0.00000	0.00000	-2679.57310	-371.75911	-10.76750
13	0.00000	0.00000	1.28418	0.22424	0.00895
14	0.00000	0.00000	-53.84446	-10.46276	-0.45566
15	0.00000	0.00000	2640.28240	990.25549	43.15418
16	30.00000	20.00000	23.14382	28.97248	29.96821
17	0.00000	0.00000	-0.01395	-0.00310	-0.00012

TABLE V-2

PARAMETER DEFINITIONS FOR THE CORIOLIS RESONANCE TEST CASE

Parameter Number	Definition
1	$\nu_{0\perp}$
2	$\nu_{0\parallel}$
3	ζ^{Z}
4	$\alpha_{\perp}^{A}$ (10^{3})
5	$\alpha_{\perp}^{B}$ (10^{3})
6	$\alpha_{\parallel}^{A}$ (10^{3})
7	$\alpha_{\parallel}^{B}$ (10^{3})
8	η^{J} (10^{3})
9	η^{K} (10^{3})
10	$\beta_{\perp}^{J}$ (10^{6})
11	$\beta_{\perp}^{JK}$ (10^{6})
12	$\beta_{\perp}^{K}$ (10^{6})
13	$\beta_{\parallel}^{J}$ (10^{6})
14	$\beta_{\parallel}^{JK}$ (10^{6})
15	$\beta_{\parallel}^{K}$ (10^{6})
16	C (10^{3})
17	1/2 q (10^{3})

TABLE V-3

STANDARD DEVIATIONS FOR CORIOLIS RESONANCE FITTING CASE 1
(in cm^{-1})

Iteration	σ_P	σ_Q	σ_R	σ_{total}
1	3.2692	0.4989	2.1461	2.7316
2	1.6354	0.4201	1.0703	1.3663
3	0.8180	0.3379	0.5414	0.6870
4	0.4090	0.3118	0.2819	0.3503
5	0.2046	0.3327	0.1607	0.1892
6	0.1024	0.3502	0.1103	0.1188
7	0.0513	0.3620	0.0931	0.0937
8	0.0257	0.3694	0.0881	0.0867
9	0.0130	0.0526	0.0205	0.0189
10	0.0066	0.0254	0.0102	0.0094
11	0.0033	0.0125	0.0051	0.0047
12	0.0017	0.0062	0.0026	0.0024
13	0.0009	0.0031	0.0013	0.0012
14	0.0005	0.0016	0.0007	0.0006
15	0.0002	0.0008	0.0003	0.0003

Q and R branches, respectively. The column headed σ_{total} gives the standard deviation for all the observations. Note that the standard deviation initially drops by a factor of two at each iteration, slows down for iterations six and seven, drops sharply at iterations eight and nine, then starts decreasing by half for iterations ten through fifteen. The recovery of the parameters is excellent in this example.

V-2. SIMULATED CORIOLIS RESONANCE CASE 2: PARALLEL BAND OBSERVED

The data set simulated in Section V-1 was modified by deleting all the parallel band observations. The test was repeated with the same starting parameters and the damping factor was kept at one-half. The performance of the algorithm in this test was inadequate. The parameter recovery was very poor for the parallel band parameters. The parameters for the perpendicular band could be determined from the nonshift frequencies much better than in this example. The parameters from the fit are given in Table V-4. The standard deviations are listed in Table V-5.

V-3. SIMULATED CORIOLIS RESONANCE CASE 3: PERPENDICULAR BAND PLUS RESONANCE ENHANCED PARALLEL BAND LINES

The Coriolis resonance data set is generated for a third case. In this simulation, the parallel band is assumed to have no intensity in the absence of the resonance but is assumed to be observed if the state mixing produces a resonance enhanced intensity one-tenth that

TABLE V-4

PARAMETER VALUES FOR CORIOLIS RESONANCE FITTING CASE 2
(in cm^{-1} except parameter 3)

Parameter Number	Value in Simulation	Starting Value	Five Iterations	Ten Iterations	Fifteen Iterations
1	2059.7000	2057.7000	2059.6490	2059.7101	2059.7122
2	2086.0000	2085.9200	2062.7614	2058.2685	2067.2231
3	-0.2800	-0.3000	-0.2778	-0.2770	-0.2770
4	10.0000	12.0000	7.3012	6.9783	7.0201
5	20.0000	18.8000	-3218.7023	-3581.9948	-4282.7738
6	18.0000	20.0000	18.1115	18.0391	18.0379
7	5.0000	4.5000	112.0302	123.2272	325.7940
8	0.0000	0.0000	5.4950	8.0897	8.7293
9	0.0000	0.0000	-137.2133	-155.0719	-155.0182
10	0.0000	0.0000	-0.0029	-0.0217	-0.0229
11	0.0000	0.0000	9.6862	12.8139	13.6068
12	0.0000	0.0000	-4780.2975	-5271.7581	-5213.0810
13	0.0000	0.0000	-141.8469	-75.7503	62.9734
14	0.0000	0.0000	7431.5876	6141.7637	10493.5030
15	0.0000	0.0000	-105263.3600	-104972.4700	-142755.1100
16	30.0000	20.0000	-13.2999	6.6007	-9.3270
17	0.0000	0.0000	-0.0281	-0.0286	-0.0289

TABLE V-5

STANDARD DERIVATIONS FOR CORIOLIS RESONANCE FITTING CASE 2
(in cm^{-1} except parameter 3)

Iteration	σ_P	σ_R	σ_{total}
1	3.2692	2.1461	2.7653
2	1.6409	1.1239	1.4064
3	0.8212	0.5685	0.7062
4	0.4110	0.2964	0.3583
5	0.2061	0.1691	0.1885
6	0.1040	0.1219	0.1133
7	0.0520	0.0963	0.0774
8	0.0295	0.0947	0.0701
9	0.0241	0.0892	0.0654
10	0.0146	0.0878	0.0629
11	0.0103	0.0874	0.0622
12	0.0084	0.0888	0.0631
13	0.0080	0.0881	0.0625
14	0.0078	0.0885	0.0628
15	0.0073	0.0879	0.0624

of the corresponding transition in the perpendicular band. This assumption produced a total of 16 parallel band transitions in the two crossing regions. These additional data points are sufficient to stabilize the fitting process. The parameters for this case are listed in Table V-6 and the standard deviation in Table V-7.

Note that the parallel band parameters are not close to the simulation values (column 2) even after five iterations. The $\alpha_{\parallel}^{B}$ parameter is reasonably well characterized in the resonance region, but $\nu_{0,\parallel}$ and $\alpha_{\parallel}^{A}$ are determined essentially from the two crossing points in the K=6 and K=7 subbands. Had the intensities of the two bands been reversed, the parallel band being observed with a few resonance enhanced perpendicular band observations, the procedure would not have converged as well. For the reversed case three parameters, $\nu_{0\perp}$, $\alpha_{\perp}^{A}$ and $A\zeta$, must be determined from the two crossing points and it should be expected that $\nu_{0,\perp}$, $\alpha_{\perp}^{A}$ and $A\zeta$ would not be well determined.

V-4. FITTING SUBBANDS WITH LOCAL CROSSINGS

The data set for this test is the $\nu_4^{-1}:2\nu_2$ K=2 subbands of $^{13}CD_3F$. These states cross between J=14 and J=15. The model used has three subband parameters for each state and one resonance parameter.

$$H_{11} = \nu_4(2) + \alpha_4^B(2)J(J+1) + \beta_4^J(2)J^2(J+1)^2 \qquad (5\text{-}1)$$

$$H_{22} = \nu_{22}(2) + \alpha_{22}^B(2)J(J+1) + \beta_{22}^J(2)J^2(J+1)^2 \qquad (5\text{-}2)$$

$$H_{12} = H_{21} = C_{422}\sqrt{J(J+1)-K(K-1)} \qquad (5\text{-}3)$$

TABLE V-6

PARAMETER VALUES FOR CORIOLIS RESONANCE FITTING CASE 3
(in cm^{-1} except parameter 3)

Parameter Number	Simulation Value	Starting Value	Five Iterations	Ten Iterations	Fifteen Iterations
1	2059.70000	2057.70000	2059.64100	2059.69960	2059.70000
2	2086.00000	2085.92000	2086.00000	2086.00010	2086.00010
3	-0.28000	-0.30000	-0.27985	-0.27999	-0.28000
4	10.00000	12.00000	9.31891	9.98189	9.99935
5	20.00000	18.80000	20.18928	20.00480	20.00006
6	18.00000	20.00000	18.07741	18.00083	18.00004
7	5.00000	4.50000	4.97144	4.99953	5.00002
8	0.00000	0.00000	1.55243	0.04789	0.00247
9	0.00000	0.00000	-36.06428	-0.94134	-0.04172
10	0.00000	0.00000	0.00082	-0.00003	0.00001
11	0.00000	0.00000	2.80876	0.08101	0.00497
12	0.00000	0.00000	-1295.85090	-32.59228	-1.27525
13	0.00000	0.00000	0.00363	0.00012	0.00003
14	0.00000	0.00000	-0.27335	-0.00702	-0.00013
15	0.00000	0.00000	2.16715	0.04918	0.00064
16	30.00000	20.00000	25.99907	29.90868	29.99718
17	0.00000	0.00000	-0.00706	-0.00019	-0.00001

TABLE V-7

STANDARD DEVIATIONS FOR CORIOLIS RESONANCE FITTING CASE 3
(in cm^{-1})

Iteration	σ_P	σ_Q	σ_R	σ_{total}
1	3.2692	0.2114	2.1461	2.2611
2	1.6346	0.1301	1.0831	1.1346
3	0.8174	0.1132	0.5559	0.5744
4	0.4088	0.0801	0.2841	0.2911
5	0.2044	0.0819	0.1616	0.1577
6	0.1022	0.0841	0.1110	0.0997
7	0.0511	0.0856	0.0940	0.0791
8	0.0256	0.0127	0.0212	0.0205
9	0.0032	0.0016	0.0026	0.0025
10	0.0016	0.0008	0.0013	0.0013
11	0.0008	0.0004	0.0007	0.0006
12	0.0004	0.0002	0.0003	0.0003
13	0.0002	0.0001	0.0002	0.0002
14	0.0001	0.0001	0.0001	0.0001
15	0.0000	0.0001	0.0000	0.0001

The two in parentheses is to indicate that the parameters apply to the K=2 subband. Starting values were chosen to insure a crossing of the two calculated states. Ten iterations were performed which reduced the unweighted standard deviation to 3.1×10^{-3} cm^{-1}. The $2\nu_2$ line positions, except in the resonance region, are weak and most of the larger residuals belong to low J $2\nu_2$ lines which are blended with the K=0 and K=1 $2\nu_2$ lines of the same J. Table V-8 gives the values of all the parameters at each iteration. Table V-9 gives the observed and calculated transition frequency for each observation. The columns under S and S' are the assigned state index (1 for ν_4^{-1}, 2 for $2\nu_2$) and the algorithm reassigned state, respectively. For this case, no assignment switching was done on the last iteration. The calculated value of the resonance induced shift is listed in the last column of Table V-9, where negative shifts are to lower frequencies. Note that the standard deviations apply to the parameter set of the previous iteration. The fit in the region of the local resonance, $13 \leq J \leq 17$ is very good with the residuals less than 1% of the resonance induced shift.

TABLE V-8

PARAMETERS FOR ν_4:$2\nu_2$ K=2 SUBBAND FIT
(all values in cm^{-1})

Iteration	$\nu_4(2)$	$2\nu_2(2)$	$\alpha_4^B \times 10^3$	$\alpha_{22}^B \times 10^3$	$\beta_4^J \times 10^6$	$\beta_{22}^J \times 10^6$	$C_{422} \times 10^3$	Standard Deviation
0	2237.5017	2234.0058	0.4000	-12.0000	0.0000	0.0000	30.2383	-
1	2237.5546	2234.0395	1.0803	-14.5751	1.3796	-1.7113	30.1906	0.6237
2	2237.5539	2234.0846	0.7544	-15.2049	0.8666	-1.3574	28.9721	0.3072
3	2237.5532	2234.1079	0.5585	-15.4827	0.5381	-1.1001	27.7830	0.1530
4	2237.5526	2234.1199	0.4507	-15.6108	0.3552	-0.9508	27.0539	0.0764
5	2237.5522	2234.1260	0.3941	-15.6719	0.2588	-0.8710	26.6566	0.0382
6	2237.5520	2234.1290	0.3651	-15.7018	0.2094	-0.8298	26.4498	0.0193
7	2237.5519	2234.1305	0.3504	-15.7166	0.1843	-0.8090	26.3442	0.0100
8	2237.5519	2234.1313	0.3429	-15.7234	0.1713	-0.7975	26.2907	0.0057
9	2237.5519	2234.1319	0.3389	-15.7242	0.1642	-0.7875	26.2651	0.0039
10	2237.5519	2234.1326	0.3367	-15.7209	0.1597	-0.7768	26.2536	0.0034

TABLE V-9

OBSERVED AND CALCULATED FREQUENCIES
FOR THE ν_4:$2\nu_2$ SUBBAND FIT

K	J	S	S'	Observed Frequency	Calculated Frequency	Observed-Calculated	Shift
2	2	1	1	2237.5532	2237.5507	0.0025	0.0008
2	3	1	1	2237.5481	2237.5500	-0.0019	0.0021
2	4	1	1	2237.5479	2237.5492	-0.0013	0.0040
2	4	2	2	2234.4315	2234.4427	-0.0112	-0.0040
2	5	1	1	2237.5481	2237.5485	-0.0004	0.0066
2	5	2	2	2234.6062	2234.5970	0.0092	-0.0066
2	6	1	1	2237.5431	2237.5480	-0.0049	0.0100
2	6	2	2	2234.7850	2234.7815	0.0035	-0.0100
2	7	1	1	2237.5490	2237.5482	0.0008	0.0147
2	7	2	2	2234.9926	2234.9959	-0.0033	-0.0147
2	8	1	1	2237.5522	2237.5496	0.0026	0.0211
2	8	2	2	2235.2408	2235.2394	0.0014	-0.0211
2	9	1	1	2237.5542	2237.5530	0.0012	0.0301
2	9	2	2	2235.5136	2235.5110	0.0026	-0.0301
2	10	1	1	2237.5590	2237.5604	-0.0014	0.0436
2	10	2	2	2235.8107	2235.8089	0.0018	-0.0436
2	11	1	1	2237.5790	2237.5751	0.0039	0.0649
2	11	2	2	2236.1278	2236.1293	-0.0015	-0.0649
2	12	1	1	2237.6079	2237.6054	0.0025	0.1021
2	12	2	2	2236.4678	2236.4640	0.0038	-0.1021
2	13	1	1	2237.6727	2237.6721	0.0006	0.1762
2	13	2	2	2236.7904	2236.7919	-0.0015	-0.1762
2	14	1	1	2237.8233	2237.8252	-0.0019	0.3370
2	14	2	2	2237.0636	2237.0628	0.0008	-0.3370
2	15	1	1	2237.2236	2237.2231	0.0005	-0.2572
2	15	2	2	2238.1164	2238.1181	-0.0017	0.2572
2	16	1	1	2237.2964	2237.2958	0.0006	-0.1763
2	16	2	2	2238.5278	2238.5276	0.0002	0.1763
2	17	1	1	2237.3278	2237.3280	-0.0002	-0.1358
2	17	2	2	2239.0072	2239.0063	0.0009	0.1358
2	18	1	1	2237.3434	2237.3426	0.0008	-0.1129
2	18	2	2	2239.5359	2239.5312	0.0047	0.1129
2	19	1	1	2237.3488	2237.3486	0.0002	-0.0985
2	19	2	2	2240.0918	2240.0929	-0.0011	0.0985
2	20	1	1	2237.3474	2237.3500	-0.0026	-0.0887
2	20	2	2	2240.6909	2240.6871	0.0038	0.0887
2	21	1	1	2237.3480	2237.3488	-0.0008	-0.0817
2	21	2	2	2241.3148	2241.3116	0.0032	0.0817
2	22	1	1	2237.3494	2237.3460	0.0034	-0.0765
2	22	2	2	2241.9652	2241.9650	0.0002	0.0765

CHAPTER VI

BACKGROUND INFORMATION FOR $^{13}CD_3F$

VI-1. THE HIGH RESOLUTION INFRARED SPECTRUM OF $^{13}CD_3F$

The infrared spectrum of $^{13}CD_3F$ was recorded on The University of Tennessee 5-m Littrow spectrometric system (Jennings, 1974). The spectrometer uses a 41 x 20 cm, 31.6/mm grating blazed at 65°. The spectrometer is computer controlled during a scan with a PDP11/20 computer used to control the grating angle, the prism predisperser angle and the ditital filtering of the incoming data.

The spectrum of $^{13}CD_3F$ was recorded at pressures of 0.40 Torr and 3.00 Torr using a 1-meter sample cell. The spectrum was recorded three times for each pressure under identical conditions and the three runs were averaged. The signal-to-noise ratio in each scan ranged from 30 to 80 depending on angle and grating order. The spectrum was recorded in three approximately equal sections of 95 cm^{-1} for each pressure. The three sections of the spectrum were individually calibrated using the CO fundamental recorded in 12th order. The CO line positions were determined in a separate piecewise scan of the entire region in which only the CO lines and selected, well-isolated lines of $^{13}CD_3F$ were scanned. The $^{13}CD_3F$ sample contains a 10% impurity of $^{12}CD_3F$ and a trace amount of CO_2. The standard deviation of the calibration fits and the prediction of the

CO_2 line frequencies indicate that the calibration accuracy ranges from 0.0008 cm^{-1} to 0.0014 cm^{-1} depending on angle and order.

All data were recorded with a fix nominal slit width of 400 μm yielding a resolution of 0.016 cm^{-1} with 0.0012 cm^{-1}/data point. The spectral records were averaged, smoothed, baseline corrected and deconvolved in the manner described by Blass and Halsey (1981). The resolution after deconvolution was 0.006 cm^{-1}. The calibration was repeated after deconvolution with no appreciable improvement since well-isolated single lines had been used in the initial calibration.

The transition frequencies for the entire spectral record were computer measured using a simple peak finding routine. The peak finding routine stored the frequency and peak height in a permanent file. This frequency list was used primarily to produce Loomis-Wood type plots. Many of the assigned transition frequencies particularly those belonging to the ν_1 band were remeasured using a CRT display with a light pen controlled cursor. Approximately 4000 transition frequencies were recorded with nearly one-third of these belonging to $^{12}CD_3F$.

VI-2. THE GROUND STATE CONSTANTS OF $^{13}CD_3F$

The ground state constants for $^{13}CD_3F$ were determined from the ν_1 transition frequencies measured in both the low and high pressure runs. The constants B_0, D_0^J and D_0^{JK} were determined from a biweighted fit of 501 combination differences. After 8 iterations the 412 non-zero weighted combination differences fit to a standard deviation

of 1.29×10^{-2} cm^{-1}. Since the uncertainty in a combination difference is $\sqrt{2}$ times the uncertainty in the measurement of a transition frequency the process was terminated after this iteration. The results are shown in Table VI-1.

TABLE VI-1

GROUND STATE CONSTANTS OF $^{13}CD_3F$ IN CM^{-1}*

B_0	= .6708360(40)
D_0^J	= $1.1004(44) \times 10^{-6}$
D_0^{JK}	= $7.292(42) \times 10^{-6}$

*Values in parentheses are the standard error of the parameters in units of the last digit quoted.

Various subsets of the ground state combination differences such as high pressure run R transitions minus low pressure run P transitions were also fitted to see if the calibrations had any detectable systematic error. All such combinations gave essentially the same results. An attempt to determine the higher order ground state constants H_0^J, H_0^{JK} and H_0^{KJ} failed. These constants were not statistically significant in the ν_1 ground state combination difference fit. The ground state parameters A_0 and D_0^K were assumed to be the same as for $^{12}CD_3F$ (Daunt, 1979).

$$A_0 = 2.604 \text{ cm}^{-1} \quad (6\text{-}1)$$

$$D_0^K = 16.2 \times 10^{-6} \text{ cm}^{-1} \quad (6\text{-}2)$$

There are no reported values for the ground state constants of $^{13}CD_3F$.

VI-3. THE MOLECULAR PARAMETERS OF $^{13}CD_3F$

One problem in interpreting and analyzing the spectrum of an isotopically substituted molecule such as $^{13}CD_3F$ is the lack of previously determined molecular parameters. Four of the fundamental vibrations of $^{13}CD_3F$ lie in the 10 μm spectral region and have not been studied in any detail. These bands have overtones and binary combination bands in the 5 μm region and most participate in the resonance network and are of interest in this work.

The molecular parameters for $^{13}CD_3F$ can be borrowed from $^{12}CD_3F$, $^{12}CH_3F$ and $^{13}CH_3F$ and to a lesser extent from other methyl halides. In many instances the methyl fluoride molecular parameters do not resemble the parameters of other methyl halides because the molecular geometry is different (Duncan, 1968). The CH bond length is increased for methyl fluorides.

The spectrum of $^{12}CD_3F$ has been studied at 10 μm. The laser Stark data of Duxbury and Freund (1977) were reanalyzed by Blass (1982) using a perturbation analysis method similar to the algorithm developed in Chapter IV. These results will be used as estimates for ν_3 and ν_6 of $^{13}CD_3F$.

The ν_2 and ν_5 bands of $^{12}CD_3F$ were analyzed by Caldow and Halonen (1982). The molecular parameters for $^{13}CD_3F$ ν_2 and ν_5 are assumed to be equal to the values obtained in their $^{12}CD_3F$ analysis. These

values are included in Table VI-2 for α_2^A, α_2^B, α_5^A, α_5^B, ζ_5^Z and ζ_{25}^X. The parameters for ν_1 and ν_4 of $^{13}CD_3F$ in Table VI-2 are from a preliminary analysis of the high resolution data of this work. The α_1^B parameters were adjusted to account for the coupling scheme $\nu_1:2\nu_5:\nu_2+\nu_5:2\nu_2$.

The band centers are obtained from three sources. A 0.2 cm^{-1} resolution FTIR spectrum of $^{13}CD_3F$ gives the band centers for ν_2, ν_3, and $2\nu_3$. A 0.3 cm^{-1} resolution Raman spectrum of $^{13}CD_3F$ gives the band center for $\nu_2+\nu_3$ and $2\nu_2$. The ν_6 band center was calculated from matrix isolation spectra studies (Gauthier-Roy, 1981). The ν_5 fundamental is not well known at this time. It is assumed to be 5 cm^{-1} below ν_5 for $^{12}CD_3F$.

The initial estimates for the molecular parameters for $^{13}CD_3F$ are listed in Table VI-2. The α and ζ parameters for the combination bands and overtone bands are just the sum of the α and ζ parameters for the fundamentals. The Fermi resonance parameters are estimated from Champion (1982). The Fermi parameter W_{155} is adjusted downward to give relative intensities for ν_1 and $2\nu_5$ in agreement with the estimated band strengths from the FTIR spectra $I(\nu_1)/I(2\nu_5) = 6$. The Fermi parameters were also scaled proportional to the vibrational energies, i.e.,

$$W_{122}(^{13}CD_3F) = W_{122}(CH_3F)\,\frac{\nu_1+2\nu_2(^{13}CD_3F)}{\nu_1+2\nu_2(CH_3F)}\,. \qquad (6\text{-}1)$$

TABLE VI-2

ESTIMATED MOLECULAR PARAMETERS FOR $^{13}CD_3F$
(all values in cm^{-1} except ζ's)

	ν_0	α^A	α^B	ζ^Z
ν_1	2102.1	0.0188	-0.0035	
ν_2	1114.1	-0.0056	0.0033	
ν_3	986.0	0.0012	0.0029	
ν_4	2241.35	0.0120	0.0004	0.179
ν_5	1077	0.0142	-0.0033	-0.2969
ν_6	907.0	-0.0063	0.0054	0.2543
$\nu_2+\nu_3$	2092.5	-0.0044	0.0061	
$2\nu_5$ (ℓ=0)	2131.8	0.0284	-0.0066	
$2\nu_2$	2228.8	-0.0112	0.0066	
$\nu_2+\nu_5$	2183	0.0086	0.0000	-0.2969
$\nu_3+\nu_5$	2058	0.0154	-0.0004	-0.2969
$\nu_2+\nu_6$	2021	-0.0119	0.0087	0.2543

$\zeta^X_{25} = 0.5422$

$\zeta^X_{36} = 0.4313$

$W_{155} = 18.6$

$W_{122} = 27.0$

$W_{2255} = -5.8$

CHAPTER VII

THE ν_1 BAND OF $^{13}CD_3F$

VII-1. OVERALL APPEARANCE OF THE ν_1 BAND

The ν_1 band from 2048.75 cm^{-1} to 2133.0 cm^{-1} of $^{13}CD_3F$ is shown in a Loomis-Wood type plot in Figure VII-1. In this plot the value of B, one-half the width of each section of the spectrum, was varied from 0.6248 cm^{-1} at the bottom of the plot to 0.6712 cm^{-1} at the band center to 0.7256 cm^{-1} at the top of the plot. This plot covers the ν_1 band from P_{29} through R_{34}. In the R-side of this band there are many scattered lines which have been assigned to $2\nu_5^0$.

In Figure VII-1, the value of B was varied so that the low K subbands formed nearly straight lines for J less than 20. The low K subbands all bent downward at higher values of J indicating the effects of a nonlocalized interaction. There are also several local resonances affecting the K=5 through K=9 subbands. The ν_1 spectrum has been assigned through K=16 including doubled transitions in the K=5 through 8 subbands. There are also weaker localized interactions in the K=0, 4, 6, 7, and 14 subbands which are not evident in the condensed plot shown in Figure VII-1.

VII-2. NON-PERTURBATION FIT

The assigned transition frequencies for ν_1 are converted to effective Q-branch transition frequencies using the ground state

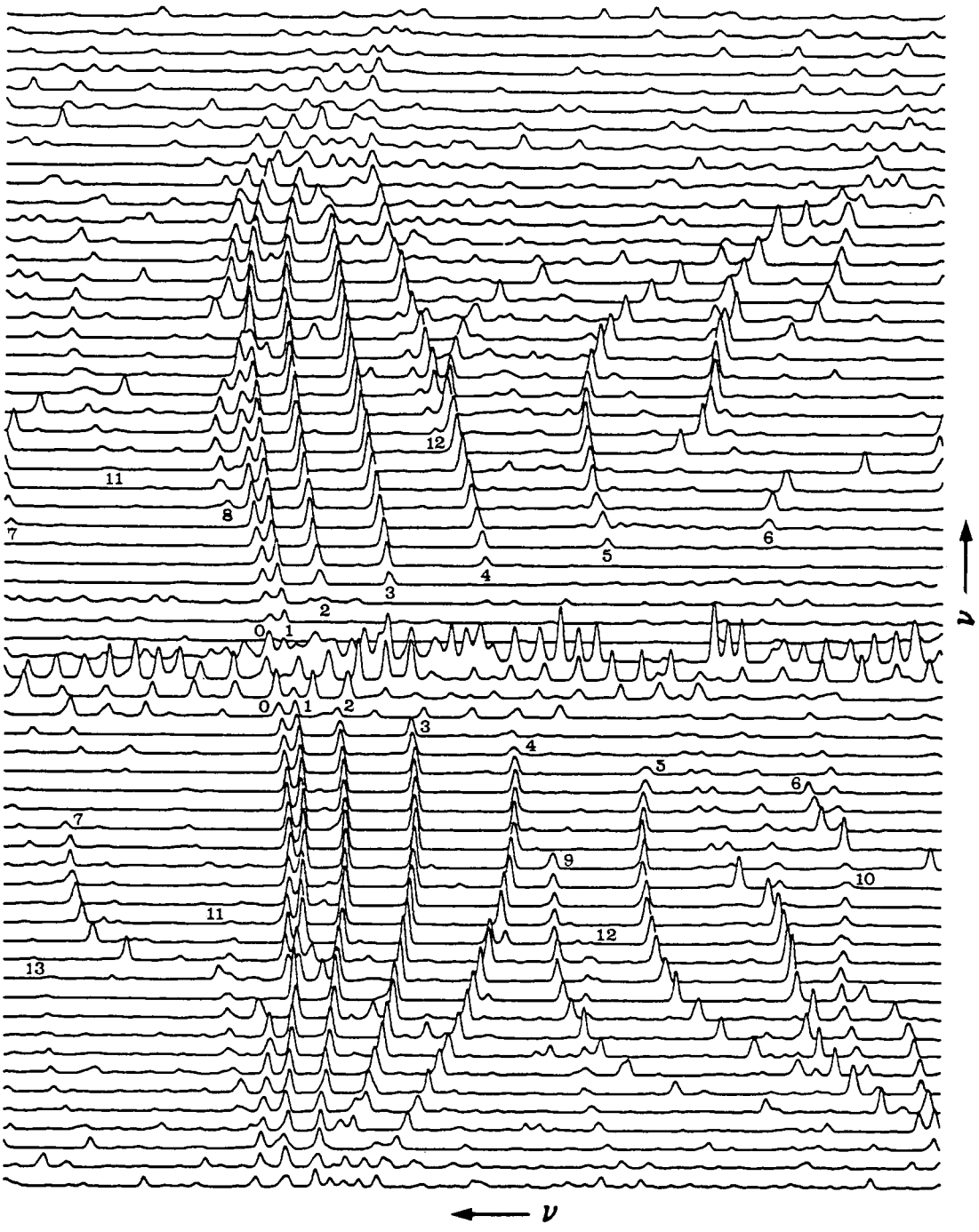


Figure VII-1. The ν_1 band of $^{13}CD_3F$.

parameters from Table VI-1 (p. 65). Over 300 Q-branch frequencies were fitted to a fourth order Hamiltonian model to yield approximate effective molecular parameters for the ν_1 band. In this bi-weighted fit a 3σ cutoff was used and approximately half of the observations were eventually given a weight of zero. The final weighted standard deviation after 10 iterations was 2.1×10^{-3} cm^{-1}, or approximately twice the experimental uncertainty in a measured transition frequency. The parameters from this fit are given in Table VII-1. The values for the β coefficients, particularly β^K are larger than expected from the order of magnitude estimate for h_4'' parameters as described in Chapter I, indicating that the β coefficient are accommodating a resonance effect.

TABLE VII-1

EFFECTIVE PARAMETERS FOR THE ν_1 BAND OF $^{13}CD_3F$*
(all values in cm^{-1})

ν_0	2085.9125(21)
α^A	1.88120(9)
α^B	-1.694(6)
β^J	$-5.4(12) \times 10^{-8}$
β^{JK}	$8.2(3) \times 10^{-7}$
β^K	$-4.85(5) \times 10^{-6}$
Weighted σ	2.1×10^{-3}

*Values in parentheses are the standard errors in units of the last digit.

VII-3. THE ν_1 SHIFT FOR THE $\nu_1:2\nu_5:\nu_2+\nu_5:2\nu_2$ COUPLING

Using the estimated parameters established in Chapter VI the ν_1 shift for the $\nu_1:2\nu_5:\nu_2+\nu_5:2\nu_2$ coupling can be estimated. In this calculation the seven state Hamiltonian shown in Figure VII-2 is diagonalized for K_{max} = 12 and J_{max} = 30 and the ν_1 shifts are fitted in the same manner as a set of parallel band Q-branch transition frequencies. The results are shown in Table VII-2 for the parameters listed in Table VII-3.

The induced rotational effects from the $\nu_1:2\nu_5:\nu_2+\nu_5:2\nu_2$ resonance chain are seen to be poorly described by this six parameter model. The large value for the standard deviation indicates that the ν_1 shift cannot be effectively absorbed into the ν_1 parameters even if β parameters are included. The $\Delta\beta_1^K$ parameter is dramatically changed when the J value for shifts included in the fit is limited to 20. In neither case do the induced $\Delta\beta_1$ terms reflect the β_1 parameters from the ν_1 non-perturbation fit. This might be remedied by reducing the Fermi resonance parameters W_{122} and W_{155}.

VII-4. THE $\nu_1:2\nu_5^{-2}$ CROSSING

Part of the discrepancy in the ν_1 shift fits is due to a crossing between $\nu_1(K)$ and $2\nu_5(K-2,\ell=-2)$. This is a curious interaction and is indicative of the problems involved in fitting a complex system of vibration-rotation interactions. This is termed a second order interaction because there is no direct coupling between these states in the

$2\nu_2(K)$	C_{25}^{-1}	C_{25}^{+1}		W_{2255}		W_{122}
C_{25}^{-1}	$\nu_2+\nu_5(K-1,-1)$	Q_5	C_{25}^{-2}	C_{25}^{-1}		
C_{25}^{+1}	Q_5	$\nu_2+\nu_5(K+1,+1)$		C_{25}^{+}	C_{25}^{+2}	
	C_{25}^{-2}		$2\nu_5(K-2,-2)$	Q_5^{-}		
W_{2255}	C_{25}^{-1}	C_{25}^{+1}	Q_5^{-}	$2\nu_5(K)$	Q_5^{+}	W_{155}
		C_{25}^{+2}		Q_5^{+}	$2\nu_5(K+2,+2)$	
W_{122}				W_{155}		$\nu_1(K)$

$$C_{25}^{-1} = C_{25}\sqrt{J(J+1)-K(K-1)}$$

$$C_{25}^{+1} = C_{25}\sqrt{J(J+1)-K(K+1)}$$

$$C_{25}^{-2} = C_{25}^{-}\sqrt{J(J+1)-(K-1)(K-2)}$$

$$C_{25}^{+2} = C_{25}^{+}\sqrt{J(J+1)-(K+1)(K+2)}$$

$$Q_5 = 1/2\ q_5\sqrt{J(J+1)-K(K+1)}\sqrt{J(J+1)-K(K-1)}$$

$$Q_5^{-} = 1/2\ q_5\sqrt{J(J+1)-K(K-1)}\sqrt{J(J+1)-(K-1)(K-2)}$$

$$Q_5^{+} = 1/2\ q_5\sqrt{J(J+1)-K(K+1)}\sqrt{J(J+1)-(K+1)(K+2)}$$

Figure VII-2. The $\nu_1:2\nu_5:\nu_2+\nu_5:2\nu_2$ approximate Hamiltonian.

TABLE VII-2

ESTIMATE FOR THE ν_1 SHIFT FOR THE $\nu_1:2\nu_5:\nu_2+\nu_5:2\nu_2$ Hamiltonian
(all values in cm^{-1})

	$J_{max} = 30$	$J_{max} = 20$
$\Delta\nu_1$:	-16.194	-16.191
$\Delta\alpha_1^A$:	-0.00188	-0.00064
$\Delta\alpha_1^B$:	0.00325	0.00315
$\Delta\beta_1^J$:	-5.3×10^{-7}	-7.0×10^{-7}
$\Delta\beta_1^{JK}$:	-9.2×10^{-6}	-9.9×10^{-6}
$\Delta\beta_1^K$:	-1.13×10^{-5}	2.33×10^{-6}
	$\sigma = 0.029$	$\sigma = 0.007$

TABLE VII-3

ESTIMATED PARAMETERS FOR THE $\nu_1:2\nu_5:\nu_2+\nu_5:2\nu_2$ HAMILTONIAN
(all values in cm^{-1} except ζ_5^Z)

ν_1	=	2102.0943
α_1^A	=	0.018812
α_1^B	=	-0.0034
ν_{55}^0	=	2131.875
$\nu_{55}^{\pm 2}$	=	2139.070
α_{55}^A	=	0.024
α_{55}^B	=	0.0
ζ_5^Z	=	-0.29
$\nu_2+\nu_5$	=	2174.5
α_{25}^A	=	0.008
α_{25}^B	=	0.0
$2\nu_2$	=	2228.785
α_{22}^A	=	-0.012
α_{22}^B	=	0.0
W_{155}	=	21.6
W_{122}	=	27.5
W_{2255}	=	-3.88
C_{25}	=	0.55
q_5	=	0.0025

Hamiltonian used in the simulation. However, if the Fermi resonance between ν_1 and $2\nu_5(\ell=0)$, the ℓ-doubling in $2\nu_5$ and the Coriolis resonances linking $2\nu_5$, $\nu_2+\nu_5$ and $2\nu_2$ exists there must be a local resonance effect where ν_1 and $2\nu_5^{-2}$ cross. The band center for $2\nu_5^{\pm 2}$ must be adjusted so that the crossing between ν_1 and $2\nu_5^{-2}$ corresponds to an observed local crossing in ν_1. The parameter X_{155} is defined as the effective resonance parameter for the ν_1:$2\nu_5^{-2}$ second order interaction.

With the simulation parameters of Table VII-3 the $2\nu_5^{-2}$ and ν_1 states cross at K=5, J=22→23 in ν_1. The crossing point is nearly independent of q_5 for values of q_5 from -0.01 cm^{-1} to 0.01 cm^{-1}. The average shift for J=22 and J=23 is a good measure of the effective resonance parameter X_{155} between ν_1 and $2\nu_5^{-2}$. Values of X_{155} and q_5 are listed in Table VII-4. This represents an instance where if a resonance is to be properly fitted the sign as well as the magnitude of the resonance parameters must be correct. This resonance is indicated as X_{155} in Figure VII-3.

VII-5. LOCALIZED CROSSINGS IN THE ν_1 BAND

The K=5 through K=8 subband residuals are plotted against J in Figure VII-3 through Figure VII-6. The residuals are the observed effective Q-branch transition frequencies minus the frequencies calculated using the effective ν_1 parameters listed in Table VII-1. There are localized resonances in each of these subbands which have been unambiguously assigned. The $\nu_3+\nu_5$ band interacts with ν_1 with

TABLE VII-4

EFFECTIVE RESONANCE PARAMETER X_{155} FOR THE $2\nu_5^{-2}:\nu_1$ SECOND ORDER INTERACTION

$1/2\ q_5$ (10^{-3} cm^{-1})	X_{155} (cm^{-1})
-2.00	1.743
-1.50	1.647
-1.00	1.551
-0.50	1.454
0.00	1.357
0.50	1.263
1.00	1.164
1.50	1.067
2.00	0.970
2.50	0.874

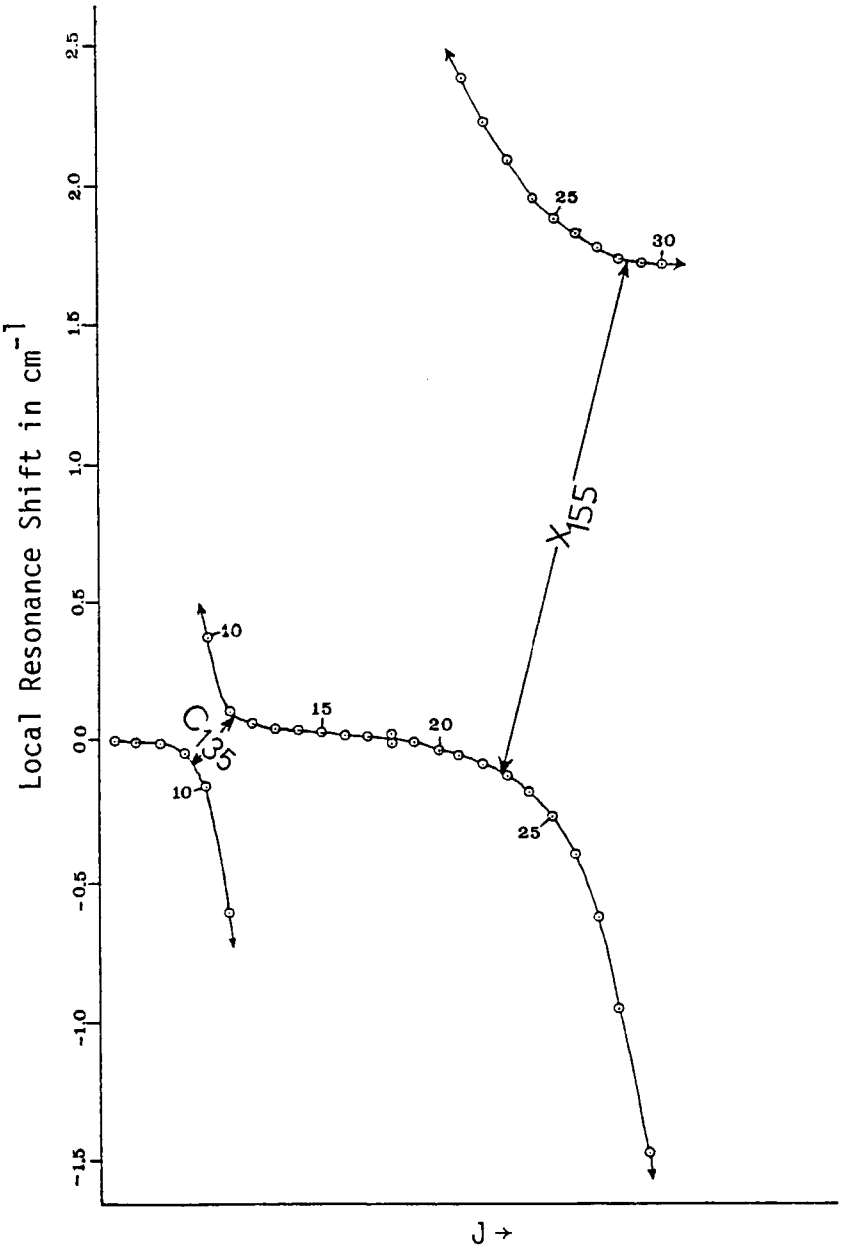


Figure VII-3. The K=6 subband of ν_1, the $\Delta K=+1$, $\Delta \ell=+1$ resonance with $\nu_3+\nu_5^{+1}$ and the $\Delta K=-2$, $\Delta \ell=-2$ resonance with $2\nu_5^{-2}$.

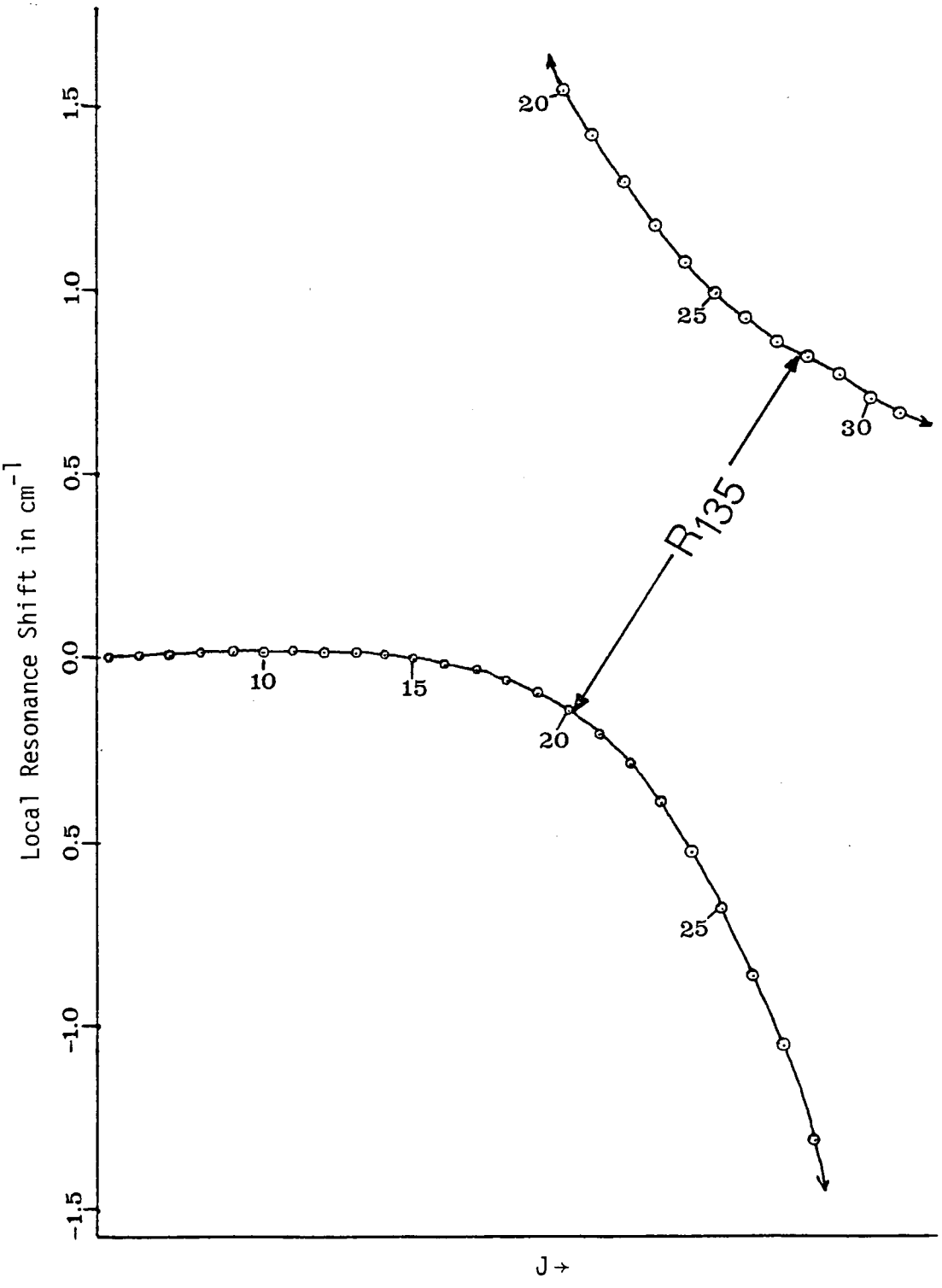


Figure VII-4. The K=5 subband of ν_1, the $\Delta K=+2$, $\Delta \ell=-1$ resonance with $\nu_3+\nu_5^{-1}$.

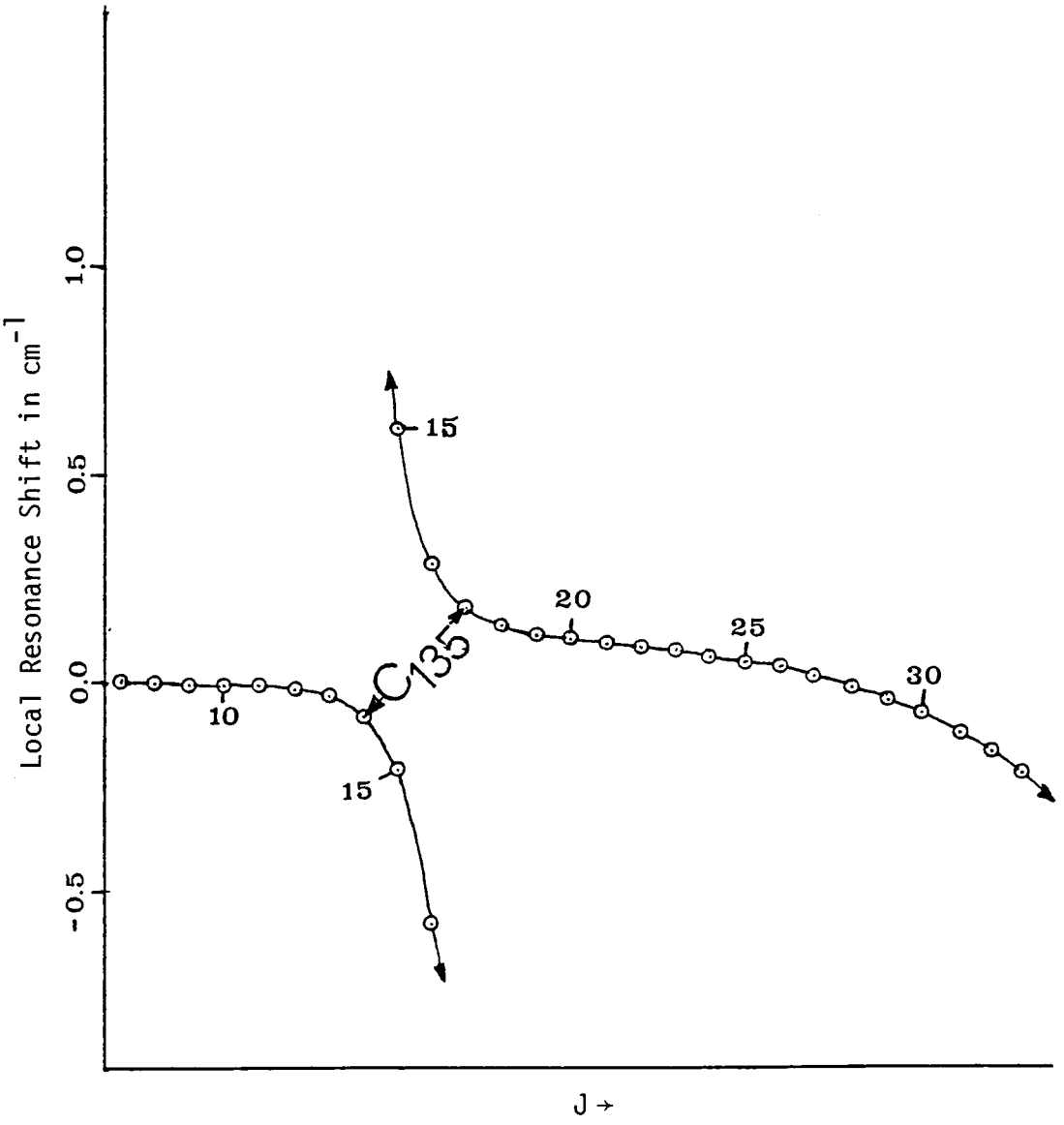


Figure VII-5. The K=7 subband of ν_1, the $\Delta K=+1$, $\Delta \ell=+1$ resonance with $\nu_3+\nu_5^{+1}$.

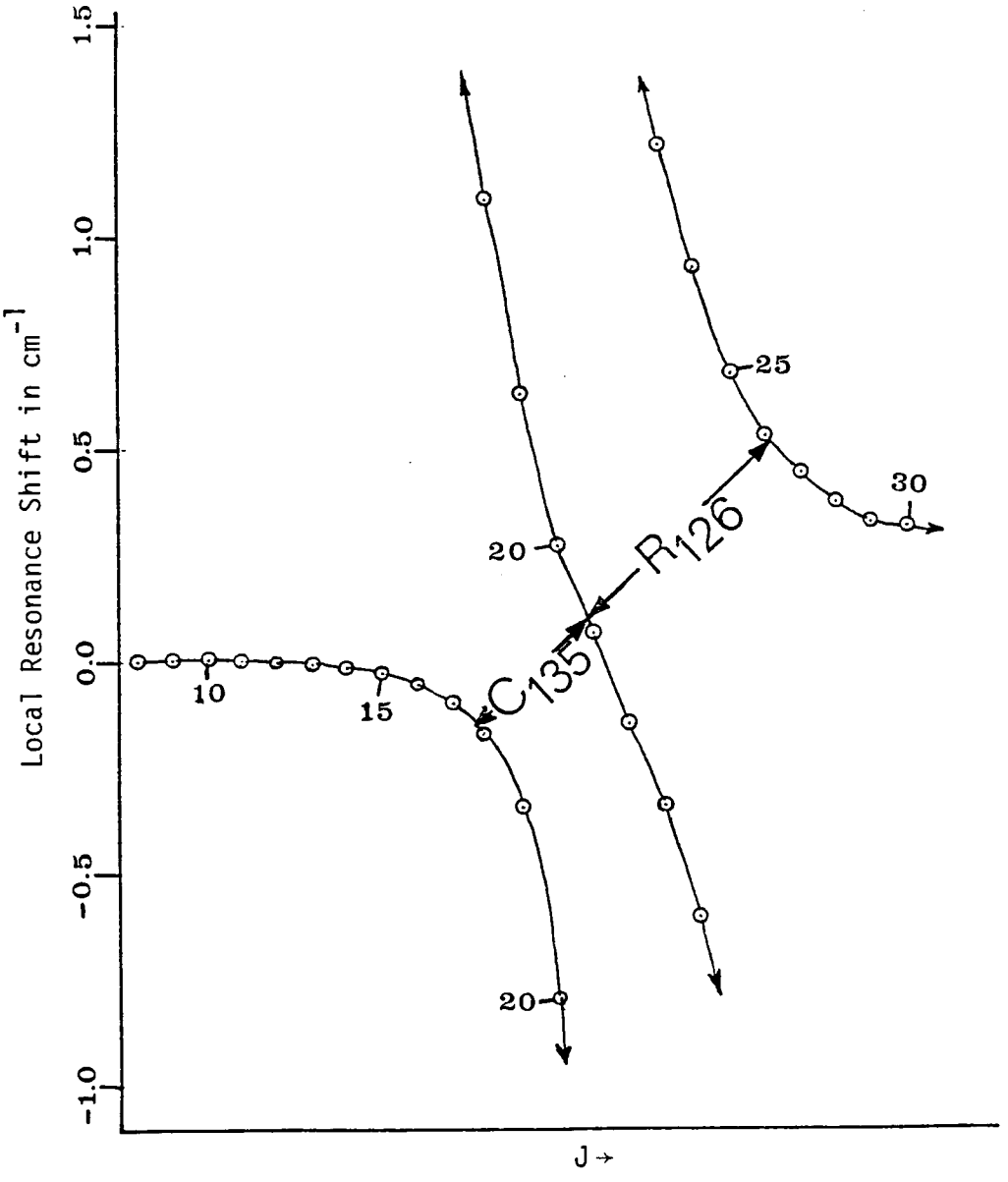


Figure VII-6. The K=8 subband of ν_1, the $\Delta K=+1$, $\Delta \ell=+1$ resonance with $\nu_3+\nu_5^{+1}$ and the $\Delta K=+2$, $\Delta \ell=-1$ resonance with $\nu_2+\nu_6^{-1}$.

both a Coriolis (type II) and a type IV rotational resonance. The $\Delta K=\Delta\ell=\pm 1$ resonance produces crossings in ν_1 at K=6, J_x=10.5; K=7, J_x=15.5; and K=8, J_x=19, where J_x is the approximate value of J at exact resonance. The effect is observed for the K=9, 10, 11, and 12 subbands also, but transitions for $J>J_x$ for those interactions have not yet been assigned. The $\Delta K=\Delta\ell=\pm 1$ crossings are indicated by C_{135} in the residual plots.

The K=5 subband of ν_1 exhibits a localized crossing with J_x = 24. This has been assigned as a $\Delta K=+2$, $\Delta\ell=-1$ (type IV) resonance between ν_1 and $\nu_3+\nu_5^{-1}$. This resonance effect is indicated by R_{135} in the residual plots. The two resonances between ν_1 and $\nu_3+\nu_5$ can only be realized if the resonances between $\nu_3+\nu_5$ and $\nu_2+\nu_3$, a strong Coriolis resonance, and the resonance between ν_1 and $\nu_2+\nu_3$, a weak Fermi resonance are taken into account. Using the estimated values for α^A_{2+3}, α^B_{2+3}, α^A_{3+5}, α^B_{3+5}, ζ^Z_5, W_{123} and C_{25} from Chapter VI, the band centers of $\nu_2+\nu_3$ and $\nu_3+\nu_5$ can be found by trial and error to be:

$$\nu_2+\nu_3 \approx 2092.8$$

$$\nu_3+\nu_5 \approx 2053.4$$

These estimates give a reasonable agreement for the crossing J values for both resonances. However, the crossing in the ν_1(K=8) subband is not with $\nu_3+\nu_5$ but with $\nu_2+\nu_3$ for this parameter set. The K=8 subbands of $\nu_2+\nu_3$ and $\nu_3+\nu_5$ are almost identical and the state which actually crosses ν_1 is almost an equal mixture of the two states since the C_{25} resonance parameter is large.

There is one additional localized crossing which has been assigned. This occurs in the K=8 subband at about J_x=25. The exact crossing point is difficult to estimate since it is very near to the $\Delta K=\Delta \ell=+1$ crossing with $\nu_2+\nu_3:\nu_3+\nu_5$. This interaction is labeled R_{126} in the residual plots. The resonance parameters for these interactions can be estimated from the separation of the doubled transitions where $\Delta E \approx 0$ for the two bands since the coupling types are known. These are listed in Table VII-5.

TABLE VII-5

COUPLING CONSTANTS FOR THE LOCAL CROSSINGS IN ν_1

C_{135} = ±0.0299	K=6
C_{135} = ±0.0290	K=7
C_{135} = ±0.0279	K=8
R_{135} = ±0.00149	K=5
R_{126} = ±0.00166	K=8

CHAPTER VIII

THE $2\nu_5(\ell=0)$ BAND OF $^{13}CD_3F$

The ν_2 and ν_5 bands of methyl halides characteristically exhibit a strong Coriolis (type II) interaction. In addition the Fermi resonance between ν_1 and $2\nu_5(\ell=0)$ is strong. These effects combine to produce very strong perturbation effects in $2\nu_5(\ell=0)$ of $^{13}CD_3F$.

VIII-1. SUBBAND FITS FOR $2\nu_5(\ell=0)$

The close proximity of both ν_1 ($\Delta\nu \approx 30$ cm^{-1}) and $\nu_2+\nu_5$ ($\Delta\nu \approx 45$ cm^{-1}) and the large interaction parameters ($C_{25} \approx 0.55$ cm^{-1} and $W_{155} \approx 20$ cm^{-1}) combine to produce a highly irregular band labeled as $2\nu_5(\ell=0)$ but containing a substantial contribution from both ν_1 and $\nu_2+\nu_5$. The strong rotational effects induced by the Coriolis resonance render the Loomis-Wood technique of little use for the $2\nu_5(\ell=0)$ band. The $2\nu_5(\ell=0)$ band has been assigned for K=0 through 14 for J up to 25 for low K values and J up to about K+6 for the higher K values. For subbands with $K \leq 8$ the strong Coriolis resonance with $\nu_2+\nu_5$ pushes the $2\nu_5(\ell=0)$ states downward and for subbands with $K \geq 9$ this same interaction pushes the $2\nu_5(\ell=0)$ levels upward. The effective α^B parameter for $2\nu_5(\ell=0)$ can be written using the effective parameter method described in Section III-4 as

$$\alpha^B_{obs}(K) \approx \alpha^B_{true} + \frac{(C_{25})^2}{\Delta E - wK} + \frac{(C_{25})^2}{\Delta E + wK} . \qquad (8\text{-}1)$$

Here $\alpha^B_{obs}(K)$ is the effective α^B parameter for the K-th subband,

α^B_{true} is α^B_{55} in the absence of the Coriolis resonance, $C_{25} \simeq \sqrt{2}\ B\ \zeta^x_{25}$ is the interaction parameter and $\Delta E \pm wK$ the subband energy differences between $2\nu_5(\ell=0)$ and $\nu_2+\nu_5(\ell=\pm 1)$. The parameter w is defined by

$$w = 2(A-B-A\zeta^Z_5) = 5.375\ cm^{-1} \tag{8-2}$$

for $\zeta^Z_5 = -0.29\ cm^{-1}$. Equation (8-1) can be rewritten

$$\alpha^B_{obs}(K) \approx \alpha^B_{true} + \frac{(C_{25})^2}{w}\ 2K_x/(K_x^2-K^2) \tag{8-3}$$

where K_x is the estimated value of K for which $2\nu_5(\ell=0)$ and $\nu_2+\nu_5(\ell=-1)$ are equal. The measured values of $\alpha^B(K)$ are given in Table VIII-1. Since $\alpha^B(8) \approx -\alpha^B(9)$ $K_x = 8.5$ is assumed. Then Eq. (8-3) is least squares fitted to the measured α^B values to yield

$$\alpha^B_{true} = -0.00018\ cm^{-1} \tag{8-4}$$

$$(C_{25})^2/w = 0.0631\ cm^{-1}\ . \tag{8-5}$$

From Eq. (8-5) and Eq. (8-2), C_{25} is determined to be $-0.582\ cm^{-1}$ in agreement with the value determined by Robiette (1981), $C_{25} = -0.514$ for $^{12}CD_3F$ in a force field calculation. The sign of C_{25} is taken to be negative to agree with the force field calculation since the argument here can only determine C^2_{25}. Since $\Delta E - wK_x = 0$, ΔE can be estimated.

$$\Delta E = wK_x = 45.69\ cm^{-1}\ . \tag{8-6}$$

TABLE VIII-1

SUBBAND FITS FOR $2\nu_5(\ell=0)$ OF $^{13}CD_3F$
(all values except K and number of lines in cm^{-1})

K	No. of Lines	$\nu(K)$	$\alpha^B(K)$	$\beta^J(K)$	"QK,K-1"
0	17	2142.8730	0.2110E -01	-0.8866E -05	2142.8730
1	23	2142.7494	0.1342E -01	0.8625E -05	2142.7494
2	22	2142.7268	0.1469E -01	0.6849E -05	2142.6974
3	22	2142.6551	0.1596E -01	0.6844E -05	2142.5596
4	22	2142.5644	0.1802E -01	0.8217E -05	2142.3494
5	20	2142.4679	0.2126E -01	0.1128E -04	2142.0471
6	12	2142.7599	0.3235E -01	0.3440E -04	2141.8202
7	8	2143.4295	0.5367E -01	0.9428E -04	2141.3416
8	5	2144.5806	0.7524E -01	0.1166E -03	2140.7328
9	17	2139.4627	-0.3663E -01	-0.2216E -04	2141.9851
10	7	2136.8762	-0.4310E -01	-0.3773E -04	2140.4498
11	7	2136.2509	-0.3558E -01	-0.2912E -04	2139.8129
12	4	2136.3625	-0.2505E -01	-0.2359E -04	2139.2585
13	3	2136.4473	-0.1572E -01	-0.1214E -04	2138.6041
14	3	2136.4787	-0.8314E -02	-0.9280E -06	2137.9612

The Coriolis resonance between $2\nu_5(\ell=0)$ and $\nu_2+\nu_5(\ell=\pm1)$ cannot be considered a localized resonance. The $\nu_2+\nu_5(\ell=+1)$ and $\nu_2+\nu_5(\ell=-1)$ components leave nearly equal effects on $2\nu_5(\ell=0)$ for low K subbands. The effects of the $\Delta K=\Delta\ell=+1$ resonance decrease gradually as K increases while the $\Delta K=\Delta\ell=-1$ resonance increases markedly as K approaches $K_x=8.5$. The upper state of the $2\nu_5(\ell=0)$ transitions for K=J are not perturbed by the $\Delta K=\Delta\ell=+1$ interaction since the interaction term $C_{25}\sqrt{J(J+1)-K(K+1)}$ goes to zero. The $\Delta K=\Delta\ell=-1$ resonance term $C_{25}\sqrt{J(J+1)-K(K-1)}$ is not zero until J=K-1, which is not possible since J must not be less than K. However the resonance effect smoothly approaches zero as J decreases toward K. If the "QK,K-1" transition is calculated based on the subband fit α^A_{55} and ν_0. can be estimated from the equation

$$QK,K-1 \approx \nu_0-\alpha^A_{55}K^2+\alpha^B_{55}K \approx \nu_0-\alpha^A_{55}K^2 \ . \tag{8-7}$$

The $\alpha^B_{55}K$ term is neglected since α^B_{55} is very small. Equation (8-7) is least-squares fitted to determine ν_0 and α^A for $2\nu_5(\ell=0)$. In this fit the QK,K-1 value for the K=8 and K=9 subbands do not fit because the approximations break down where the resonance is nearly exact. These values are excluded from the final fit used to determine ν_0 and α^A for $2\nu_5(\ell=0)$.

$$\nu_0 = 2142.80 \text{ cm}^{-1} \tag{8-8}$$

$$\alpha^A = 0.0247 \text{ cm}^{-1} \ . \tag{8-9}$$

The α^A value is in good agreement with the value of α_5^A for $^{12}CD_3F$ determined by Caldow and Halonen (1982) in fitting the ν_2 and ν_5 fundamentals. This value yields

$$\alpha_{55}^A = 2\alpha_5^A = 2(0.0142 \text{ cm}^{-1}) = 0.0284 \text{ cm}^{-1} . \quad (8\text{-}10)$$

The frequencies of the Q-branch transitions are shown in Figure VIII-1 for $K \leq 8$. In this representation a dot is placed at the coordinates $(K^2, V(J,K))$. The QK,K-1 pseudo frequencies are indicated with an open circle and the line connecting the open circles represents Eq. (8-7) for the parameter values given in Eq. (8-8) and Eq. (8-9). The K=0 and K=1 subbands were omitted in Figure VIII-1 to avoid crowding but were included in both the α^B and QK,K-1 fits. The agreement in α_{55}^A and C_{25} and the quality of the QK,K-1 fit indicate that the $2\nu_5(\ell=0)$ assignments are correct. It is possible that the transitions for the K=8 and K=9 subbands but not both might later be reassigned to $\nu_2+\nu_5(\ell=-1)$. The parameters determined in this analysis are summarized in Table VII-2.

VIII-2. OTHER INTERACTIONS IN THE $2\nu_5(\ell=0)$ BAND

In the subband analysis in the preceding section some simplifications had to be made. The Fermi resonances between $2\nu_5(\ell=0)$ and ν_1 and between $2\nu_5(\ell=0)$ and $2\nu_2$ were ignored. The $2\nu_5(\ell=0)$ spectrum is also affected by the Coriolis resonances between $2\nu_2$ and $\nu_2+\nu_5$ and between $\nu_2+\nu_5$ and $2\nu_5(\ell=\pm2)$. The interaction constant for these Coriolis resonances should be approximately

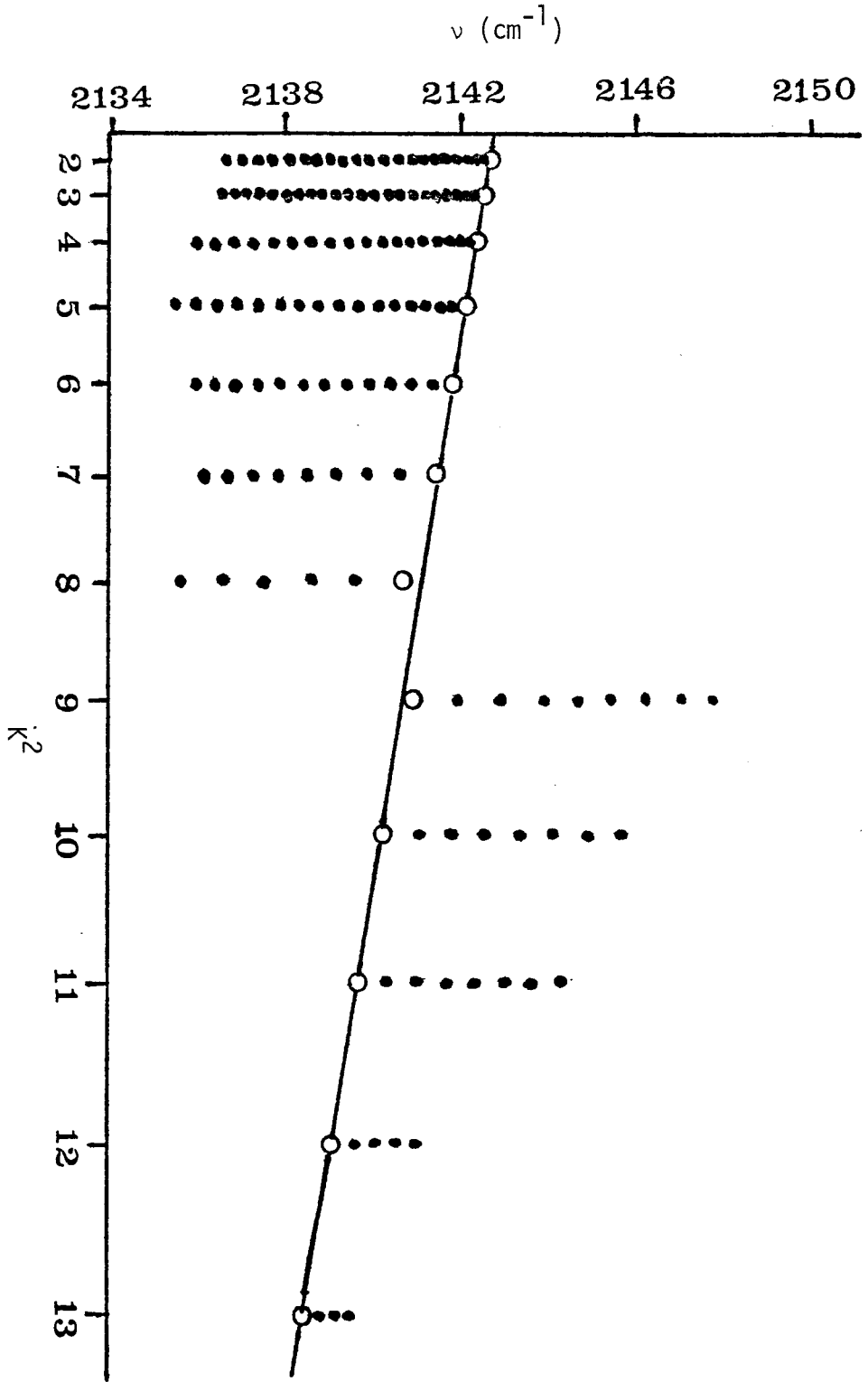


Figure VIII-1. The $2\nu_5(\ell=0)$ band of $^{13}CD_3F$. (Solid dots represent observed Q-branch frequencies, open dots represent the calculated "QK_1K-1" frequencies.)

equal to the value of C_{25} determined from the $2\nu_5(\ell=0)$ subband analysis. Since the Coriolis and Fermi resonance parameters are large it is likely that higher order interaction terms may be necessary to define these resonances. These terms have proven to be significant in the analysis of CH_3F (Champion, 1982).

TABLE VIII-2

ESTIMATED PARAMETERS FOR THE $2\nu_5(\ell=0)$ BAND OF $^{13}CD_3F$
(all values in cm^{-1})

ν_0	=	2142.80
α^A	=	0.0247
α^B	=	-0.00018
C_{25}	=	-0.582
$\nu_2+\nu_5$	=	2185.80

The parameters listed in Table VIII-2 were used to estimate the total rotational perturbation shift for the $2\nu_5(\ell=0)$ effective Q-branch transitions. These are used to generate Figure VIII-2. The solid lines of Figure VIII-2 represent lines of constant rotational perturbation shift Δ, for Δ = -1, -2, ... , -10 cm^{-1}, where a negative shift implies a shift to lower frequencies. For each value of K the value of J corresponding to each value of Δ is determined using a linear interpolation between J values. That is, if the shift is -3.4 at K=2, J=13 and the shift is -4.2 at K=2, J=14, the shift is

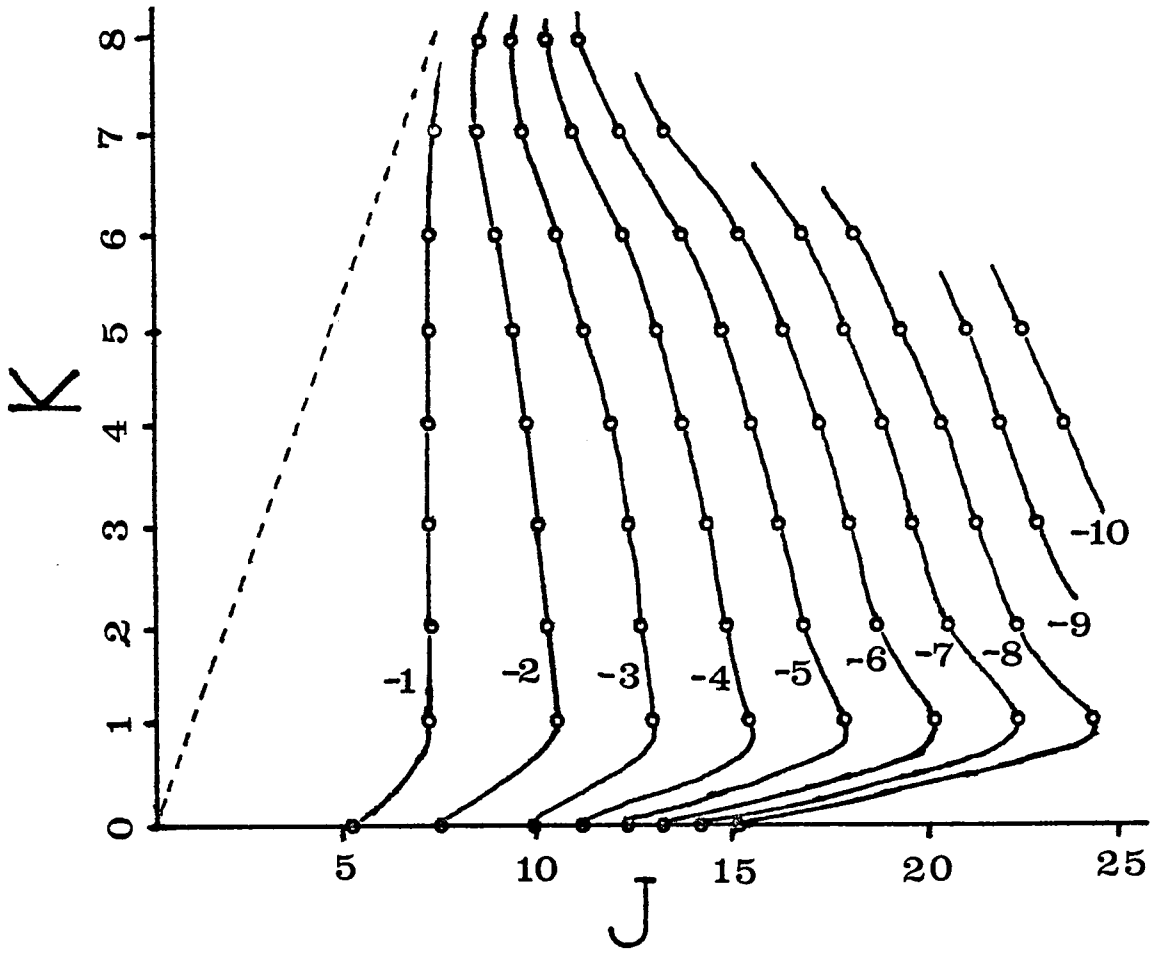


Figure VIII-2. Lines of constant rotational shift in the $2\nu_5(\ell=0)$ band of $^{13}CD_3F$.

assumed to be -4.0 for J=13.75. The shifts are plotted only for $K \leq 8$ because the number of observations for $K \geq 9$ ($\Delta > 0$) is not sufficient to produce a meaningful plot.

The K=0 and K=1 subbands are seen to behave differently than the other subbands for $K \leq 8$. This is evident in the $\alpha(K)$ and $\beta(K)$ values in Table VIII-1 and in the perturbation plot of Figure VIII-2. Since no vibrational levels other than $2\nu_5(\pm 2)$ are near $2\nu_5(\ell=0)$ for K=0 or 1, this can only be explained as an ℓ-resonance effect. There are two possibilities for an ℓ-resonance corresponding to $\Delta K = \Delta\ell = \pm 2$ and $\Delta K = \pm 1$, $\Delta\ell = \mp 2$. The $(K,\ell)=(0,0)$ subband would be linked to the $(K,\ell)=(2,2)$ and $(K,\ell)=(1,-2)$ subbands, respectively, for these two cases.

The difference in the subband energies for the $\Delta K = \Delta\ell = \pm 2$ case is

$$\begin{aligned} \Delta E_{\pm 2,\pm 2} &\approx 2\nu_5(K=2,\ell=2) - 2\nu_5(K=0,\ell=0) \\ &= G_5 - F_{155} + (A_0 - B_0)2^2 - 2A\zeta_5^Z(2)(2) \\ &= G_5 - F_{155} + 13.77 \text{ cm}^{-1} , \end{aligned} \tag{8-10}$$

where G_5 is the difference between $2\nu_5(\ell=\pm 2)$ and $2\nu_5(\ell=0)$ in the absence of any resonance and F_{155} is the shift in $2\nu_5(\ell=0)$ due to the $\nu_1 : 2\nu_5(\ell=0)$ Fermi resonance. The parameters in Table VI-2 (p. 68) give an estimate of $F_{155} = 8 \text{ cm}^{-1}$. For ΔE in Eq. (8-10) to be near zero G_5 must be approximately -5.8 cm^{-1}. Normally the E band ($\Delta\ell = \pm 2$) of the overtone of a degenerate fundamental lies above the A band ($\Delta\ell = 0$).

The subband energy difference for the $\Delta K = \pm 1$, $\Delta\ell = \mp 2$ ℓ-resonance is given by

$$\Delta E_{\pm 1,\mp 2} \approx G_5 - F_{155} + (A_0 - B_0)1^2 - 2A\zeta_5(1)(-2)$$

$$= G_5 - F_{155} - 1.09 \ . \qquad (8\text{-}11)$$

This gives an estimate of $G_5 \approx 9.1\ cm^{-1}$ for $\Delta E_{\pm 1,\mp 2} \approx 0$. This is in agreement with the value of G_5 determined by Champion (1982) for CH_3F where G_5 was found to be $9.35\ cm^{-1}$. For a value of $G_5 = 9.1\ cm^{-1}$ the (K=1,ℓ=0) subband lies just above the (K=2,=ℓ-2) subband possibly causing the high J states of the (K=1,ℓ=0) subband to be pushed upward explaining the K=1 shifts seen in Figure VIII-2. It seems clear that the (±1,∓2) ℓ-resonance is important in describing the $2\nu_5$(ℓ=0) band but this resonance parameter is difficult to estimate since both states are highly perturbed by the strong Coriolis resonances. The value of $G_5 = 9.35\ cm^{-1}$ is consistent with the crossing of $2\nu_5$(ℓ=-2) and ν_1 occurring in the K=6 subband of ν_1.

CHAPTER IX

THE ν_4 BAND OF $^{13}CD_3F$

IX-1. OVERALL APPEARANCE OF THE ν_4 BAND

The ν_4 band of $^{13}CD_3F$ from 2160 cm^{-1} to 2220 cm^{-1} is shown in Figure IX-1 and from 2200 cm^{-1} to 2300 cm^{-1} is shown in Figure IX-2. The B value for these Loomis-Wood type plots was not varied across the band and was equal to B_0, the ground state B value. Several conclusions can be immediately drawn from the ν_4 plots in Figure IX-1 and Figure IX-2. First, the ν_4 band is relatively unperturbed compared to other bands of $^{13}CD_3F$ in this region. Second, the value of α_4^B must be relatively small.

There are several local resonances seen in ν_4. The RRO,J and RPO,J transitions are pushed to higher frequency while RQO,J is pushed downward indicating a $(\pm2,\pm2)$ ℓ-resonance. There is a strong local interaction affecting the $K\Delta K=-1$ and $K\Delta K=-2$ subbands. The $K\Delta K=-6$ subband is pushed to high frequencies and there are weak crossings in subbands for $K\Delta K=-7$, -8, -9, -10, -11, +9, and +10. These interactions are the result of a Coriolis (type II) interaction with $2\nu_2$ and a type IV, $\Delta K=\Delta\ell=\pm2$ interaction with $\nu_2+\nu_5$. An additional coupling term is needed to explain the crossings at high K. The $2\nu_2$ and $\nu_2+\nu_5$ bands interact through a very strong Coriolis resonance. For K less than seven $2\nu_2(K)$ is pushed to higher frequencies and $\nu_2+\nu_5$ $(K+1,\ell=+1)$ is pushed to lower frequencies. For K greater than

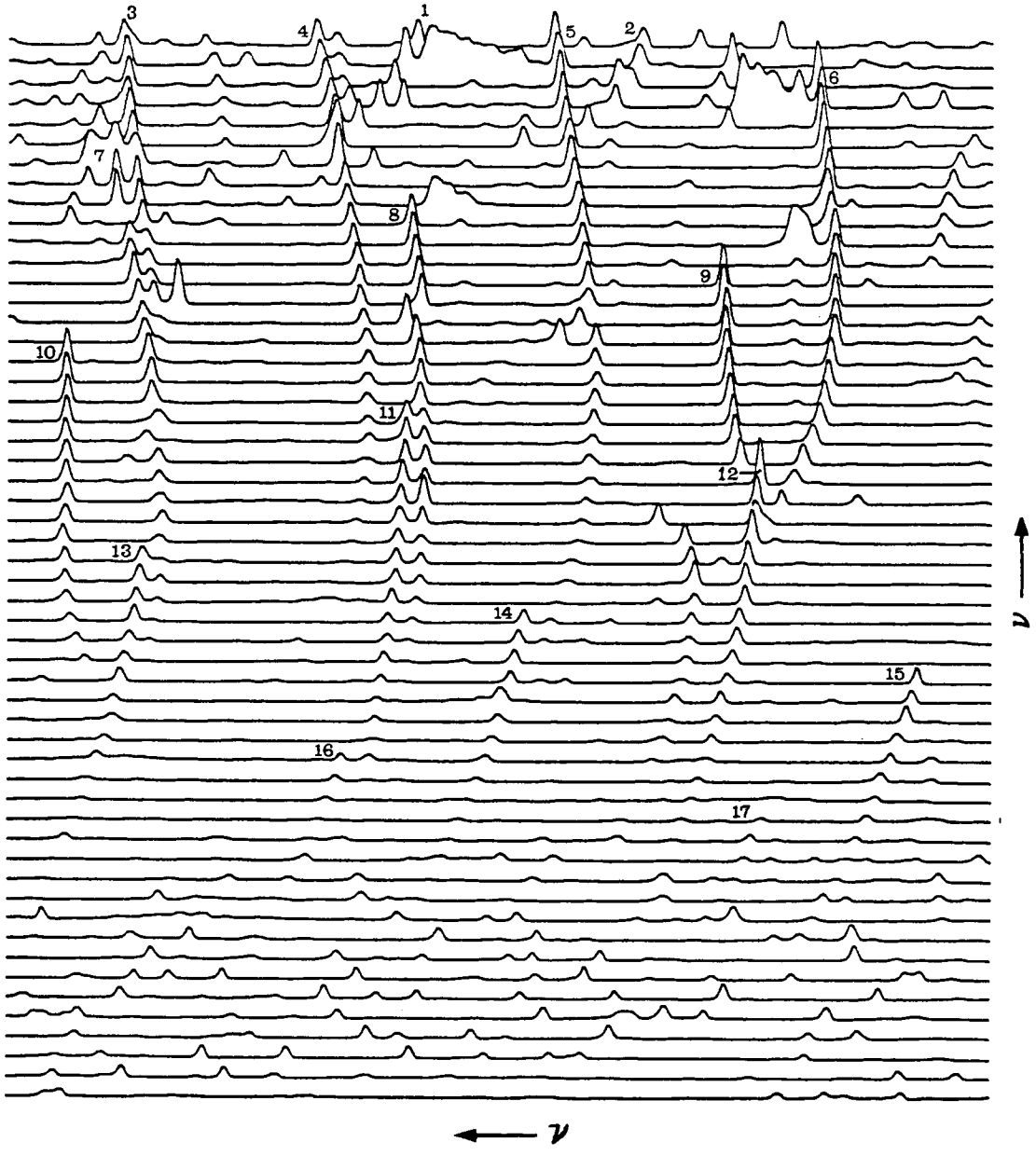


Figure IX-1. The ν_4 band of $^{13}CD_3F$ below 2200 cm^{-1}.

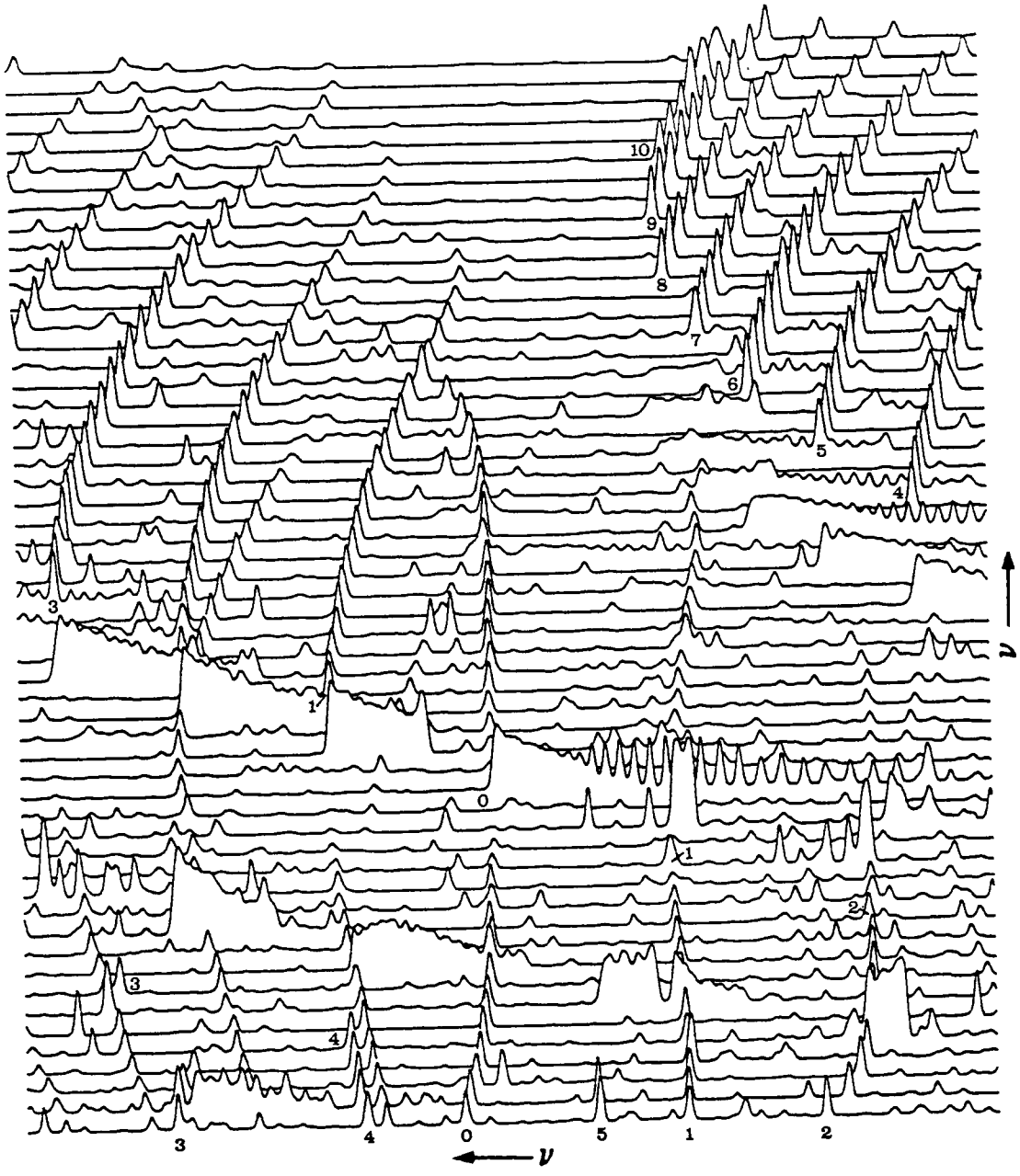


Figure IX-2. The ν_4 band of $^{13}CD_3F$ above 2200 cm^{-1}.

seven the subband order is reversed for these two bands. This allows $\nu_2+\nu_5^{+1}$ to cross ν_4^{-1} from below for K=5 and from above for $K\geq 6$. Thus PQ_6 of ν_4^{-1} is crossed from below and $PQ_7 \rightarrow PQ_{11}$ are crossed from above. This second order interaction causes the weak splittings in RQ_9 and RQ_{10} also. The ν_4 band has been assigned for $K\Delta K$ from -18 to +16. In addition about 130 $2\nu_2$ transitions have been assigned for $K\leq 6$, mostly in the regions where $2\nu_2$ and ν_4 have local interactions.

IX-2. NON-PERTURBATION FIT OF ν_4

The observed transition frequencies for ν_4 were converted to effective Q-branch transitions and fitted to an energy expression using elements from the Hamiltonian through h_3'' and the β terms from h_4'', This was a biweighted fit with $J_{max}=30$ and $K_{max}=16$. The weighted standard deviation was reduced to 1.4×10^{-3} cm^{-1} when approximately half of the 600 ν_4 observations were zero weighted after 30 iterations. The results of this fit are listed in Table IX-1.

The values of the parameters are in agreement with the assumption that ν_4 is relatively unperturbed. The η and β parameters are not indicative of global resonance effects.

IX-3. LOCAL RESONANCES

The ℓ-resonance in ν_4 affects only the K=0 subband. The residuals from the non-perturbation fit of ν_4 for the RR_0 and RP_0

TABLE IX-1

EFFECTIVE PARAMETERS FOR ν_4 OF $^{13}CD_3F$ FROM A NONPERTURBATION FIT (all values in cm^{-1})

ν_0	=	2242.4408
$A\zeta_4^Z$	=	0.45952
α_4^A	=	1.2022×10^{-2}
α_4^B	=	3.4994×10^{-4}
η_4^J	=	-6.026×10^{-6}
η_4^K	=	2.003×10^{-5}
β_4^J	=	5.036×10^{-8}
β_4^{JK}	=	2.790×10^{-7}
β_4^K	=	6.23×10^{-8}
$\sigma_{weighted}$	=	1.4×10^{-3}

upper state (effective PQ_0 transitions) are plotted in Figure IX-3. The RQ_0 subband assignment is based on the assumption that the two subbands are symmetrically perturbed for lower values of J. This is not the case for J>20 as the RR_0 subband is pushed up at high J by the Coriolis interaction with $2\nu_2$. The ℓ-doubling parameter is estimated from the shift at J=10 to be

$$q_4^+ = \pm 0.74 \times 10^{-3}\ cm^{-1}\ . \qquad (9\text{-}1)$$

The ν_4:$2\nu_2$ Coriolis interaction is difficult to analyze because of the nature of the $2\nu_2$ band. The $2\nu_2$ band is part of the

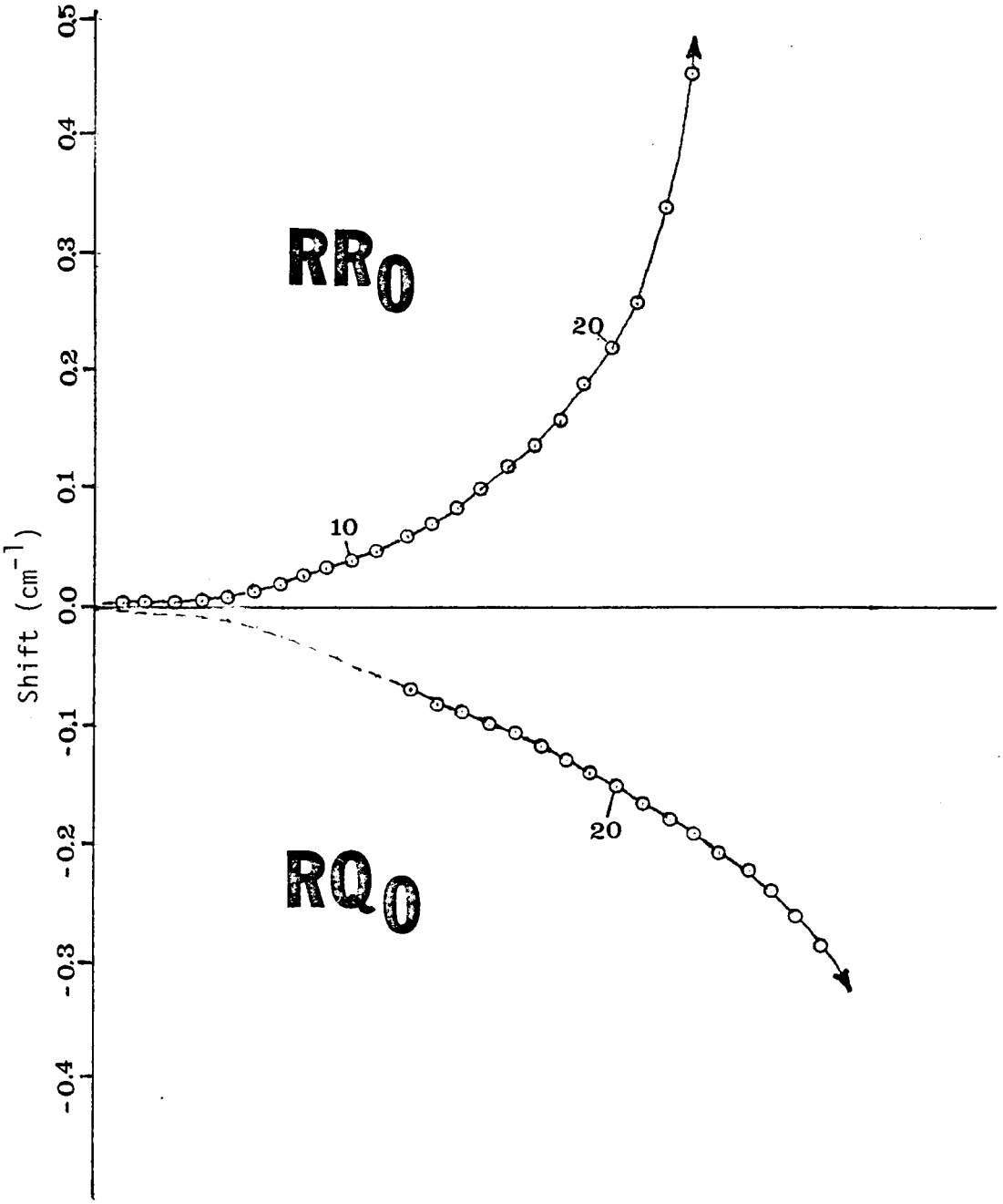


Figure IX-3. Residuals for the RR_0 and RQ_0 subbands.

$2\nu_2:\nu_2+\nu_5:2\nu_5:\nu_1$ interaction system. The effective interaction constants when only ν_4 and $2\nu_2$ are considered exhibit a decrease as K increases. The individual subbands can be fitted with a simple model however. The resonance parameter from the K=2 subband fit where the overall fit is good is

$$C_{422} = 0.0263 \text{ cm}^{-1} . \tag{9-2}$$

For the secondary resonance effect producing crossings in the PQ_7, PQ_8, PQ_9, PQ_{10} and PQ_{11} subbands the resonance parameter is seen to become smaller as K increases. This parameter is estimated from the doubled transitions in PQ_9.

$$R_{425} = 0.00072 \text{ cm}^{-1} . \tag{9-3}$$

This resonance produces crossings in RQ_9 and RQ_{10} but the resonance parameter is difficult to estimate for this case because the RR subband structure is overlapped for K=8 through 14. For the localized resonance in the ℓ=-1 component of ν_4, the intensity sharing is such as to deplete $2\nu_2$ below the crossing point and enhance $2\nu_2$ above the crossing point. There is a second crossing in the PQ_2 subband at J=25 which has been assigned as a $\Delta K=-2$, $\Delta\ell=+1$ resonance with $2\nu_2$. The interaction parameter from doubled transitions is estimated to be

$$R_{422} = 0.00030 \text{ cm}^{-1} . \tag{9-4}$$

The PQ_1 and PQ_2 subband resonance shifts are plotted in Figure IX-4.

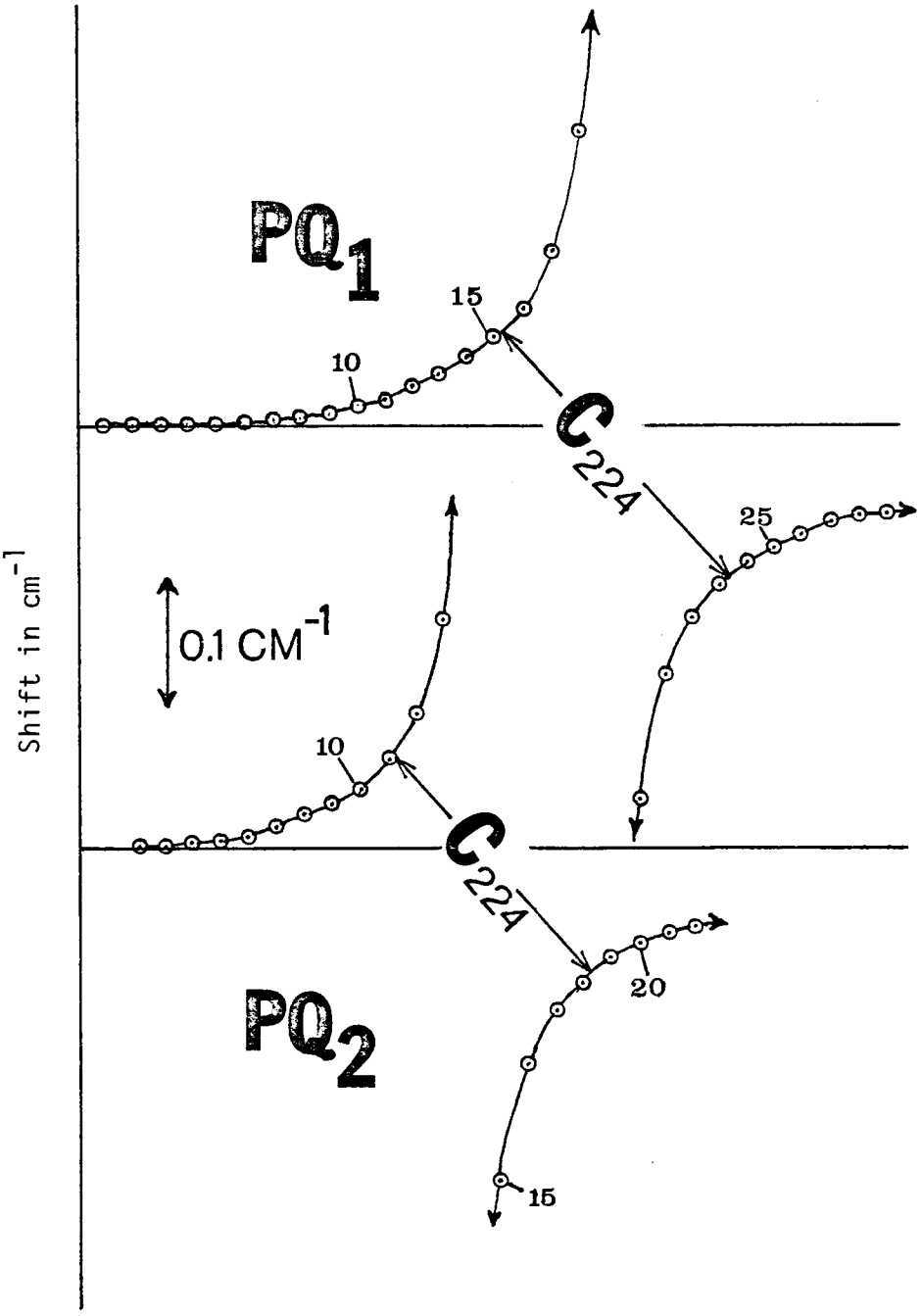


Figure IX-4. Local resonance shifts in PQ_1 and PQ_2 of ν_4 of $^{13}CD_3F$.

IX-4. THE $2\nu_2$ BAND

The $2\nu_2$ band has been assigned for K=0 through K=5. These subbands have been fitted separately along with the ν_4 subbands. The $2\nu_2$ results are listed in Table IX-2. A three state Coriolis analysis was not successful for ν_4 and $2\nu_2$ because of the strong Fermi and Coriolis effects in $2\nu_2$.

TABLE IX-2

SUBBAND FITS FOR $2\nu_2$ OF $^{13}CD_3F$

K	# Lines	$\nu_0(K)$	$\alpha^B(K)\times10^3$	$\beta^J(K)\times10^6$
0	18	2234.1560	-14.61	0.87
1*	22	2234.1642	-14.96	-0.82
2*	19	2234.1358	-15.72	-0.74
3*	25	2234.0988	-17.14	-1.09
4	16	2233.9123	-18.33	-1.91
5	12	2233.7626	-23.41	-3.08

*ν_4^{-1}:$2\nu_2$ crossing included in fit. All values in cm^{-1}.

The estimated value for α_{22}^A from the subband fits is α_{22}^A = -0.0165 cm^{-1} in modest agreement with the value obtained from the analysis of ν_2 of $^{12}CD_3F$ (Caldow and Halonen, 1982)

$$\alpha_{22}^A = 2 \cdot \alpha_2^A = -0.0112\ cm^{-1} \quad . \tag{9-5}$$

The α_{22}^B values from the subband fits does not agree with the value of $\alpha_{22}^B \approx 0.0066\ cm^{-1}$ from the ν_2 analysis because of the strong Coriolis resonance with $\nu_2+\nu_5(\ell=\pm1)$. The resonance parameter linking

these states differs from the resonance parameter for the $2\nu_5(\ell=0):\nu_2+\nu_5(\ell=\pm1)$ coupling by a factor of $\sqrt{2}$. When the $2\nu_2:\nu_2+\nu_5$ coupling is considered the α^B_{22} subband values are not unreasonable.

CHAPTER X

FITTING THE 5 μm SPECTRUM OF $^{13}CD_3F$

X-1. THE HAMILTONIAN

At this point only twelve of the 24 vibrational levels of $^{13}CD_3F$ near 5 μm are under consideration. These levels are $\nu_4(\ell=\pm1)$, $2\nu_2$, $\nu_2+\nu_5(\ell=\pm1)$, $2\nu_5(\ell=0,\pm2)$, $\nu_2+\nu_3$, ν_1 and $\nu_3+\nu_5(\ell=\pm1)$. The omitted levels are $\nu_2+\nu_6(\ell=\pm1)$, $\nu_5+\nu_6(\ell_5=\pm1,\ell_6=\pm1)$, $2\nu_3$, $\nu_3+\nu_6(\ell=\pm1)$ and $2\nu_6(\ell=0,\pm2)$ and are found at lower frequencies. The omitted levels are coupled to the levels being considered through several interactions, but only the $\Delta K=+2,\Delta\ell=-1$ interaction between ν_1 and $\nu_2+\nu_6(\ell=-1)$ produces a directly observable effect. The observed transition frequencies above 2045 cm^{-1} are assigned principally to ν_1, ν_4, $2\nu_5(\ell=0)$ and $2\nu_2$. Local resonances give rise to transitions assigned to $\nu_2+\nu_3$, $\nu_2+\nu_5$, $2\nu_5(\ell=-2)$ and $\nu_3+\nu_5(\ell=+1)$. The Hamiltonian describing the twelve states under consideration is very complex and in this work only interactions with $\Delta K-\Sigma\Delta\ell=0$ are considered. The Hamiltonian used in this analysis does include all possible $\Delta K-\Sigma\Delta\ell=0$ interaction terms which result in a local resonance or a strong global resonance. Some weaker global resonances are being omitted at this time.

The Hamiltonian model used in this analysis is found in Table X-1 and Table X-2. In Table X-2, C_{nt} is symbolic for a $\Delta K=\Delta\ell=\pm1$ Coriolis resonance parameter, Q_t is symbolic for a

TABLE X-1

DIAGONAL TERMS IN THE 12 STATE HAMILTONIAN
FOR $\Delta K - \sum \Delta \ell = 0$

$H_{1,1}$	$= \nu_4(K-1, \ell_4=-1)$
$H_{2,2}$	$= \nu_4(K+1, \ell_4=+1)$
$H_{3,3}$	$= 2\nu_2(K)$
$H_{4,4}$	$= \nu_2+\nu_5(K-1, \ell_5=-1)$
$H_{5,5}$	$= \nu_2+\nu_5(K+1, \ell_5=+1)$
$H_{6,6}$	$= 2\nu_5(K-2, \ell_5=-2)$
$H_{7,7}$	$= 2\nu_5(K, \ell_5=0)$
$H_{8,8}$	$= 2\nu_5(K+2, \ell_5=+2)$
$H_{9,9}$	$= \nu_1(K)$
$H_{10,10}$	$= \nu_2+\nu_3(K)$
$H_{11,11}$	$= \nu_3+\nu_5(K-1, \ell_5=-1)$
$H_{12,12}$	$= \nu_3+\nu_5(K+1, \ell_5=+1)$

TABLE X-2

OFF-DIAGONAL TERMS IN THE 12 STATE HAMILTONIAN
FOR $\Delta K-\sum\Delta\ell=0$

$H_{1,2}$	$= Q_4 f_{+1} f_{-1}$
$H_{1,3}$	$= C_{224} f_{-1}$
$H_{1,4}$	$= W_{245}$
$H_{1,7}$	$= C_{455} f_{-1}$
$H_{2,3}$	$= C_{224} f_{+1}$
$H_{2,5}$	$= W_{245}$
$H_{2,7}$	$= C_{455} f_{+1}$
$H_{3,4}$	$= (C_{25}-C_{25}^{J}J(J+1)-C_{25}^{K}K^2) f_{-1}\sqrt{2}$
$H_{3,5}$	$= (C_{25}-C_{25}^{J}J(J+1)-C_{25}^{K}K^2) f_{+1}\sqrt{2}$
$H_{4,5}$	$= Q_5 f_{+1} f_{-1}$
$H_{4,6}$	$= (C_{25}-C_{25}^{J}J(J+1)-C_{25}^{K}K^2) f_{-1}\sqrt{2}$
$H_{4,7}$	$= (C'_{25}-C'^{J}_{25}J(J+1)-C'^{K}_{25}K^2) f_{-1}$
$H_{4,9}$	$= C_{125} f_{-1}$
$H_{5,7}$	$= (C'_{25}-C'^{J}_{25}J(J+1)-C'^{K}_{25}K^2) f_{+1}$
$H_{5,8}$	$= (C_{25}-C_{25}^{J}J(J+1)-C_{25}^{K}K^2) f_{-2}\sqrt{2}$
$H_{5,9}$	$= C_{125} f_{+1}$
$H_{6,7}$	$= Q_5 f_{-1} f_{-2}$
$H_{6,11}$	$= C_{35} f_{-2}\sqrt{2}$
$H_{7,8}$	$= Q_5 f_{+1} f_{+2}$
$H_{7,9}$	$= W_{155}-W_{155}^{J}J(J+1)-W_{155}^{K}K^2$
$H_{7,10}$	$= W_{2255}$
$H_{7,11}$	$= C_{35} f_{-1}$

TABLE X-2 (continued)

$H_{7,12}$	$= C_{35}\ f_{+1}$
$H_{8,12}$	$= C_{35}\ f_{+2}\sqrt{2}$
$H_{3,9}$	$= W_{122}-W^{J}_{122}J(J+1)-W^{K}_{122}K^{2}$
$H_{3,7}$	$= W_{2255}$
$H_{10,11}$	$= C''_{25}\ f_{-1}$
$H_{10,12}$	$= C''_{25}\ f_{+2}$
$H_{11,12}$	$= Q_{5}\ f_{+1}f_{-1}$
$H_{9,12}$	$= C_{135}\ f_{+1}$
$H_{9,11}$	$= C_{135}\ f_{-1}$
$H_{9,10}$	$= W_{123}$
$H_{1,5}$	$= R_{425}\ f_{-1}f_{-2}$
$H_{2,4}$	$= R_{425}\ f_{+1}f_{+2}$
$H_{1,9}$	$= C_{14}\ f_{-1}$
$H_{2,9}$	$= C_{14}\ f_{+1}$
H_{ij}	$= H_{ji}$

$\Delta K=\Delta\ell=\pm 2$ ℓ-resonance parameter, and R_{nt} is symbolic for a $\Delta K=\Delta\ell=\pm 2$ type IV coupling parameter. The functions $f_{\pm n}$ are defined by

$$f_{\pm 1} = \sqrt{J(J+1)-K(K\pm 1)} \tag{10-1}$$

$$f_{\pm 2} = \sqrt{J(J+1)-(K\pm 1)(K\pm 2)} \tag{10-2}$$

The strong Coriolis coupling between states with ν_2 and ν_5 components and the strong Fermi resonances coupling ν_1, $2\nu_5(\ell=0)$ and $2\nu_2$ were expanded to include the first higher order terms with coefficients $J(J+1)$ and K^2, where K is the K of the $\ell=0$ states. The C_{25} Coriolis parameter is separated for the various $\nu_2:\nu_5$ interactions since the coupling parameters may differ slightly. Note that the Coriolis couplings for $2\nu_2:\nu_2+\nu_5$, $\nu_2+\nu_5:2\nu_5(\ell=\pm 2)$ and $\nu_3+\nu_5:2\nu_5(\ell=-2)$ have an additional factor of $\sqrt{2}$ (Grenier-Besson, 1960). The α^A and α^B parameters for $2\nu_2$, $\nu_2+\nu_5$ and $2\nu_5$ are not constrained to force internal consistency among these parameters. There are a total of 54 parameters used in the Hamiltonian model. Of these 28 are diagonal and 26 are off-diagonal or resonance parameters.

X-2. RESULTS

The diagonal and off-diagonal parameters estimated in Chapters VI, VII, VIII, and IX give a qualitative fit to the observed 5 μm spectrum of $^{13}CD_3F$ when the Hamiltonian of Table X-1 and Table X-2 is used. The standard deviation is 3.72 cm^{-1} with the largest residuals corresponding to transitions affected by resonances with $\Delta K-\Sigma\Delta\ell=\pm 3$ which are not included in the model Hamiltonian. The

region of close resonance between $\nu_2+\nu_5(\ell=-1)$ and $2\nu_5(\ell=0)$ exhibits large residuals also but there are many terms in the model Hamiltonian which can affect these transitions and it is reasonable to assume that these residuals can be greatly reduced with the restricted Hamiltonian model through the process of refining the parameter set. For all the parameter refinements reported in this work only transitions with $J\leq 27$ and $K\leq 12$ were considered. Also, those transitions noticeably shifted by resonances with $\Delta K-\Sigma\Delta\ell\neq 0$ are excluded.

In the first attempt to refine the parameter set, all η^J and η^K parameters and the higher order Coriolis and Fermi resonance parameters were initialized to zero. All parameters were refined simultaneously using a damping factor of one-half. This refinement process was generally successful when fitting simulated data, but was not successful for the 5 μm $^{13}CD_3F$ observations. In fact the refinement process diverged in only a few iterations with most of the parameter values becoming unreasonable. Failure to converge when all parameters are simultaneously refined is not surprising when the complexity of the model Hamiltonian is considered. The high degree of correlation between the Fermi parameters and the $\ell=0$ band centers is a problem since these parameters seem to diverge most rapidly.

In additional attempts to refine the parameter set, the problems encountered when simultaneously refining all the parameters were minimized by refining the parameters in subsets. One effective method of dividing the parameters into subsets is to refine only

diagonal or only off-diagonal parameters. This greatly stabilized the refinement process. The parameters for $\nu_2+\nu_3$ and $\nu_3+\nu_5$ were still unstable. When these parameters were held constant and the remaining diagonal and off-diagonal parameters alternately refined the standard deviation was reduced to less than 0.1 cm^{-1} in 20 iterations. At this point most of the parameters had reasonable values except α^A_{25}, α^B_{25} and ζ^Z_5. Other parameters which had reasonable size values did not agree well with their initial values. The largest residuals for this refinement are in ν_1, possibly because the $\nu_2+\nu_3$ and $\nu_3+\nu_5$ parameters have not been refined. The ν_1 observations account for two-thirds of the total variance. The refinement process was repeated with ζ^Z_5, α^A_{25} and α^B_{25} fixed. The standard deviation after the diagonal and off-diagonal parameters were alternately refined three times was 0.82 cm^{-1}. These parameters are listed in Table X-3.

X-3. CONCLUSIONS

An algorithm for fitting perturbed spectra of axially symmetric molecules has been developed and tested. This method has been tested with simulated and real spectra. The tests are not completely conclusive at this time but the results are encouraging. The algorithm was able to fit a simulated spectrum where the Hamiltonian included 12 vibrational states with local resonances and strong global resonances. The algorithm gave satisfying results when the local resonances between $\nu_4(\ell=-1)$ and $2\nu_2$ of $^{13}CD_3F$ were fitted. The local resonances between ν_1 and $\nu_3+\nu_5$ could not be fitted satisfactorily due to the complex state mixing for both these states.

TABLE X-3

REFINED VALUES FOR THE $^{13}CD_3F$ PARAMETER SET
(all values in cm^{-1} except ζ^Z)

	ν_0	$\alpha^A \times 10^3$	$\alpha^B \times 10^3$	ζ^Z
ν_4	2242.4096	11.05	1.35	0.1755
$2\nu_2$	2227.3695	-6.14	10.29	
$\nu_2+\nu_5$	2178.7252	8.60*	0.00	-0.2970*
$2\nu_5(\ell=0)$	2135.9357	12.36	8.73	
$2\nu_5(\ell=\pm2)$	2146.3620	12.36	8.73	-0.2970*
$\nu_2+\nu_3$	2092.8000*	-4.40*	6.10	
ν_1	2099.3803	11.83	-17.49	
$\nu_3+\nu_5$	2053.4000*	15.56	-0.40*	-0.2970*

$\eta_4^J = 8.01\times10^{-7}$	$\eta_4^K = -8.13\times10^{-5}$	
$\eta_5^5 = 0.0$*	$\eta_5^K = 0.0$*	
$C_{25} = -0.5435$	$C_{25}^J = -3.56\times10^{-5}$	$C_{25}^K = -2.07\times10^{-4}$
$C'_{25} = -0.9203$	$C'^J_{25} = -1.21\times10^{-5}$	$C'^K_{25} = -8.05\times10^{-5}$
$C''_{25} = -0.5422$*		
$W_{155} = 24.49$	$W_{155}^J = 8.29\times10^{-3}$	$W_{155}^K = -3.21\times10^{-3}$
$W_{122} = 21.58$	$W_{122}^J = 9.44\times10^{-3}$	$W_{122}^K = -1.09\times10^{-2}$
$W_{2255} = 13.96$		
$W_{123} = -2.18$		
$C_{14} = 0.310$*	$R_{425} = 7.2\times10^{-4}$*	
$C_{224} = 2.75\times10^{-2}$*	$Q_4 = -2.34\times10^{-4}$	
$C_{135} = 3.00\times10^{-2}$*	$Q_5 = -1.05\times10^{-3}$*	
$C_{455} = -0.20$*		

*Parameter fixed at this value.

The 5 μm absorption spectrum of $^{13}CD_3F$ was recorded at high resolution. Over 1400 effective Q-branch transition frequencies have been determined. The ν_1, $2\nu_5(\ell=0)$, and ν_4 bands have been individually analyzed to give approximate values for their diagonal parameters. Rotational resonance parameters have been determined for all local resonances. The Fermi parameters linking ν_1, $2\nu_5(\ell=0)$, and $2\nu_2$ were estimated from reported values of these parameters for CH_3F. The ν_1, $2\nu_5(\ell=0)$, and $2\nu_2$ band centers, α_1^A and α_1^B, were adjusted to take the Fermi resonances into account.

The initial parameter set describing the 5 μm spectrum of $^{13}CD_3F$ gives a qualitative fit to the observed spectrum. The standard deviation for observations with $J\leq 27$ and $K\leq 12$ is 2.81 cm^{-1}. This parameter set was refined using the technique discussed in Chapter IV. The procedure did not produce satisfactory results unless 24 of the 54 parameters were held constant. The magnitude of all the refined parameters remained reasonable although some of the parameters were not close to their initial values. The final results of this parameter refinement were used to create Appendix A and Appendix B.

There are three ways in which the analysis of the 5 μm region of $^{13}CD_3F$ could be further improved. In fitting the spectrum of CH_3F, Champion (1982) used a novel approach to constrain the parameters in a manner which ties the parameters to their initial values with a "spring-like" restoring force. The method was developed by Bartel (1975) and seeks to minimize the quantity

$$\sum_i w_i (E_i^{obs} - E_i^{calc})^2 + \sum_j W_j (p_j^0 - p_j^n)^2$$

where p_j^0 is the initial value of the j-th parameter, p_j^n is the value of p_j at the n-th iteration, W_j is a weight which controls the strength of the spring tying p_j to p_j^0, $E_i^{obs}-E_i^{calc}$ is the residual for the i-th observation and W_i is the weight for that observation. This damping method would be easy to implement but it is not clear how one should chose the W_j values.

Secondly, there are several resonance terms with $\Delta K-\Delta \ell = 3$ which have been excluded in this analysis. The first order effect of these resonances have been minimized by excluding the affected transitions in the parameter refinement process. The second order effects of these resonances are difficult to predict.

The third suggestion for improving the analysis of the $^{13}CD_3F$ spectrum is to improve the data set. The spectrum of $^{13}CD_3F$ is difficult to analyze partly because only five of the twelve states included in this analysis are observed over a range of K and J values. The $\nu_2+\nu_3$ band of $^{13}CD_3F$ lies very close to the ν_1 band and exhibits a Raman intensity approximately 1% of the ν_1 Raman intensity. If this region could be recorded with a high resolution Raman spectrometer ($\Delta\nu \leq 0.01$ cm^{-1}) it would seem likely that many $\nu_2+\nu_3$ Raman transitions could be assigned. The band is important in unraveling the 5 μm spectrum because it is linked to ν_1 with a Fermi resonance, to $\nu_2+\nu_5$ with the C_{35} Coriolis resonance, and with $\nu_3+\nu_5$ with the C_{25} Coriolis resonance.

resonance.

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APPENDICES

APPENDIX A

CURRENT RESULTS FOR THE ANALYSIS OF THE 5 μm SPECTRUM OF $^{13}CD_3F$

The current results for the analysis of the 5 μm spectrum of $^{13}CD_3F$ are tabulated in Appendix A. The values listed under J and K are the ground state rotational quantum numbers for the Q-branch transition frequencies listed under observed. The numbers in the columns headed S and S' refer to the initial vibrational state assignment and the reassigned vibrational state based on the assumption that the correct assignment corresponds to the state with the calculated value closest to the observed value. Here state 1 is ν_4^{-1}, state 2 is ν_4^{+1}, state 3 is $2\nu_2$, state 4 is $\nu_2+\nu_5^{-1}$, state 5 is $\nu_2+\nu_5^{+1}$, state 6 is $2\nu_5^{-2}$, state 7 is $2\nu_5^{0}$, state 8 is $2\nu_5^{+2}$, state 9 is ν_1, state 10 is $\nu_2+\nu_3$, state 11 is $\nu_3+\nu_5^{-1}$ and state 12 is $\nu_3+\nu_5^{+1}$. The calculated frequencies listed under calculated are based on the parameter set found in Table X-3 (p. 111). The column headed O-C contains the observed Q-branch frequency minus the calculated value. Under total shift are the calculated transition frequencies minus the calculated transition frequencies when all resonance parameters are set to zero. The total shift values give an estimate of the total perturbation for a given state but can be misleading for states such as $2\nu_5(\ell=0)$ which is pushed to higher frequencies by the vibrational resonance with ν_1 and to lower frequencies for $K\leq 8$ by the Coriolis interaction with $\nu_2+\nu_5$.

TABLE A-1

CURRENT RESULTS FOR THE ANALYSIS OF THE 5 μm SPECTRUM OF $^{13}CD_3F$

K	J	S	S'	Obs.	Calc.	O-C	Total Shift
0	1	1	1	2243.4388	2243.4199	0.0189	0.0040
0	1	3	3	2234.2260	2234.2604	-0.0344	6.9115
0	1	7	7	2142.7651	2142.6090	0.1561	6.6908
0	1	9	9	2085.9146	2085.3175	0.5971	-14.0977
0	2	1	1	2243.4377	2243.4225	0.0152	0.0120
0	2	3	3	2234.2630	2234.3170	-0.0540	7.0092
0	2	7	7	2142.7016	2142.5389	0.1627	6.6555
0	2	9	9	2085.9216	2085.3465	0.5751	-14.1388
0	3	1	1	2243.4399	2243.4263	0.0136	0.0240
0	3	3	3	2234.3453	2234.4020	-0.0567	7.1560
0	3	7	7	2142.6121	2142.4339	0.1782	6.6029
0	3	9	9	2085.9317	2085.3893	0.5424	-14.2010
0	4	1	1	2243.4414	2243.4313	0.0101	0.0399
0	4	3	3	2234.4604	2234.5156	-0.0552	7.3520
0	4	7	7	2142.4693	2142.2945	0.1748	6.5333
0	4	9	9	2085.9457	2085.4453	0.5004	-14.2849
0	5	1	1	2243.4407	2243.4376	0.0031	0.0598
0	5	3	3	2234.6064	2234.6579	-0.0515	7.5972
0	5	7	7	2142.2744	2142.1211	0.1533	6.4472
0	5	9	9	2085.9619	2085.5135	0.4484	-14.3916
0	6	1	1	2243.4413	2243.4449	-0.0036	0.0834
0	6	3	3	2234.7854	2234.8291	-0.0437	7.8919
0	6	7	7	2142.0236	2141.9145	0.1091	6.3453
0	6	9	9	2085.9824	2085.5929	0.3895	-14.5221
0	7	1	1	2243.4410	2243.4533	-0.0123	0.1109
0	7	3	3	2234.9894	2235.0293	-0.0399	8.2363
0	7	7	7	2141.7101	2141.6755	0.0346	6.2285
0	7	9	9	2086.0070	2085.6822	0.3248	-14.6778
0	8	1	1	2243.4430	2243.4627	-0.0197	0.1420
0	8	3	3	2235.2196	2235.2589	-0.0393	8.6306
0	8	7	7	2141.3365	2141.4053	-0.0688	6.0979
0	8	9	9	2086.0327	2085.7798	0.2529	-14.8602
0	9	1	1	2243.4420	2243.4729	-0.0309	0.1768
0	9	3	3	2235.4895	2235.5180	-0.0285	9.0749
0	9	7	7	2140.9155	2141.1053	-0.1898	5.9550
0	9	9	9	2086.0640	2085.8840	0.1800	-15.0709
0	10	1	1	2243.4441	2243.4840	-0.0399	0.2151
0	10	3	3	2235.8283	2235.8067	0.0216	9.5695
0	10	7	7	2140.4312	2140.7773	-0.3461	5.8015
0	10	9	9	2086.0952	2085.9929	0.1023	-15.3119
0	11	1	1	2243.4465	2243.4958	-0.0493	0.2569
0	11	3	3	2236.1306	2236.1252	0.0054	10.1145
0	11	7	7	2139.8997	2140.4232	-0.5235	5.6395
0	11	9	9	2086.1341	2086.1044	0.0297	-15.5853
0	12	1	1	2243.4510	2243.5082	-0.0572	0.3020
0	12	3	3	2236.4617	2236.4735	-0.0118	10.7099
0	12	7	7	2139.3196	2140.0456	-0.7260	5.4713
0	12	9	9	2086.1737	2086.2163	-0.0426	-15.8933
0	13	1	1	2243.4522	2243.5212	-0.0690	0.3503
0	13	3	3	2236.7922	2236.8517	-0.0595	11.3557
0	13	7	7	2138.6998	2139.6471	-0.9473	5.2997
0	13	9	9	2086.2171	2086.3260	-0.1089	-16.2383
0	14	1	2	2243.4549	2243.5346	-0.0797	0.0496
0	14	3	3	2237.1589	2237.2597	-0.1008	12.0519
0	14	7	7	2138.0388	2139.2309	-1.1921	5.1278
0	14	9	9	2086.2615	2086.4311	-0.1696	-16.6231
0	15	1	1	2243.4620	2243.5483	-0.0863	0.4564
0	15	3	3	2237.5469	2237.6972	-0.1503	12.7983
0	15	7	7	2137.3432	2138.8005	-1.4573	4.9592
0	15	9	9	2086.3136	2086.5287	-0.2151	-17.0504
0	16	1	1	2243.4669	2243.5623	-0.0954	0.5140
0	16	3	3	2237.9480	2238.1641	-0.2161	13.5947
0	16	7	7	2136.5107	2138.3595	-1.8488	4.7974
0	16	9	9	2086.3602	2086.6159	-0.2557	-17.5231
0	17	1	1	2243.4739	2243.5767	-0.1028	0.5746
0	17	3	3	2238.3518	2238.6599	-0.3081	14.4405
0	17	7	7	2135.5680	2137.9120	-2.3440	4.6467
0	17	9	9	2086.4049	2086.6895	-0.2846	-18.0442
0	18	1	1	2243.4846	2243.5914	-0.1068	0.6383
0	18	3	3	2238.7562	2239.1840	-0.4278	15.3351
0	18	9	9	2086.5103	2086.7466	-0.2363	-18.6170
0	19	1	1	2243.5004	2243.6067	-0.1063	0.7053
0	19	9	9	2086.5549	2086.7837	-0.2288	-19.2447
0	20	1	1	2243.5244	2243.6232	-0.0988	0.7762
0	20	9	9	2086.6162	2086.7976	-0.1814	-19.9305
0	21	1	1	2243.5464	2243.6420	-0.0956	0.8522
0	21	9	9	2086.6841	2086.7852	-0.1011	-20.6777
0	22	1	1	2243.6163	2243.6661	-0.0498	0.9363
0	22	9	9	2086.7525	2086.7432	0.0093	-21.4895
0	23	1	1	2243.7074	2243.7040	0.0034	1.0367
0	23	9	9	2086.8270	2086.6687	0.1583	-22.3689
0	24	1	2	2243.8813	2243.7858	0.0955	0.1438
0	24	9	9	2086.9012	2086.5586	0.3426	-23.3187
0	25	9	9	2086.9793	2086.4104	0.5689	-24.3416
0	26	9	9	2087.0573	2086.2217	0.8356	-25.4401
0	27	9	7	2087.1434	2085.9905	1.1529	21.4573
0	28	9	7	2087.2286	2085.7150	1.5136	20.2523
0	29	9	7	2087.3159	2085.3940	1.9219	19.0567
0	30	9	7	2087.4049	2085.0265	2.3784	17.8733
0	31	9	7	2087.4963	2084.6120	2.8843	16.7044
0	32	9	7	2087.5859	2084.1504	3.4355	15.5519
0	33	9	7	2087.7054	2083.6419	4.0635	14.4171
1	1	1	1	2240.5086	2240.4770	0.0316	0.0025
1	1	7	7	2142.7495	2142.6096	0.1399	6.6950
1	1	9	9	2085.8929	2085.2982	0.5947	-14.0877
1	2	1	1	2240.5064	2240.4766	0.0298	0.0075
1	2	2	2	2246.3449	2246.3359	0.0090	0.0042
1	2	3	3	2234.2630	2234.3096	-0.0466	6.9854
1	2	7	7	2142.7020	2142.5382	0.1638	6.6585
1	2	9	9	2085.8998	2085.3272	0.5726	-14.1287

TABLE A-1 (continued)

K	J	S	S'	Obs.	Calc.	O-C	Total Shift
1	3	1	1	2240.5058	2240.4760	0.0298	0.0150
1	3	2	2	2246.3455	2246.3339	0.0116	0.0104
1	3	3	3	2234.3453	2234.3957	-0.0504	7.1333
1	3	7	7	2142.6121	2142.4310	0.1811	6.6037
1	3	9	9	2085.9099	2085.3701	0.5398	-14.1908
1	4	1	1	2240.5040	2240.4752	0.0288	0.0250
1	4	2	2	2246.3435	2246.3313	0.0122	0.0188
1	4	3	3	2234.4604	2234.5107	-0.0503	7.3307
1	4	7	7	2142.5017	2142.2880	0.2137	6.5305
1	4	9	9	2085.9243	2085.4262	0.4981	-14.2747
1	5	1	1	2240.5016	2240.4741	0.0275	0.0373
1	5	2	2	2246.3397	2246.3280	0.0117	0.0292
1	5	3	3	2234.6065	2234.6548	-0.0483	7.5777
1	5	7	7	2142.3632	2142.1091	0.2541	6.4388
1	5	9	9	2085.9406	2085.4946	0.4460	-14.3813
1	6	1	1	2240.4962	2240.4726	0.0236	0.0521
1	6	2	2	2246.3349	2246.3240	0.0109	0.0417
1	6	3	3	2234.7852	2234.8282	-0.0430	7.8746
1	6	7	7	2142.2005	2141.8945	0.3060	6.3289
1	6	9	9	2085.9618	2085.5740	0.3878	-14.5117
1	7	1	1	2240.4954	2240.4708	0.0246	0.0691
1	7	2	2	2246.3338	2246.3193	0.0145	0.0563
1	7	3	3	2234.9900	2235.0311	-0.0411	8.2216
1	7	7	7	2142.0137	2141.6444	0.3693	6.2010
1	7	9	9	2085.9865	2085.6633	0.3232	-14.6674
1	8	1	1	2240.4917	2240.4686	0.0231	0.0884
1	8	2	2	2246.3269	2246.3140	0.0129	0.0730
1	8	3	3	2235.2195	2235.2636	-0.0441	8.6189
1	8	7	7	2141.8106	2141.3596	0.4510	6.0558
1	8	9	9	2086.0111	2085.7608	0.2503	-14.8498
1	9	1	1	2240.4877	2240.4658	0.0219	0.1099
1	9	2	2	2246.3222	2246.3080	0.0142	0.0917
1	9	3	3	2235.4753	2235.5260	-0.0507	9.0665
1	9	7	7	2141.5886	2141.0410	0.5476	5.8943
1	9	9	9	2086.0434	2085.8648	0.1786	-15.0607
1	10	1	1	2240.4864	2240.4625	0.0239	0.1335
1	10	2	2	2246.3119	2246.3013	0.0106	0.1125
1	10	3	3	2235.8282	2235.8184	0.0098	9.5648
1	10	7	7	2141.3485	2140.6901	0.6584	5.7180
1	10	9	9	2086.0753	2085.9735	0.1018	-15.3019
1	11	1	1	2240.4806	2240.4585	0.0221	0.1592
1	11	2	2	2246.3080	2246.2939	0.0141	0.1354
1	11	3	3	2236.1273	2236.1409	-0.0136	10.1138
1	11	9	9	2086.1142	2086.0846	0.0296	-15.5757
1	12	1	1	2240.4802	2240.4538	0.0264	0.1868
1	12	2	2	2246.3004	2246.2859	0.0145	0.1603
1	12	3	3	2236.4657	2236.4935	-0.0278	10.7134
1	12	9	9	2086.1536	2086.1960	-0.0424	-15.8842
1	13	1	1	2240.4802	2240.4483	0.0319	0.2164
1	13	2	2	2246.2948	2246.2772	0.0176	0.1874
1	13	3	3	2236.8198	2236.8762	-0.0564	11.3638
1	13	9	9	2086.1966	2086.3052	-0.1086	-16.2298
1	14	1	1	2240.4761	2240.4420	0.0341	0.2478
1	14	2	2	2246.2841	2246.2679	0.0162	0.2166
1	14	3	3	2237.2246	2237.2887	-0.0641	12.0646
1	14	9	9	2086.2426	2086.4096	-0.1670	-16.6154
1	15	1	1	2240.4759	2240.4349	0.0410	0.2812
1	15	2	2	2246.2769	2246.2579	0.0190	0.2479
1	15	3	3	2237.6516	2237.7309	-0.0793	12.8155
1	15	9	9	2086.2956	2086.5063	-0.2107	-17.0435
1	16	1	1	2240.4905	2240.4273	0.0632	0.3166
1	16	2	2	2246.2674	2246.2475	0.0199	0.2815
1	16	3	3	2238.0959	2238.2019	-0.1060	13.6160
1	16	9	9	2086.3468	2086.5924	-0.2456	-17.5172
1	17	1	1	2240.5029	2240.4194	0.0835	0.3546
1	17	2	2	2246.2604	2246.2366	0.0238	0.3173
1	17	3	3	2238.5699	2238.7009	-0.1310	14.4650
1	17	9	9	2086.4049	2086.6649	-0.2600	-18.0396
1	18	1	1	2240.5366	2240.4131	0.1235	0.3967
1	18	2	2	2246.2488	2246.2254	0.0234	0.3556
1	18	3	3	2239.0458	2239.2254	-0.1796	15.3601
1	18	9	9	2086.4609	2086.7205	-0.2596	-18.6138
1	19	1	1	2240.6192	2240.4164	0.2028	0.4512
1	19	2	2	2246.2375	2246.2141	0.0234	0.3966
1	19	3	3	2239.4984	2239.7665	-0.2681	16.2924
1	19	9	9	2086.5224	2086.7560	-0.2336	-19.2430
1	20	1	3	2240.8196	2240.5254	0.2942	0.3156
1	20	2	2	2246.2308	2246.2032	0.0276	0.4406
1	20	3	1	2239.8625	2240.2268	-0.3643	17.4630
1	20	9	9	2086.5861	2086.7682	-0.1821	-19.9306
1	21	1	1	2240.0617	2240.3150	-0.2533	0.4603
1	21	2	2	2246.2242	2246.1931	0.0311	0.4883
1	21	3	3	2241.2013	2241.0302	0.1711	18.4002
1	21	9	9	2086.6546	2086.7538	-0.0992	-20.6799
1	22	1	1	2240.1513	2240.3114	-0.1601	0.5160
1	22	2	2	2246.2163	2246.1849	0.0314	0.5406
1	22	3	3	2241.7166	2241.6483	0.0683	19.4712
1	22	9	9	2086.7214	2086.7095	0.0119	-21.4939
1	23	1	1	2240.1838	2240.2958	-0.1120	0.5623
1	23	2	2	2246.2085	2246.1804	0.0281	0.5994
1	23	3	3	2242.2994	2242.2972	0.0022	20.5936
1	23	9	9	2086.7957	2086.6324	0.1633	-22.3758
1	24	1	1	2240.1976	2240.2753	-0.0777	0.6065
1	24	2	2	2246.2119	2246.1834	0.0285	0.6683
1	24	9	9	2086.8686	2086.5195	0.3491	-23.3285
1	25	1	1	2240.2023	2240.2514	-0.0491	0.6500
1	25	2	2	2246.2212	2246.2014	0.0198	0.7551
1	25	9	9	2086.9458	2086.3681	0.5777	-24.3545
1	26	1	1	2240.1974	2240.2246	-0.0272	0.6933
1	26	2	2	2246.2556	2246.2534	0.0022	0.8786

TABLE A-1 (continued)

K	J	S	S'	Obs.	Calc.	O-C	Total Shift
1	26	9	9	2087.0217	2086.1760	0.8457	-25.4564
1	27	1	1	2240.1925	2240.1951	-0.0026	0.7365
1	27	2	2	2246.3397	2246.3893	-0.0496	1.0888
1	27	9	7	2087.1025	2085.9411	1.1614	20.8301
1	28	1	1	2240.1795	2240.1628	0.0167	0.7797
1	28	2	2	2246.4411	2246.7131	-0.2720	1.4895
1	28	9	7	2087.1856	2085.6617	1.5239	19.6055
1	29	1	1	2240.1650	2240.1278	0.0372	0.8228
1	29	9	7	2087.2669	2085.3366	1.9303	18.3915
1	30	1	1	2240.1541	2240.0900	0.0641	0.8659
1	30	9	7	2087.3536	2084.9648	2.3888	17.1899
1	31	1	1	2240.1391	2240.0493	0.0898	0.9088
1	31	9	7	2087.4328	2084.5459	2.8869	16.0022
1	32	1	1	2240.1218	2240.0058	0.1160	0.9514
1	32	9	7	2087.5182	2084.0798	3.4384	14.8284
1	33	1	1	2240.1045	2239.9593	0.1452	0.9939
1	33	9	7	2087.5989	2083.5668	4.0321	13.6674
1	34	9	7	2087.6831	2083.0077	4.6754	12.5157
2	2	1	1	2237.5532	2237.5150	0.0382	0.0065
2	2	7	7	2142.6601	2142.5405	0.1196	6.6717
2	2	9	9	2085.8410	2085.2693	0.5717	-14.0987
2	3	1	1	2237.5481	2237.5167	0.0314	0.0162
2	3	2	2	2249.2322	2249.2297	0.0025	0.0060
2	3	7	7	2142.5666	2142.4328	0.1338	6.6163
2	3	9	9	2085.8492	2085.3126	0.5366	-14.1604
2	4	1	1	2237.5479	2237.5191	0.0288	0.0292
2	4	2	2	2249.2264	2249.2265	-0.0001	0.0139
2	4	3	3	2234.4315	2234.4915	-0.0600	7.2621
2	4	7	7	2142.4431	2142.2935	0.1496	6.5468
2	4	9	9	2085.8646	2085.3691	0.4955	-14.2438
2	5	1	1	2237.5481	2237.5222	0.0259	0.0457
2	5	2	2	2249.2246	2249.2226	0.0020	0.0238
2	5	3	3	2234.6062	2234.6396	-0.0334	7.5132
2	5	7	7	2142.2981	2142.1259	0.1722	6.4665
2	5	9	9	2085.8810	2085.4378	0.4432	-14.3500
2	6	1	1	2237.5431	2237.5261	0.0170	0.0656
2	6	2	2	2249.2194	2249.2178	0.0016	0.0357
2	6	3	3	2234.7850	2234.8176	-0.0326	7.8147
2	6	7	7	2142.1212	2141.9335	0.1877	6.3788
2	6	9	9	2085.9019	2085.5176	0.3843	-14.4802
2	7	1	1	2237.5490	2237.5312	0.0178	0.0894
2	7	2	2	2249.2154	2249.2122	0.0032	0.0495
2	7	3	3	2234.9926	2235.0254	-0.0328	8.1666
2	7	7	7	2141.9190	2141.7199	0.1991	6.2874
2	7	9	9	2085.9268	2085.6069	0.3199	-14.6358
2	8	1	1	2237.5522	2237.5378	0.0144	0.1173
2	8	2	2	2249.2112	2249.2058	0.0054	0.0653
2	8	3	3	2235.2408	2235.2626	-0.0218	8.5685
2	8	7	7	2141.6961	2141.4882	0.2079	6.1953
2	8	9	9	2085.9523	2085.7042	0.2481	-14.8184
2	9	1	1	2237.5542	2237.5467	0.0075	0.1503
2	9	2	2	2249.2065	2249.1986	0.0079	0.0831
2	9	3	3	2235.5136	2235.5287	-0.0151	9.0199
2	9	7	7	2141.4469	2141.2414	0.2055	6.1056
2	9	9	9	2085.9844	2085.8078	0.1766	-15.0297
2	10	1	1	2237.5590	2237.5595	-0.0005	0.1897
2	10	2	2	2249.1969	2249.1906	0.0063	0.1029
2	10	3	3	2235.8107	2235.8222	-0.0115	9.5193
2	10	7	7	2141.1813	2140.9816	0.1997	6.0204
2	10	9	9	2086.0179	2085.9156	0.1023	-15.2718
2	11	1	1	2237.5790	2237.5792	-0.0002	0.2387
2	11	2	2	2249.1919	2249.1817	0.0102	0.1246
2	11	3	3	2236.1278	2236.1400	-0.0122	10.0636
2	11	7	7	2140.8912	2140.7108	0.1804	5.9415
2	11	9	9	2086.0553	2086.0256	0.0297	-15.5467
2	12	1	1	2237.6079	2237.6132	-0.0053	0.3048
2	12	2	2	2249.1811	2249.1721	0.0090	0.1483
2	12	3	3	2236.4678	2236.4746	-0.0068	10.6453
2	12	7	7	2140.5838	2140.4302	0.1536	5.8704
2	12	9	9	2086.0959	2086.1354	-0.0395	-15.8567
2	13	1	1	2237.6727	2237.6811	-0.0084	0.4073
2	13	2	2	2249.1733	2249.1617	0.0116	0.1741
2	13	3	3	2236.7904	2236.8064	-0.0160	11.2447
2	13	7	7	2140.2680	2140.1408	0.1272	5.8078
2	13	9	9	2086.1405	2086.2426	-0.1021	-16.2044
2	14	1	3	2237.8233	2237.8313	-0.0080	-0.1499
2	14	2	2	2249.1648	2249.1506	0.0142	0.2018
2	14	3	1	2237.0636	2237.0865	-0.0229	12.5578
2	14	7	7	2139.9355	2139.8433	0.0922	5.7547
2	14	9	9	2086.1871	2086.3446	-0.1575	-16.5924
2	15	1	1	2237.2236	2237.2566	-0.0330	0.0602
2	15	2	2	2249.1531	2249.1388	0.0143	0.2316
2	15	3	3	2238.1164	2238.1217	-0.0053	13.1571
2	15	7	7	2139.5940	2139.5383	0.0557	5.7115
2	15	9	9	2086.2391	2086.4384	-0.1993	-17.0234
2	16	1	1	2237.2964	2237.3355	-0.0391	0.1817
2	16	2	2	2249.1440	2249.1263	0.0177	0.2636
2	16	3	3	2238.5278	2238.5330	-0.0052	13.8978
2	16	7	7	2139.2406	2139.2264	0.0142	5.6789
2	16	9	9	2086.2909	2086.5211	-0.2302	-17.5005
2	17	1	1	2237.3278	2237.3716	-0.0438	0.2632
2	17	2	2	2249.1316	2249.1132	0.0184	0.2977
2	17	3	3	2239.0072	2239.0160	-0.0088	14.7308
2	17	7	7	2138.8834	2138.9083	-0.0249	5.6575
2	17	9	9	2086.3484	2086.5896	-0.2412	-18.0269
2	18	1	1	2237.3434	2237.3887	-0.0453	0.3283
2	18	2	2	2249.1195	2249.0998	0.0197	0.3343
2	18	3	3	2239.5359	2239.5460	-0.0101	15.6314
2	18	7	7	2138.5180	2138.5846	-0.0666	5.6479
2	18	9	9	2086.4078	2086.6406	-0.2328	-18.6056

TABLE A-1 (continued)

K	J	S	S'	Obs.	Calc.	O-C	Total Shift
2	19	1	1	2237.3488	2237.3960	-0.0472	0.3863
2	19	2	2	2249.1053	2249.0861	0.0192	0.3734
2	19	3	3	2240.0918	2240.1127	-0.0209	16.5893
2	19	7	7	2138.1516	2138.2562	-0.1046	5.6511
2	19	9	9	2086.4700	2086.6709	-0.2009	-19.2401
2	20	1	1	2237.3474	2237.3973	-0.0499	0.4410
2	20	2	2	2249.0979	2249.0724	0.0255	0.4153
2	20	3	3	2240.6909	2240.7111	-0.0202	17.5995
2	20	7	7	2137.7822	2137.9242	-0.1420	5.6682
2	20	9	9	2086.5340	2086.6772	-0.1432	-19.9337
2	21	1	1	2237.3480	2237.3945	-0.0465	0.4941
2	21	2	2	2249.0797	2249.0593	0.0204	0.4604
2	21	3	3	2241.3148	2241.3380	-0.0232	18.6587
2	21	7	7	2137.4126	2137.5898	-0.1772	5.7003
2	21	9	9	2086.6032	2086.6560	-0.0528	-20.6897
2	22	1	1	2237.3494	2237.3883	-0.0389	0.5466
2	22	2	2	2249.0673	2249.0472	0.0201	0.5094
2	22	3	3	2241.9652	2241.9906	-0.0254	19.7642
2	22	7	7	2137.0375	2137.2546	-0.2171	5.7491
2	22	9	9	2086.6720	2086.6041	0.0679	-21.5113
2	23	2	2	2249.0577	2249.0372	0.0205	0.5633
2	23	3	3	2242.6257	2242.6664	-0.0407	20.9135
2	23	7	7	2136.6793	2136.9203	-0.2410	5.8162
2	23	9	9	2086.7468	2086.5185	0.2283	-22.4017
2	24	2	2	2249.0459	2249.0308	0.0151	0.6235
2	24	3	3	2243.3162	2243.3623	-0.0461	22.1036
2	24	9	9	2086.8210	2086.3961	0.4249	-23.3638
2	25	2	2	2249.0343	2249.0305	0.0038	0.6927
2	25	3	3	2244.0724	2244.0744	-0.0020	23.3304
2	25	9	9	2086.8989	2086.2345	0.6644	-24.4002
2	26	2	2	2249.0252	2249.0409	-0.0157	0.7753
2	26	9	9	2086.9779	2086.0311	0.9468	-25.5133
2	27	2	2	2249.0226	2249.0704	-0.0478	0.8798
2	27	9	7	2087.0606	2085.7841	1.2765	23.1517
2	28	2	2	2249.0272	2249.1354	-0.1082	1.0226
2	28	9	7	2087.1444	2085.4918	1.6526	21.8823
2	29	2	2	2249.0554	2249.2697	-0.2143	1.2375
2	29	9	7	2087.2293	2085.1531	2.0762	20.5979
2	30	9	7	2087.3123	2084.7673	2.5450	19.3036
2	31	9	7	2087.3995	2084.3341	3.0654	18.0047
2	32	9	7	2087.4894	2083.8537	3.6357	16.7073
2	33	9	7	2087.5734	2083.3264	4.2470	15.4174
2	34	9	7	2087.6477	2082.7533	4.8944	14.1413
3	3	1	1	2234.5836	2234.5830	0.0006	0.0614
3	3	7	7	2142.4979	2142.4317	0.0662	6.6334
3	3	9	9	2085.7477	2085.2158	0.5319	-14.1105
3	4	1	1	2234.6259	2234.6753	-0.0494	0.1642
3	4	2	2	2252.0898	2252.0986	-0.0088	0.0076
3	4	3	3	2234.3658	2234.3196	0.0462	7.0080
3	4	7	7	2142.3631	2142.2759	0.0872	6.5474
3	4	9	9	2085.7621	2085.2736	0.4885	-14.1926
3	5	1	3	2234.7230	2234.8123	-0.0893	-0.1498
3	5	2	2	2252.0880	2252.0941	-0.0061	0.0171
3	5	3	1	2234.4384	2234.3481	0.0903	7.6036
3	5	7	7	2142.1977	2142.0861	0.1116	6.4448
3	5	9	9	2085.7793	2085.3436	0.4357	-14.2976
3	6	1	1	2234.4670	2234.3675	0.0995	-0.1146
3	6	2	2	2252.0830	2252.0887	-0.0057	0.0286
3	6	3	3	2234.8703	2234.9921	-0.1218	7.9070
3	6	7	7	2142.0030	2141.8652	0.1378	6.3287
3	6	9	9	2085.8010	2085.4243	0.3767	-14.4268
3	7	1	1	2234.4820	2234.3814	0.1006	-0.0822
3	7	2	2	2252.0776	2252.0824	-0.0048	0.0419
3	7	3	3	2235.1148	2235.2114	-0.0966	8.2704
3	7	7	7	2141.7807	2141.6163	0.1644	6.2020
3	7	9	9	2085.8254	2085.5141	0.3113	-14.5819
3	8	1	1	2234.4880	2234.3922	0.0958	-0.0503
3	8	2	2	2252.0732	2252.0752	-0.0020	0.0571
3	8	3	3	2235.3802	2235.4681	-0.0879	8.6918
3	8	7	7	2141.5284	2141.3427	0.1857	6.0679
3	8	9	9	2085.8540	2085.6114	0.2426	-14.7646
3	9	1	1	2234.4832	2234.4012	0.0820	-0.0176
3	9	2	2	2252.0671	2252.0671	0.0000	0.0743
3	9	3	3	2235.6805	2235.7610	-0.0805	9.1700
3	9	7	7	2141.2560	2141.0475	0.2085	5.9298
3	9	9	9	2085.8843	2085.7142	0.1701	-14.9767
3	10	1	1	2234.4789	2234.4090	0.0699	0.0166
3	10	2	2	2252.0563	2252.0581	-0.0018	0.0933
3	10	3	3	2236.0131	2236.0895	-0.0764	9.7044
3	10	7	7	2140.9608	2140.7338	0.2270	5.7907
3	10	9	9	2085.9209	2085.8205	0.1004	-15.2202
3	11	1	1	2234.4747	2234.4159	0.0588	0.0527
3	11	2	2	2252.0488	2252.0482	0.0006	0.1143
3	11	3	3	2236.3782	2236.4533	-0.0751	10.2947
3	11	7	7	2140.6468	2140.4048	0.2420	5.6536
3	11	9	9	2085.9576	2085.9282	0.0294	-15.4974
3	12	1	1	2234.4751	2234.4222	0.0529	0.0906
3	12	2	2	2252.0422	2252.0375	0.0047	0.1372
3	12	3	3	2236.7783	2236.8520	-0.0737	10.9405
3	12	7	7	2140.3088	2140.0630	0.2458	5.5213
3	12	9	9	2086.0009	2086.0349	-0.0340	-15.8106
3	13	1	1	2234.4709	2234.4279	0.0430	0.1306
3	13	2	2	2252.0314	2252.0258	0.0056	0.1621
3	13	3	3	2237.2162	2237.2852	-0.0690	11.6413
3	13	7	7	2139.9558	2139.7112	0.2446	5.3964
3	13	9	9	2086.0468	2086.1381	-0.0913	-16.1623
3	14	1	1	2234.4633	2234.4329	0.0304	0.1726
3	14	2	2	2252.0192	2252.0134	0.0058	0.1889
3	14	3	3	2237.6853	2237.7525	-0.0672	12.3968
3	14	7	7	2139.5899	2139.3518	0.2381	5.2813

TABLE A-1 (continued)

K	J	S	S'	Obs.	Calc.	O-C	Total Shift
3	14	9	9	2086.0950	2086.2351	-0.1401	-16.5551
3	15	1	1	2234.4558	2234.4372	0.0186	0.2164
3	15	2	2	2252.0083	2252.0002	0.0081	0.2178
3	15	3	3	2238.1900	2238.2531	-0.0631	13.2062
3	15	7	7	2139.2110	2138.9870	0.2240	5.1783
3	15	9	9	2086.1491	2086.3230	-0.1739	-16.9921
3	16	1	1	2234.4493	2234.4407	0.0086	0.2622
3	16	2	2	2252.0003	2251.9864	0.0139	0.2488
3	16	3	3	2238.7162	2238.7862	-0.0700	14.0687
3	16	7	7	2138.8228	2138.6189	0.2039	5.0895
3	16	9	9	2086.2050	2086.3988	-0.1938	-17.4761
3	17	1	1	2234.4412	2234.4433	-0.0021	0.3096
3	17	2	2	2251.9843	2251.9718	0.0125	0.2820
3	17	3	3	2239.2833	2239.3508	-0.0675	14.9834
3	17	7	7	2138.4226	2138.2496	0.1730	5.0169
3	17	9	9	2086.2648	2086.4592	-0.1944	-18.0106
3	18	1	1	2234.4328	2234.4449	-0.0121	0.3587
3	18	2	2	2251.9719	2251.9568	0.0151	0.3174
3	18	3	3	2239.8761	2239.9457	-0.0696	15.9489
3	18	7	7	2138.0280	2137.8810	0.1470	4.9624
3	18	9	9	2086.3256	2086.5008	-0.1752	-18.5987
3	19	1	1	2234.4239	2234.4454	-0.0215	0.4094
3	19	2	2	2251.9579	2251.9415	0.0164	0.3554
3	19	3	3	2240.4973	2240.5697	-0.0724	16.9641
3	19	7	7	2137.5955	2137.5149	0.0806	4.9280
3	19	9	9	2086.3925	2086.5204	-0.1279	-19.2440
3	20	1	1	2234.4157	2234.4446	-0.0289	0.4614
3	20	2	2	2251.9434	2251.9261	0.0173	0.3961
3	20	3	3	2241.1407	2241.2211	-0.0804	18.0273
3	20	7	7	2137.1887	2137.1533	0.0354	4.9154
3	20	9	9	2086.4607	2086.5142	-0.0535	-19.9500
3	21	1	1	2234.4056	2234.4426	-0.0370	0.5148
3	21	2	2	2251.9290	2251.9109	0.0181	0.4398
3	21	3	3	2241.8297	2241.8983	-0.0686	19.1368
3	21	7	7	2136.7647	2136.7981	-0.0334	4.9268
3	21	9	9	2086.5350	2086.4790	0.0560	-20.7199
3	22	1	1	2234.3950	2234.4390	-0.0440	0.5693
3	22	2	2	2251.9138	2251.8964	0.0174	0.4870
3	22	3	3	2242.5325	2242.5994	-0.0669	20.2909
3	22	7	7	2136.3452	2136.4514	-0.1062	4.9640
3	22	9	9	2086.6114	2086.4114	0.2000	-21.5573
3	23	1	1	2234.3887	2234.4339	-0.0452	0.6249
3	23	2	2	2251.8966	2251.8832	0.0134	0.5384
3	23	3	3	2243.2692	2243.3223	-0.0531	21.4872
3	23	7	7	2135.9250	2136.1153	-0.1903	5.0294
3	23	9	9	2086.6887	2086.3082	0.3805	-22.4653
3	24	2	2	2251.8805	2251.8724	0.0081	0.5949
3	24	3	3	2244.0626	2244.0644	-0.0018	22.7235
3	24	7	7	2135.5100	2135.7921	-0.2821	5.1251
3	24	9	9	2086.7826	2086.1664	0.6162	-23.4469
3	25	2	2	2251.8630	2251.8655	-0.0025	0.6580
3	25	3	3	2244.8325	2244.8229	0.0096	23.9967
3	26	2	2	2251.8466	2251.8646	-0.0180	0.7301
3	26	3	3	2245.6192	2245.5941	0.0251	25.3032
3	27	2	2	2251.8321	2251.8736	-0.0415	0.8149
3	27	3	3	2246.3880	2246.3727	0.0153	26.6377
3	28	2	2	2251.8179	2251.8988	-0.0809	0.9186
3	29	2	2	2251.8087	2251.9512	-0.1425	1.0524
3	30	2	2	2251.8079	2252.0509	-0.2430	1.2362
3	31	2	2	2251.8264	2252.2330	-0.4066	1.5052
3	32	2	2	2251.9306	2252.5477	-0.6171	1.9096
4	4	1	1	2231.5623	2231.5161	0.0462	0.0011
4	4	3	3	2234.6968	2234.4053	0.2915	6.9786
4	4	7	7	2142.2700	2142.2764	-0.0064	6.5733
4	4	9	9	2085.6167	2085.1373	0.4794	-14.1235
4	5	1	1	2231.5561	2231.5063	0.0498	0.0044
4	5	2	2	2254.9274	2254.9417	-0.0143	0.0092
4	5	3	3	2234.8418	2234.6024	0.2394	7.2788
4	5	7	7	2142.0729	2142.0582	0.0147	6.4423
4	5	9	9	2085.6361	2085.2121	0.4240	-14.2237
4	6	1	1	2231.5517	2231.4967	0.0550	0.0105
4	6	2	2	2254.9207	2254.9357	-0.0150	0.0203
4	6	3	3	2235.0090	2234.8381	0.1709	7.6380
4	6	7	7	2141.8461	2141.8056	0.0405	6.2945
4	6	9	9	2085.6580	2085.2965	0.3615	-14.3492
4	7	1	1	2231.5418	2231.4880	0.0538	0.0200
4	7	2	2	2254.9161	2254.9288	-0.0127	0.0332
4	7	3	3	2235.1968	2235.1123	0.0845	8.0563
4	7	7	7	2141.5874	2141.5228	0.0646	6.1339
4	7	9	9	2085.6842	2085.3887	0.2955	-14.5020
4	8	1	1	2231.5347	2231.4804	0.0543	0.0334
4	8	2	2	2254.9097	2254.9209	-0.0112	0.0479
4	8	3	3	2235.4277	2235.4249	0.0028	8.5335
4	8	7	7	2141.2967	2141.2138	0.0829	5.9645
4	8	9	9	2085.7145	2085.4867	0.2278	-14.6840
4	9	1	1	2231.5285	2231.4743	0.0542	0.0507
4	9	2	2	2254.9021	2254.9120	-0.0099	0.0645
4	9	3	3	2235.7319	2235.7759	-0.0440	9.0699
4	9	7	7	2140.9872	2140.8826	0.1046	5.7904
4	9	9	9	2085.7460	2085.5885	0.1575	-14.8971
4	10	1	1	2231.5200	2231.4697	0.0503	0.0723
4	10	2	2	2254.8939	2254.9022	-0.0083	0.0830
4	10	3	3	2236.1157	2236.1654	-0.0497	9.6653
4	10	7	7	2140.6475	2140.5330	0.1145	5.6153
4	10	9	9	2085.7845	2085.6921	0.0924	-15.1433
4	11	1	1	2231.5088	2231.4666	0.0422	0.0979
4	11	2	2	2254.8832	2254.8914	-0.0082	0.1034
4	11	3	3	2236.5367	2236.5932	-0.0565	10.3195
4	11	7	7	2140.2897	2140.1684	0.1213	5.4427
4	11	9	9	2085.8248	2085.7954	0.0294	-15.4249

TABLE A-1 (continued)

K	J	S	S'	Obs.	Calc.	O-C	Total Shift
4	12	2	2	2254.8773	2254.8796	-0.0023	0.1256
4	12	3	3	2236.9944	2237.0589	-0.0645	11.0323
4	12	7	7	2139.9119	2139.7922	0.1197	5.2760
4	12	9	9	2085.8697	2085.8961	-0.0264	-15.7441
4	13	1	1	2231.5012	2231.4644	0.0368	0.1610
4	13	2	2	2254.8655	2254.8670	-0.0015	0.1498
4	13	3	3	2237.4915	2237.5620	-0.0705	11.8030
4	13	7	7	2139.5147	2139.4075	0.1072	5.1181
4	13	9	9	2085.9176	2085.9916	-0.0740	-16.1035
4	14	1	1	2231.4887	2231.4649	0.0238	0.1980
4	14	2	2	2254.8554	2254.8534	0.0020	0.1759
4	14	3	3	2238.0213	2238.1015	-0.0802	12.6308
4	14	7	7	2139.1134	2139.0170	0.0964	4.9719
4	14	9	9	2085.9799	2086.0790	-0.0991	-16.5059
4	15	1	1	2231.4827	2231.4661	0.0166	0.2385
4	15	2	2	2254.8440	2254.8391	0.0049	0.2040
4	15	3	3	2238.5876	2238.6763	-0.0887	13.5144
4	15	7	7	2138.6940	2138.6233	0.0707	4.8401
4	15	9	9	2086.0293	2086.1554	-0.1261	-16.9543
4	16	1	1	2231.4747	2231.4679	0.0068	0.2820
4	16	2	2	2254.8277	2254.8239	0.0038	0.2342
4	16	3	3	2239.1878	2239.2851	-0.0973	14.4526
4	16	7	7	2138.2619	2138.2290	0.0329	4.7250
4	16	9	9	2086.0922	2086.2176	-0.1254	-17.4520
4	17	1	1	2231.4677	2231.4699	-0.0022	0.3285
4	17	2	2	2254.8147	2254.8081	0.0066	0.2665
4	17	3	3	2239.8205	2239.9262	-0.1057	15.4437
4	17	7	7	2137.8267	2137.8364	-0.0097	4.6291
4	17	9	9	2086.1545	2086.2620	-0.1075	-18.0025
4	18	1	1	2231.4563	2231.4719	-0.0156	0.3775
4	18	2	2	2254.7998	2254.7917	0.0081	0.3011
4	18	3	3	2240.4820	2240.5977	-0.1157	16.4858
4	18	7	7	2137.3823	2137.4476	-0.0653	4.5545
4	18	9	9	2086.2220	2086.2850	-0.0630	-18.6092
4	19	1	1	2231.4487	2231.4737	-0.0250	0.4289
4	19	2	2	2254.7850	2254.7749	0.0101	0.3382
4	19	3	3	2241.1737	2241.2977	-0.1240	17.5770
4	19	7	7	2136.9364	2137.0650	-0.1286	4.5035
4	19	9	9	2086.2946	2086.2830	0.0116	-19.2760
4	20	1	1	2231.4407	2231.4750	-0.0343	0.4824
4	20	2	2	2254.7692	2254.7579	0.0113	0.3778
4	20	3	3	2241.8868	2242.0240	-0.1372	18.7150
4	20	7	7	2136.4852	2136.6906	-0.2054	4.4781
4	20	9	9	2086.3676	2086.2523	0.1153	-20.0066
4	21	1	1	2231.4305	2231.4756	-0.0451	0.5379
4	21	2	2	2254.7540	2254.7409	0.0131	0.4203
4	21	3	3	2242.6057	2242.7743	-0.1686	19.8977
4	21	7	7	2136.0336	2136.3266	-0.2930	4.4807
4	21	9	9	2086.4456	2086.1891	0.2565	-20.8046
4	22	1	1	2231.4193	2231.4752	-0.0559	0.5950
4	22	2	2	2254.7358	2254.7244	0.0114	0.4661
4	22	7	7	2135.5852	2135.9752	-0.3900	4.5133
4	22	9	9	2086.5291	2086.0900	0.4391	-21.6734
4	23	1	1	2231.4086	2231.4738	-0.0652	0.6536
4	23	2	2	2254.7195	2254.7088	0.0107	0.5157
4	23	7	7	2135.1351	2135.6387	-0.5036	4.5782
4	23	9	9	2086.6115	2085.9518	0.6597	-22.6164
4	24	1	1	2231.4025	2231.4710	-0.0685	0.7136
4	24	2	2	2254.6992	2254.6950	0.0042	0.5698
4	24	7	7	2134.6980	2135.3194	-0.6214	4.6777
4	24	9	9	2086.6990	2085.7716	0.9274	-23.6364
4	25	1	1	2231.3935	2231.4669	-0.0734	0.7747
4	25	2	2	2254.6832	2254.6839	-0.0007	0.6296
4	25	7	7	2134.2647	2135.0197	-0.7550	4.8144
4	25	9	9	2086.7912	2085.5471	1.2441	-24.7356
4	26	1	1	2231.3842	2231.4611	-0.0769	0.8368
4	26	2	2	2254.6593	2254.6772	-0.0179	0.6965
4	26	9	9	2086.8841	2085.2764	1.6077	-25.9160
4	27	1	1	2231.3748	2231.4536	-0.0788	0.8999
4	27	2	2	2254.6432	2254.6772	-0.0340	0.7730
4	27	9	9	2086.9758	2084.9584	2.0174	-27.1788
4	28	1	1	2231.3614	2231.4442	-0.0828	0.9636
4	28	2	2	2254.6256	2254.6878	-0.0622	0.8629
4	28	9	9	2087.0728	2084.5922	2.4806	-28.5246
4	29	1	1	2231.3538	2231.4328	-0.0790	1.0280
4	29	2	2	2254.6056	2254.7150	-0.1094	0.9722
4	29	9	7	2087.1757	2084.1780	2.9977	19.9379
4	30	1	1	2231.3457	2231.4194	-0.0737	1.0929
4	30	2	2	2254.5929	2254.7692	-0.1763	1.1114
4	30	9	7	2087.2745	2083.7161	3.5584	18.7267
4	31	1	1	2231.3373	2231.4037	-0.0664	1.1582
4	31	2	2	2254.5831	2254.8681	-0.2850	1.2981
4	31	9	7	2087.3739	2083.2075	4.1664	17.5168
4	32	1	1	2231.3291	2231.3858	-0.0567	1.2239
4	32	2	2	2254.5859	2255.0416	-0.4557	1.5623
4	32	9	7	2087.4725	2082.6536	4.8189	16.3113
4	33	1	1	2231.3233	2231.3655	-0.0422	1.2898
4	33	2	2	2254.6063	2255.3325	-0.7262	1.9466
4	33	9	7	2087.5590	2082.0560	5.5030	15.1131
4	34	1	1	2231.3296	2231.3428	-0.0132	1.3558
4	34	2	2	2254.6310	2255.7806	-1.1496	2.4911
4	34	9	7	2087.6537	2081.4169	6.2368	13.9251
5	5	1	1	2228.5353	2228.4951	0.0402	0.0057
5	5	7	7	2141.9567	2142.0545	-0.0978	6.4713
5	5	9	9	2085.4494	2085.0332	0.4162	-14.1386
5	6	1	1	2228.5276	2228.4878	0.0398	0.0140
5	6	2	2	2257.7361	2257.7579	-0.0218	0.0107
5	6	7	7	2141.6662	2141.7412	-0.0750	6.2627
5	6	9	9	2085.4748	2085.1523	0.3225	-14.2295
5	7	1	1	2228.5253	2228.4809	0.0444	0.0252

TABLE A-1 (continued)

K	J	S	S'	Obs.	Calc.	O-C	Total Shift
5	7	2	2	2257.7289	2257.7505	-0.0216	0.0233
5	7	3	3	2235.0710	2235.0761	-0.0051	7.8721
5	7	7	7	2141.3443	2141.3973	-0.0530	6.0410
5	7	9	9	2085.5016	2085.2578	0.2438	-14.3689
5	8	1	1	2228.5211	2228.4750	0.0461	0.0399
5	8	2	2	2257.7242	2257.7419	-0.0177	0.0376
5	8	3	3	2235.4168	2235.4465	-0.0297	8.4072
5	8	7	7	2140.9922	2141.0288	-0.0366	5.8122
5	8	9	9	2085.5313	2085.3579	0.1734	-14.5487
5	9	1	1	2228.5138	2228.4703	0.0435	0.0585
5	9	2	2	2257.7156	2257.7323	-0.0167	0.0538
5	9	3	3	2235.8437	2235.8659	-0.0222	9.0119
5	9	7	7	2140.6123	2140.6411	-0.0288	5.5816
5	9	9	9	2085.5652	2085.4553	0.1099	-14.7662
5	10	1	1	2228.5079	2228.4671	0.0408	0.0812
5	10	2	2	2257.7097	2257.7217	-0.0120	0.0717
5	10	3	3	2236.2905	2236.3339	-0.0434	9.6858
5	10	7	7	2140.2076	2140.2389	-0.0313	5.3539
5	10	9	9	2085.5976	2085.5500	0.0476	-15.0214
5	11	1	1	2228.5022	2228.4657	0.0365	0.1082
5	11	2	2	2257.6971	2257.7100	-0.0129	0.0916
5	11	3	3	2236.7920	2236.8498	-0.0578	10.4282
5	11	7	7	2139.7874	2139.8263	-0.0389	5.1332
5	11	9	9	2085.6349	2085.6411	-0.0062	-15.3152
5	12	1	1	2228.4938	2228.4660	0.0278	0.1395
5	12	2	2	2257.6875	2257.6974	-0.0099	0.1132
5	12	3	3	2237.3285	2237.4120	-0.0835	11.2374
5	12	7	7	2139.3542	2139.4068	-0.0526	4.9232
5	12	9	9	2085.6731	2085.7264	-0.0533	-15.6498
5	13	1	1	2228.4892	2228.4680	0.0212	0.1751
5	13	2	2	2257.6737	2257.6838	-0.0101	0.1368
5	13	3	3	2237.9096	2238.0184	-0.1088	12.1115
5	13	7	7	2138.8999	2138.9837	-0.0838	4.7270
5	13	9	9	2085.7131	2085.8033	-0.0902	-16.0277
5	14	1	1	2228.4806	2228.4715	0.0091	0.2148
5	14	2	2	2257.6616	2257.6692	-0.0076	0.1622
5	14	3	3	2238.5378	2238.6665	-0.1287	13.0478
5	14	7	7	2138.4430	2138.5598	-0.1168	4.5474
5	14	9	9	2085.7539	2085.8688	-0.1149	-16.4521
5	15	1	1	2228.4750	2228.4763	-0.0013	0.2583
5	15	2	2	2257.6501	2257.6537	-0.0036	0.1897
5	15	3	3	2239.1931	2239.3534	-0.1603	14.0435
5	15	7	7	2137.9729	2138.1376	-0.1647	4.3870
5	15	9	9	2085.7956	2085.9192	-0.1236	-16.9265
5	16	1	1	2228.4696	2228.4819	-0.0123	0.3053
5	16	2	2	2257.6348	2257.6374	-0.0026	0.2191
5	16	3	3	2239.8924	2240.0758	-0.1834	15.0953
5	16	7	7	2137.5057	2137.7195	-0.2138	4.2482
5	16	9	9	2085.8333	2085.9507	-0.1174	-17.4549
5	17	1	1	2228.4538	2228.4882	-0.0344	0.3555
5	17	2	2	2257.6237	2257.6204	0.0033	0.2507
5	17	3	3	2240.6229	2240.8303	-0.2074	16.1999
5	17	7	7	2137.0248	2137.3077	-0.2829	4.1331
5	17	9	9	2085.8736	2085.9590	-0.0854	-18.0414
5	18	1	1	2228.4538	2228.4946	-0.0408	0.4085
5	18	2	2	2257.6064	2257.6027	0.0037	0.2845
5	18	3	3	2241.3889	2241.6137	-0.2248	17.3538
5	18	7	7	2136.5563	2136.9044	-0.3481	4.0439
5	19	1	1	2228.4604	2228.5010	-0.0406	0.4639
5	19	2	2	2257.5912	2257.5845	0.0067	0.3206
5	19	7	7	2136.0891	2136.5115	-0.4224	3.9827
5	20	1	1	2228.4329	2228.5068	-0.0739	0.5215
5	20	2	2	2257.5736	2257.5659	0.0077	0.3593
5	20	7	7	2135.6029	2136.1312	-0.5283	3.9514
5	21	1	1	2228.4280	2228.5119	-0.0839	0.5808
5	21	2	2	2257.5576	2257.5473	0.0103	0.4008
5	21	7	7	2135.1294	2135.7654	-0.6360	3.9521
5	22	1	1	2228.4190	2228.5159	-0.0969	0.6417
5	22	2	2	2257.5390	2257.5290	0.0100	0.4453
5	22	7	7	2134.6784	2135.4161	-0.7377	3.9869
5	23	1	1	2228.4110	2228.5187	-0.1077	0.7039
5	23	2	2	2257.5210	2257.5113	0.0097	0.4935
5	23	7	7	2134.1485	2135.0856	-0.9371	4.0578
5	24	1	1	2228.4056	2228.5199	-0.1143	0.7672
5	24	2	2	2257.5000	2257.4950	0.0050	0.5458
5	24	7	7	2133.6349	2134.7759	-1.1410	4.1670
5	25	1	1	2228.3991	2228.5196	-0.1205	0.8315
5	25	2	2	2257.4813	2257.4809	0.0004	0.6032
5	26	1	1	2228.3905	2228.5175	-0.1270	0.8965
5	26	2	2	2257.4600	2257.4703	-0.0103	0.6670
5	27	1	1	2228.3816	2228.5135	-0.1319	0.9623
5	27	2	2	2257.4401	2257.4651	-0.0250	0.7389
5	28	1	1	2228.3746	2228.5075	-0.1329	1.0287
5	28	2	2	2257.4169	2257.4680	-0.0511	0.8220
5	29	1	1	2228.3689	2228.4996	-0.1307	1.0957
5	29	2	2	2257.3982	2257.4837	-0.0855	0.9206
5	30	1	1	2228.3600	2228.4896	-0.1296	1.1633
5	31	1	1	2228.3532	2228.4775	-0.1243	1.2313
5	32	1	1	2228.3463	2228.4634	-0.1171	1.2999
5	33	1	1	2228.3443	2228.4472	-0.1029	1.3690
5	34	1	1	2228.3378	2228.4289	-0.0911	1.4386
5	35	1	1	2228.3296	2228.4086	-0.0790	1.5087
6	6	1	1	2225.4844	2225.4544	0.0300	0.0087
6	6	7	7	2141.5140	2141.6979	-0.1839	6.2594
6	6	9	9	2085.2428	2084.9019	0.3409	-14.1572
6	7	1	1	2225.4842	2225.4485	0.0357	0.0207
6	7	2	2	2260.5205	2260.5465	-0.0260	0.0122
6	7	7	7	2141.0611	2141.2122	-0.1511	5.8959
6	7	9	9	2085.2618	2084.9312	0.3306	-14.3729
6	8	1	1	2225.4798	2225.4518	0.0280	0.0445

TABLE A-1 (continued)

K	J	S	S'	Obs.	Calc.	O-C	Total Shift
6	8	2	2	2260.5118	2260.5373	-0.0255	0.0262
6	8	7	7	2140.5860	2140.7217	-0.1357	5.5450
6	8	9	9	2085.2808	2084.9310	0.3498	-14.6529
6	9	1	1	2225.4752	2225.3664	0.1088	-0.0179
6	9	2	2	2260.5028	2260.5271	-0.0243	0.0419
6	9	7	7	2140.0914	2140.2303	-0.1389	5.2107
6	9	9	9	2085.2816	2084.8502	0.4314	-15.0487
6	10	1	1	2225.4666	2225.3832	0.0834	0.0244
6	10	2	2	2260.4939	2260.5157	-0.0218	0.0594
6	10	7	7	2139.5839	2139.7410	-0.1571	4.8958
6	10	9	12	2085.7215	2085.8521	-0.1306	-15.6707
6	10	12	9	2085.1963	2084.5781	0.6182	-2.7281
6	11	1	1	2225.4674	2225.3722	0.0952	0.0415
6	11	2	2	2260.4839	2260.5033	-0.0194	0.0788
6	11	7	7	2139.0706	2139.2558	-0.1852	4.6027
6	11	9	9	2085.5002	2085.6639	-0.1637	-14.9697
6	11	12	12	2084.7818	2084.0662	0.7156	-4.5207
6	12	1	1	2225.4593	2225.3556	0.1037	0.0556
6	12	2	2	2260.4757	2260.4898	-0.0141	0.0999
6	12	7	7	2138.5511	2138.7768	-0.2257	4.3331
6	12	9	9	2085.5017	2085.6020	-0.1003	-15.4515
6	13	1	1	2225.4525	2225.3356	0.1169	0.0689
6	13	2	2	2260.4609	2260.4752	-0.0143	0.1229
6	13	7	7	2138.0284	2138.3056	-0.2772	4.0888
6	13	9	9	2085.5317	2085.5756	-0.0439	-15.9328
6	14	1	1	2225.4497	2225.3127	0.1370	0.0818
6	14	2	2	2260.4506	2260.4596	-0.0090	0.1477
6	14	7	7	2137.5140	2137.8435	-0.3295	3.8711
6	14	9	9	2085.5672	2085.5473	0.0199	-16.4510
6	15	1	1	2225.4445	2225.2867	0.1578	0.0941
6	15	2	2	2260.4367	2260.4431	-0.0064	0.1745
6	15	7	7	2137.0011	2137.3921	-0.3910	3.6815
6	15	9	9	2085.6127	2085.4990	0.1137	-17.0241
6	16	1	1	2225.4411	2225.2573	0.1838	0.1056
6	16	2	2	2260.4221	2260.4257	-0.0036	0.2033
6	16	7	7	2136.5108	2136.9528	-0.4420	3.5214
6	16	9	9	2085.6575	2085.4195	0.2380	-17.6635
6	17	1	1	2225.4376	2225.2242	0.2134	0.1160
6	17	2	2	2260.4080	2260.4075	0.0005	0.2342
6	17	7	7	2136.0485	2136.5268	-0.4783	3.3921
6	17	9	9	2085.7056	2085.3005	0.4051	-18.3772
6	18	1	1	2225.4340	2225.1866	0.2474	0.1245
6	18	2	2	2260.3921	2260.3885	0.0036	0.2672
6	18	9	9	2085.7431	2085.1364	0.6067	-19.1712
6	19	1	1	2225.4313	2225.1440	0.2873	0.1304
6	19	2	2	2260.3764	2260.3689	0.0075	0.3025
6	19	9	9	2085.8145	2084.9232	0.8913	-20.0492
6	20	1	1	2225.4298	2225.0952	0.3346	0.1328
6	20	2	2	2260.3560	2260.3490	0.0070	0.3403
6	20	9	9	2085.8579	2084.6596	1.1983	-21.0126
6	21	1	1	2225.4287	2225.0392	0.3895	0.1304
6	21	2	2	2260.3377	2260.3288	0.0089	0.3808
6	21	6	9	2088.3323	2084.3458	3.9865	1.6092
6	21	9	9	2085.9039	2084.3458	1.5581	-22.0612
6	22	1	1	2225.4249	2224.9744	0.4505	0.1219
6	22	2	2	2260.3186	2260.3088	0.0098	0.4243
6	22	6	9	2088.2746	2083.9838	4.2908	2.0379
6	22	9	9	2085.9474	2083.9838	1.9636	-23.1930
6	23	1	1	2225.4286	2224.8990	0.5296	0.1054
6	23	2	2	2260.2984	2260.2893	0.0091	0.4712
6	23	6	9	2088.1193	2083.5766	4.5427	2.5070
6	23	9	9	2085.9806	2083.5766	2.4040	-24.4050
6	24	1	1	2225.4306	2224.8114	0.6192	0.0791
6	24	2	2	2260.2783	2260.2709	0.0074	0.5221
6	24	6	9	2088.1331	2083.1277	5.0054	3.0112
6	24	9	9	2086.0040	2083.1277	2.8763	-25.6936
6	25	1	1	2225.4358	2224.7095	0.7263	0.0411
6	25	2	2	2260.2570	2260.2545	0.0025	0.5778
6	25	6	6	2088.1483	2093.2682	-5.1199	3.5451
6	25	9	9	2085.9993	2082.6409	3.3584	-27.0552
6	26	1	1	2225.4411	2226.1260	-0.6849	1.5240
6	26	2	2	2260.2342	2260.2411	-0.0069	0.6395
6	26	6	6	2088.1704	2093.3801	-5.2097	4.1032
6	26	9	9	2085.9460	2082.1198	3.8262	-28.4860
6	27	1	1	2225.4529	2226.0315	-0.5786	1.4986
6	27	2	2	2260.2143	2260.2324	-0.0181	0.7089
6	27	6	6	2088.1856	2093.4942	-5.3086	4.6806
6	27	9	9	2085.8074	2081.5677	4.2397	-29.9828
6	28	1	1	2225.4613	2225.9444	-0.4831	1.4831
6	28	2	2	2260.1992	2260.2312	-0.0320	0.7885
6	28	6	6	2088.1932	2093.6058	-5.4126	5.2728
6	28	9	7	2085.5074	2080.9878	4.5196	20.6415
6	29	1	1	2225.4887	2225.8654	-0.3767	1.4783
6	29	2	2	2260.1685	2260.2414	-0.0729	0.8824
6	29	6	6	2088.1858	2093.7109	-5.5251	5.8756
6	29	9	7	2084.9574	2080.3826	4.5748	19.4888
6	30	1	1	2225.5123	2225.7945	-0.2822	1.4840
6	30	2	2	2260.1444	2260.2699	-0.1255	0.9976
6	30	6	6	2088.1492	2093.8060	-5.6568	6.4855
6	31	1	1	2225.5523	2225.7311	-0.1788	1.5000
6	31	2	2	2260.1465	2260.3281	-0.1816	1.1453
6	32	1	1	2225.6018	2225.6746	-0.0728	1.5253
6	33	1	1	2225.6736	2225.6241	0.0495	1.5591
6	34	1	1	2225.7695	2225.5788	0.1907	1.6008
6	35	1	1	2225.8981	2225.5380	0.3601	1.6494
7	7	1	1	2222.4174	2222.3965	0.0209	0.0114
7	7	7	7	2140.7739	2140.8355	-0.0616	5.5664
7	7	9	9	2084.9954	2084.7752	0.2202	-14.1475
7	8	1	1	2222.4162	2222.3947	0.0215	0.0298
7	8	2	2	2263.2744	2263.3063	-0.0319	0.0136

TABLE A-1 (continued)

K	J	S	S'	Obs.	Calc.	O-C	Total Shift
7	8	7	7	2140.0222	2140.0365	-0.0143	4.9069
7	8	9	9	2085.0217	2084.8841	0.1376	-14.3186
7	9	1	1	2222.4764	2222.3939	0.0825	0.0519
7	9	2	2	2263.2666	2263.2954	-0.0288	0.0290
7	9	5	1	2222.3485	2222.3939	-0.0454	-1.6810
7	9	7	7	2139.3182	2139.3557	-0.0375	4.3832
7	9	9	9	2085.0534	2085.0048	0.0486	-14.5127
7	10	1	1	2222.3929	2222.3937	-0.0008	0.0769
7	10	2	2	2263.2580	2263.2834	-0.0254	0.0461
7	10	7	7	2138.6421	2138.7402	-0.0981	3.9423
7	10	9	9	2085.0860	2085.1285	-0.0425	-14.7389
7	11	1	1	2222.3937	2222.3938	-0.0001	0.1048
7	11	2	2	2263.2483	2263.2702	-0.0219	0.0649
7	11	7	7	2137.9976	2138.1686	-0.1710	3.5627
7	11	9	9	2085.1206	2085.2404	-0.1198	-15.0120
7	12	1	1	2222.3843	2222.3940	-0.0097	0.1354
7	12	2	2	2263.2379	2263.2558	-0.0179	0.0856
7	12	7	7	2137.3867	2137.6304	-0.2437	3.2339
7	12	9	9	2085.1526	2085.3074	-0.1548	-15.3648
7	13	1	1	2222.3741	2222.3945	-0.0204	0.1688
7	13	2	2	2263.2226	2263.2404	-0.0178	0.1080
7	13	7	7	2136.8206	2137.1199	-0.2993	2.9503
7	13	9	9	2085.1804	2085.2496	-0.0692	-15.8774
7	14	1	1	2222.3653	2222.3952	-0.0299	0.2049
7	14	2	2	2263.2119	2263.2239	-0.0120	0.1323
7	14	7	7	2136.2795	2136.6338	-0.3543	2.7085
7	14	9	9	2085.1818	2084.9446	0.2372	-16.6723
7	15	1	1	2222.3589	2222.3961	-0.0372	0.2437
7	15	2	2	2263.1972	2263.2063	-0.0091	0.1585
7	15	9	10	2085.1048	2084.3988	0.7060	-15.4364
7	15	12	9	2085.9240	2086.7054	-0.7814	7.1313
7	16	1	1	2222.3520	2222.3972	-0.0452	0.2853
7	16	2	2	2263.1831	2263.1878	-0.0047	0.1866
7	16	9	9	2085.6566	2086.8128	-1.1562	-15.8888
7	16	12	10	2084.7900	2083.7344	1.0556	7.6626
7	17	1	1	2222.3417	2222.3986	-0.0569	0.3297
7	17	2	2	2263.1662	2263.1684	-0.0022	0.2168
7	17	9	9	2085.6096	2086.9793	-1.3697	-16.3171
7	18	1	1	2222.3355	2222.4003	-0.0648	0.3769
7	18	2	2	2263.1496	2263.1482	0.0014	0.2491
7	18	9	9	2085.6273	2087.1736	-1.5463	-16.7526
7	19	1	1	2222.3277	2222.4022	-0.0745	0.4269
7	19	2	2	2263.1338	2263.1274	0.0064	0.2836
7	19	9	9	2085.6706	2087.3816	-1.7110	-17.2095
7	20	2	2	2263.1119	2263.1060	0.0059	0.3206
7	20	9	9	2085.7245	2087.5955	-1.8710	-17.6953
7	21	1	1	2222.3096	2222.4071	-0.0975	0.5355
7	21	2	2	2263.0969	2263.0844	0.0125	0.3602
7	21	9	9	2085.7840	2087.8104	-2.0264	-18.2152
7	22	1	1	2222.3012	2222.4101	-0.1089	0.5941
7	22	2	2	2263.0728	2263.0629	0.0099	0.4028
7	22	9	9	2085.8512	2088.0224	-2.1712	-18.7731
7	23	1	1	2222.2878	2222.4134	-0.1256	0.6556
7	23	9	9	2085.9181	2088.2281	-2.3100	-19.3721
7	24	1	1	2222.2766	2222.4172	-0.1406	0.7201
7	24	2	2	2263.0316	2263.0217	0.0099	0.4986
7	24	9	9	2085.9803	2088.4247	-2.4444	-20.0152
7	25	1	1	2222.2695	2222.4214	-0.1519	0.7876
7	25	2	2	2263.0102	2263.0034	0.0068	0.5533
7	25	9	9	2086.0553	2088.6095	-2.5542	-20.7052
7	26	1	1	2222.2589	2222.4261	-0.1672	0.8580
7	26	2	2	2262.9882	2262.9883	-0.0001	0.6139
7	26	9	9	2086.1288	2088.7800	-2.6512	-21.4444
7	27	1	1	2222.2496	2222.4311	-0.1815	0.9313
7	27	2	2	2262.9654	2262.9781	-0.0127	0.6824
7	27	9	9	2086.1972	2088.9339	-2.7367	-22.2352
7	28	1	1	2222.2453	2222.4366	-0.1913	1.0076
7	28	2	2	2262.9429	2262.9757	-0.0328	0.7616
7	28	9	7	2086.2668	2089.0693	-2.8025	20.1817
7	29	1	1	2222.2359	2222.4424	-0.2065	1.0868
7	29	2	2	2262.9208	2262.9860	-0.0652	0.8565
7	29	9	7	2086.3409	2089.1842	-2.8433	19.0782
7	30	1	1	2222.2278	2222.4486	-0.2208	1.1688
7	30	2	2	2262.8978	2263.0173	-0.1195	0.9752
7	30	9	7	2086.4177	2089.2773	-2.8596	17.9764
7	31	1	1	2222.2191	2222.4550	-0.2359	1.2536
7	31	2	2	2262.8881	2263.0846	-0.1965	1.1330
7	31	9	7	2086.4822	2089.3473	-2.8651	16.8781
7	32	1	1	2222.2124	2222.4615	-0.2491	1.3411
7	32	2	2	2262.9077	2263.2157	-0.3080	1.3573
7	32	9	7	2086.5484	2089.3934	-2.8450	15.7845
7	33	1	1	2222.2101	2222.4679	-0.2578	1.4310
7	33	9	7	2086.6158	2089.4151	-2.7993	14.6973
7	34	9	6	2086.6830	2089.4124	-2.7294	13.6178
7	35	9	6	2086.7514	2089.3855	-2.6341	12.5472
8	8	1	1	2219.3274	2219.3224	0.0050	0.0140
8	8	7	4	2139.7731	2137.7548	2.0183	7.6565
8	8	9	9	2084.7063	2084.5626	0.1437	-14.2001
8	9	1	1	2219.3225	2219.3117	0.0108	0.0259
8	9	2	2	2266.0062	2266.0365	-0.0303	0.0150
8	9	7	4	2138.7504	2137.0710	1.6794	8.5946
8	9	9	9	2084.7375	2084.6360	0.1015	-14.4415
8	10	1	1	2219.3162	2219.2911	0.0251	0.0303
8	10	2	2	2265.9975	2266.0238	-0.0263	0.0317
8	10	7	4	2137.6963	2136.4781	1.2182	9.4713
8	10	9	9	2084.7718	2084.7156	0.0562	-14.7118
8	11	1	1	2219.3093	2219.2444	0.0649	0.0110
8	11	2	2	2265.9859	2266.0098	-0.0239	0.0501
8	11	7	4	2136.7055	2135.9412	0.7643	10.3218
8	11	9	9	2084.8071	2084.7995	0.0076	-15.0128

TABLE A-1 (continued)

K	J	S	S'	Obs.	Calc.	O-C	Total Shift
8	12	1	1	2219.3266	2219.0999	0.2267	-0.1034
8	12	2	2	2265.9727	2265.9947	-0.0220	0.0703
8	12	5	1	2219.2836	2219.0999	0.1837	-4.4040
8	12	7	4	2135.6717	2135.4450	0.2267	11.1619
8	12	9	9	2084.8457	2084.8848	-0.0391	-15.3474
8	13	1	1	2219.3106	2219.7238	-0.4132	0.5530
8	13	2	2	2265.9598	2265.9784	-0.0186	0.0922
8	13	9	9	2084.8859	2084.9665	-0.0806	-15.7206
8	14	1	1	2219.3007	2219.5507	-0.2500	0.4150
8	14	2	2	2265.9465	2265.9609	-0.0144	0.1160
8	14	9	9	2084.9233	2085.0351	-0.1118	-16.1418
8	15	1	1	2219.2974	2219.4987	-0.2013	0.4005
8	15	2	2	2265.9316	2265.9424	-0.0108	0.1416
8	15	9	9	2084.9599	2085.0720	-0.1121	-16.6298
8	16	1	1	2219.2926	2219.4779	-0.1853	0.4197
8	16	2	2	2265.9145	2265.9228	-0.0083	0.1691
8	16	9	9	2084.9909	2085.0375	-0.0466	-17.2241
8	17	1	1	2219.2823	2219.4688	-0.1865	0.4532
8	17	2	2	2265.9018	2265.9023	-0.0005	0.1986
8	17	9	9	2084.9999	2084.8582	0.1417	-17.9982
8	18	1	1	2219.2750	2219.4655	-0.1905	0.4949
8	18	2	2	2265.8864	2265.8809	0.0055	0.2302
8	18	9	10	2086.2510	2086.5013	-0.2503	-19.0157
8	18	10	9	2084.9864	2084.4705	0.5159	-4.8845
8	19	1	1	2219.2697	2219.4655	-0.1958	0.5424
8	19	2	2	2265.8654	2265.8589	0.0065	0.2641
8	19	9	9	2085.8551	2086.4310	-0.5759	-17.7201
8	19	10	10	2084.8788	2083.9085	0.9703	-7.2455
8	20	1	1	2219.2633	2219.4676	-0.2043	0.5945
8	20	2	2	2265.8474	2265.8362	0.0112	0.3003
8	20	9	10	2084.4904	2083.2499	1.2405	-18.3966
8	20	10	9	2085.5652	2086.4543	-0.8891	-7.6601
8	21	1	1	2219.2559	2219.4712	-0.2153	0.6506
8	21	2	2	2265.8302	2265.8133	0.0169	0.3392
8	22	1	1	2219.2503	2219.4758	-0.2255	0.7103
8	22	2	2	2265.8073	2265.7904	0.0169	0.3810
8	23	1	1	2219.2416	2219.4814	-0.2398	0.7734
8	23	2	2	2265.7879	2265.7681	0.0198	0.4263
8	24	1	1	2219.2359	2219.4876	-0.2517	0.8397
8	24	2	2	2265.7660	2265.7469	0.0191	0.4758
8	25	1	1	2219.2258	2219.4943	-0.2685	0.9090
8	25	2	2	2265.7438	2265.7281	0.0157	0.5305
8	26	1	1	2219.2197	2219.5015	-0.2818	0.9812
8	26	2	2	2265.7207	2265.7131	0.0076	0.5921
8	27	1	1	2219.2132	2219.5091	-0.2959	1.0563
8	27	2	2	2265.7040	2265.7049	-0.0009	0.6634
8	28	1	1	2219.2079	2219.5169	-0.3090	1.1342
8	28	2	2	2265.6929	2265.7084	-0.0155	0.7492
8	29	1	1	2219.1998	2219.5248	-0.3250	1.2146
8	29	2	2	2265.7058	2265.7327	-0.0269	0.8589
8	30	1	1	2219.1914	2219.5327	-0.3413	1.2976
8	31	1	1	2219.1894	2219.5405	-0.3511	1.3830
9	9	1	1	2216.2159	2216.2332	-0.0173	0.0166
9	9	7	7	2142.0700	2141.9545	0.1155	7.0981
9	9	9	9	2084.3765	2084.3447	0.0318	-14.2341
9	10	1	1	2216.2092	2216.2256	-0.0164	0.0337
9	10	2	2	2268.7067	2268.7361	-0.0294	0.0163
9	10	7	7	2143.0882	2142.4142	0.6740	7.7324
9	10	9	9	2084.4130	2084.4112	0.0018	-14.5176
9	11	1	1	2216.2074	2216.2153	-0.0079	0.0506
9	11	2	2	2268.6959	2268.7214	-0.0255	0.0343
9	11	7	7	2143.9964	2142.8823	1.1141	8.3925
9	11	9	9	2084.4529	2084.4807	-0.0278	-14.8330
9	12	1	1	2216.2029	2216.2010	0.0019	0.0661
9	12	2	2	2268.6844	2268.7055	-0.0211	0.0541
9	12	7	7	2144.8414	2143.3574	1.4840	9.0770
9	12	9	9	2084.4949	2084.5516	-0.0567	-15.1819
9	13	1	1	2216.1961	2216.1812	0.0149	0.0784
9	13	2	2	2268.6718	2268.6884	-0.0166	0.0755
9	13	7	7	2145.6449	2143.8382	1.8067	9.7847
9	13	9	9	2084.5389	2084.6219	-0.0830	-15.5665
9	14	1	1	2216.1897	2216.1528	0.0369	0.0846
9	14	2	2	2268.6582	2268.6700	-0.0118	0.0988
9	14	7	7	2146.4247	2144.3236	2.1011	10.5145
9	14	9	9	2084.5847	2084.6886	-0.1039	-15.9897
9	15	1	1	2216.1801	2216.1108	0.0693	0.0797
9	15	2	2	2268.6451	2268.6505	-0.0054	0.1238
9	15	7	7	2147.1801	2144.8128	2.3673	11.2655
9	15	9	9	2084.6315	2084.7473	-0.1158	-16.4558
9	16	1	1	2216.1727	2216.0460	0.1267	0.0545
9	16	2	2	2268.6290	2268.6299	-0.0009	0.1507
9	16	7	7	2147.9164	2145.3049	2.6115	12.0369
9	16	9	9	2084.6782	2084.7915	-0.1133	-16.9715
9	17	1	1	2216.1591	2215.9402	0.2189	-0.0092
9	17	2	2	2268.6133	2268.6083	0.0050	0.1797
9	17	7	7	2148.6423	2145.7993	2.8430	12.8279
9	17	9	9	2084.7246	2084.8100	-0.0854	-17.5478
9	18	1	1	2216.1280	2215.7567	0.3713	-0.1481
9	18	2	2	2268.5963	2268.5859	0.0104	0.2106
9	18	7	7	2149.3595	2146.2952	3.0643	13.6379
9	18	9	9	2084.7679	2084.7834	-0.0155	-18.2042
9	19	1	1	2215.9877	2215.4294	0.5583	-0.4284
9	19	2	2	2268.5805	2268.5627	0.0178	0.2439
9	19	7	7	2150.0646	2146.7919	3.2727	14.4663
9	19	9	9	2084.8069	2084.6779	0.1290	-18.9745
9	20	1	1	2216.2515	2217.3872	-1.1357	1.5789
9	20	2	2	2268.5643	2268.5390	0.0253	0.2796
9	20	5	5	2215.7638	2214.8910	0.8728	-15.0407
9	20	7	7	2150.7622	2147.2889	3.4733	15.3123
9	20	9	9	2084.8357	2084.4448	0.3909	-19.9074

TABLE A-1 (continued)

K	J	S	S'	Obs.	Calc.	O-C	Total Shift
9	21	1	1	2216.2087	2217.0874	-0.8787	1.3310
9	21	2	2	2268.5509	2268.5152	0.0357	0.3182
9	21	7	4	2151.4534	2147.7854	3.6680	-1.7666
9	21	9	9	2084.8391	2084.0504	0.7887	-21.0366
9	22	1	1	2216.1917	2216.9213	-0.7296	1.2193
9	22	2	2	2268.5532	2268.4917	0.0615	0.3600
9	22	7	4	2152.1370	2148.2810	3.8560	-1.5001
9	22	9	9	2084.7860	2083.5125	1.2735	-22.3443
9	23	1	1	2216.1788	2216.8259	-0.6471	1.1808
9	23	2	2	2268.5649	2268.4694	0.0955	0.4061
9	23	7	4	2152.8058	2148.7749	4.0309	-1.1900
9	23	9	9	2084.6484	2086.0797	-1.4313	-20.5819
9	24	1	1	2216.1691	2216.7681	-0.5990	1.1824
9	24	2	2	2268.3896	2268.4499	-0.0603	0.4578
9	24	7	4	2153.4989	2149.2666	4.2323	-0.8350
9	24	9	9	2084.4269	2086.0293	-1.6024	-21.4720
9	25	1	1	2216.1626	2216.7315	-0.5689	1.2077
9	25	2	2	2268.3993	2268.4357	-0.0364	0.5180
9	25	7	4	2154.2017	2149.7553	4.4464	-0.4340
9	25	9	9	2084.0197	2085.9920	-1.9723	-22.3840
9	26	1	1	2216.1556	2216.7080	-0.5524	1.2485
9	26	2	2	2268.3875	2268.4327	-0.0452	0.5921
9	27	1	1	2216.1486	2216.6928	-0.5442	1.3001
9	27	2	2	2268.3697	2268.4543	-0.0846	0.6939
9	28	1	1	2216.1434	2216.6831	-0.5397	1.3597
9	28	2	2	2268.3448	2268.5371	-0.1923	0.8599
9	29	1	1	2216.1399	2216.6774	-0.5375	1.4258
9	29	2	2	2268.3217	2268.7750	-0.4533	1.1839
9	30	1	1	2216.1356	2216.6744	-0.5388	1.4970
9	31	1	1	2216.1297	2216.6733	-0.5436	1.5726
9	32	1	1	2216.1282	2216.6735	-0.5453	1.6520
9	33	1	1	2216.1241	2216.6745	-0.5504	1.7346
10	10	1	1	2213.0816	2213.1300	-0.0484	0.0193
10	10	7	7	2141.1379	2141.5077	-0.3698	6.8949
10	10	9	9	2084.0060	2084.0943	-0.0883	-14.2772
10	11	1	1	2213.0750	2213.1236	-0.0486	0.0398
10	11	2	2	2271.3824	2271.4042	-0.0218	0.0176
10	11	7	7	2141.9297	2141.8223	0.1074	7.4014
10	11	9	9	2084.0468	2084.1455	-0.0987	-14.6108
10	12	1	1	2213.0746	2213.1155	-0.0409	0.0611
10	12	2	2	2271.3706	2271.3875	-0.0169	0.0369
10	12	7	7	2142.7017	2142.1547	0.5470	7.9433
10	12	9	9	2084.0899	2084.1965	-0.1066	-14.9797
10	13	1	1	2213.0711	2213.1055	-0.0344	0.0829
10	13	2	2	2271.3580	2271.3695	-0.0115	0.0579
10	13	7	7	2143.4719	2142.5033	0.9686	8.5188
10	13	9	9	2084.1377	2084.2455	-0.1078	-15.3856
10	14	1	1	2213.0661	2213.0929	-0.0268	0.1045
10	14	2	2	2271.3469	2271.3503	-0.0034	0.0806
10	14	7	7	2144.2441	2142.8666	1.3775	9.1265
10	14	9	9	2084.1851	2084.2904	-0.1053	-15.8305
10	15	1	1	2213.0617	2213.0770	-0.0153	0.1253
10	15	2	2	2271.3337	2271.3299	0.0038	0.1052
10	15	7	7	2145.0340	2143.2432	1.7908	9.7648
10	15	9	9	2084.2388	2084.3287	-0.0899	-16.3171
10	16	1	1	2213.0547	2213.0569	-0.0022	0.1444
10	16	2	2	2271.3197	2271.3084	0.0113	0.1317
10	16	7	7	2145.8224	2143.6316	2.1908	10.4325
10	16	9	9	2084.2899	2084.3570	-0.0671	-16.8487
10	17	1	1	2213.0504	2213.0311	0.0193	0.1602
10	17	2	2	2271.2985	2271.2860	0.0125	0.1603
10	17	9	9	2084.3441	2084.3708	-0.0267	-17.4297
10	18	1	1	2213.0477	2212.9979	0.0498	0.1710
10	18	2	2	2271.2872	2271.2630	0.0242	0.1913
10	18	9	9	2084.3970	2084.3641	0.0329	-18.0662
10	19	1	1	2213.0361	2212.9544	0.0817	0.1740
10	19	2	2	2271.2726	2271.2401	0.0325	0.2253
10	19	9	9	2084.4534	2084.3280	0.1254	-18.7671
10	20	1	1	2213.0316	2212.8965	0.1351	0.1651
10	20	2	2	2271.2591	2271.2190	0.0401	0.2642
10	20	9	9	2084.5066	2084.2496	0.2570	-19.5453
10	21	1	1	2213.0215	2212.8180	0.2035	0.1379
10	21	2	2	2271.2500	2271.2055	0.0445	0.3137
10	21	9	9	2084.5572	2084.1102	0.4470	-20.4194
10	22	1	1	2213.0085	2212.7089	0.2996	0.0827
10	22	2	2	2271.2271	2271.2340	-0.0069	0.4081
10	22	9	9	2084.6072	2083.8857	0.7215	-21.4138
10	23	1	1	2212.9918	2212.5541	0.4377	-0.0159
10	23	2	2	2271.2193	2271.0145	0.2048	0.2575
10	23	9	9	2084.5851	2083.5529	1.0322	-22.5513
10	24	1	1	2212.9686	2212.3306	0.6380	-0.1806
10	24	2	2	2271.1881	2271.0302	0.1579	0.3452
10	24	9	10	2084.5571	2085.9649	-1.4078	-23.8404
10	25	1	1	2212.9127	2212.0090	0.9037	-0.4411
10	25	2	2	2271.1676	2271.0100	0.1576	0.3999
10	26	1	1	2213.3675	2211.5622	1.8053	-0.8243
10	26	2	2	2271.1770	2270.9807	0.1963	0.4486
10	26	5	1	2212.6041	2211.5622	1.0419	10.9391
10	27	1	1	2213.2589	2214.8493	-1.5904	2.5289
10	28	1	1	2213.1460	2214.5591	-1.4131	2.3072
10	29	1	1	2213.1054	2214.3593	-1.2539	2.1783
10	30	1	1	2213.0855	2214.2206	-1.1351	2.1131
10	31	1	1	2213.0693	2214.1224	-1.0531	2.0907
10	32	1	1	2213.0641	2214.0510	-0.9869	2.0976
10	33	1	1	2213.0459	2213.9979	-0.9520	2.1252
10	34	1	1	2213.0507	2213.9574	-0.9067	2.1679
11	11	1	1	2209.9278	2210.0137	-0.0859	0.0221
11	11	7	7	2140.4333	2141.1188	-0.6855	6.7742
11	11	9	9	2083.5935	2083.8069	-0.2134	-14.3334
11	12	1	1	2209.9241	2210.0083	-0.0842	0.0457

TABLE A-1 (continued)

K	J	S	S'	Obs.	Calc.	O-C	Total Shift
11	12	7	7	2141.0997	2141.3748	-0.2751	7.2396
11	12	9	9	2083.6369	2083.8307	-0.1938	-14.7295
11	13	1	1	2209.9232	2210.0018	-0.0786	0.0707
11	13	7	7	2141.7692	2141.6475	0.1217	7.7392
11	13	9	9	2083.6859	2083.8501	-0.1642	-15.1650
11	14	1	1	2209.9214	2209.9940	-0.0726	0.0968
11	14	7	7	2142.4401	2141.9360	0.5041	8.2721
11	14	9	9	2083.7359	2083.8634	-0.1275	-15.6415
11	15	1	1	2209.9166	2209.9847	-0.0681	0.1237
11	15	7	7	2143.1123	2142.2395	0.8728	8.8374
11	15	9	9	2083.7913	2083.8684	-0.0771	-16.1614
11	16	1	1	2209.9142	2209.9735	-0.0593	0.1512
11	16	7	7	2143.7639	2142.5571	1.2068	9.4342
11	16	9	9	2083.8472	2083.8625	-0.0153	-16.7272
11	17	1	1	2209.9107	2209.9601	-0.0494	0.1790
11	17	7	7	2144.4205	2142.8877	1.5328	10.0615
11	17	9	9	2083.9044	2083.8426	0.0618	-17.3418
11	18	1	1	2209.9046	2209.9440	-0.0394	0.2064
11	18	9	9	2083.9635	2083.8051	0.1584	-18.0092
11	19	1	1	2209.9027	2209.9245	-0.0218	0.2329
11	19	9	9	2084.0242	2083.7453	0.2789	-18.7338
11	20	1	1	2209.8997	2209.9010	-0.0013	0.2577
11	20	9	9	2084.0843	2083.6575	0.4268	-19.5214
11	21	1	1	2209.8939	2209.8723	0.0216	0.2799
11	21	9	9	2084.1437	2083.5344	0.6093	-20.3793
11	22	1	1	2209.8900	2209.8372	0.0528	0.2980
11	22	9	9	2084.2065	2083.3668	0.8397	-21.3166
11	23	1	1	2209.8851	2209.7939	0.0912	0.3104
11	23	9	9	2084.2632	2083.1442	1.1190	-22.3440
11	24	1	1	2209.8811	2209.7401	0.1410	0.3145
11	24	9	9	2084.3138	2082.8548	1.4590	-23.4732
11	25	1	1	2209.8728	2209.6723	0.2005	0.3072
11	25	9	10	2084.3585	2086.2152	-1.8567	-24.7141
11	26	1	1	2209.8641	2209.5860	0.2781	0.2839
11	26	9	10	2084.3829	2085.7910	-1.4081	16.2648
11	27	1	1	2209.8594	2209.4748	0.3846	0.2379
11	27	9	10	2084.3917	2085.4113	-1.0196	15.6469
11	28	1	1	2209.8483	2209.3295	0.5188	0.1604
11	28	9	10	2084.3771	2085.0684	-0.6913	15.0175
11	29	1	1	2209.8304	2209.1380	0.6924	0.0391
11	29	9	10	2084.2925	2084.7513	-0.4588	14.3771
11	30	1	1	2209.8080	2208.8848	0.9232	-0.1416
11	31	1	1	2209.7744	2208.5526	1.2218	-0.3988
11	32	1	1	2209.7290	2208.1275	1.6015	-0.7465
11	33	1	3	2209.6542	2207.6048	2.0494	3.6032
12	12	1	1	2206.7527	2206.8853	-0.1326	0.0250
12	12	7	7	2139.6909	2140.7333	-1.0424	6.6815
12	12	9	9	2083.1334	2083.4766	-0.3432	-14.4089
12	13	1	1	2206.7510	2206.8810	-0.1300	0.0518
12	13	7	7	2140.1571	2140.9830	-0.8259	7.1582
12	13	9	9	2083.1822	2083.4549	-0.2727	-14.8855
12	14	1	1	2206.7524	2206.8759	-0.1235	0.0802
12	14	7	7	2140.5682	2141.2482	-0.6800	7.6677
12	14	9	9	2083.2377	2083.4241	-0.1864	-15.4062
12	15	1	1	2206.7510	2206.8700	-0.1190	0.1101
12	15	7	7	2141.0212	2141.5280	-0.5068	8.2093
12	15	9	9	2083.2940	2083.3822	-0.0882	-15.9729
12	16	1	1	2206.7489	2206.8631	-0.1142	0.1415
12	16	9	9	2083.3514	2083.3272	0.0242	-16.5877
12	17	1	1	2206.7440	2206.8550	-0.1110	0.1741
12	17	9	9	2083.4125	2083.2566	0.1559	-17.2532
12	18	1	1	2206.7448	2206.8457	-0.1009	0.2078
12	18	9	9	2083.4746	2083.1675	0.3071	-17.9721
12	19	1	1	2206.7410	2206.8348	-0.0938	0.2423
12	19	9	9	2083.5384	2083.0567	0.4817	-18.7477
12	20	1	1	2206.7399	2206.8221	-0.0822	0.2775
12	20	9	9	2083.6051	2082.9206	0.6845	-19.5836
12	21	1	1	2206.7366	2206.8073	-0.0707	0.3129
12	21	9	9	2083.6665	2082.7550	0.9115	-20.4840
12	22	1	1	2206.7381	2206.7899	-0.0518	0.3482
12	22	9	9	2083.7350	2082.5551	1.1799	-21.4537
12	23	1	1	2206.7348	2206.7697	-0.0349	0.3829
12	23	9	9	2083.7929	2082.3158	1.4771	-22.4978
12	24	1	1	2206.7319	2206.7459	-0.0140	0.4165
12	24	9	9	2083.8519	2082.0313	1.8206	-23.6220
12	25	1	1	2206.7284	2206.7178	0.0106	0.4483
12	25	9	4	2083.9060	2081.6964	2.2096	12.2507
12	26	1	1	2206.7319	2206.6846	0.0473	0.4772
12	26	9	10	2083.9466	2086.5602	-2.6136	11.4911
12	27	1	1	2206.7235	2206.6451	0.0784	0.5023
12	27	9	10	2083.9693	2086.0643	-2.0950	13.6433
12	28	1	1	2206.7246	2206.5977	0.1269	0.5219
12	28	9	10	2083.9475	2085.5908	-1.6433	13.0847
12	29	1	1	2206.7198	2206.5406	0.1792	0.5341
12	33	1	1	2206.7077	2206.1467	0.5610	0.4415
13	13	1	1	2203.5630	2203.7458	-0.1828	0.0280
13	13	7	7	2138.9061	2140.3342	-1.4281	6.6001
13	13	9	9	2082.6335	2083.0934	-0.4599	-14.5137
13	14	1	1	2203.5615	2203.7427	-0.1812	0.0580
13	14	7	7	2139.2130	2140.6325	-1.4195	7.1427
13	14	9	9	2082.6885	2082.9989	-0.3104	-15.0980
13	15	1	1	2203.5591	2203.7391	-0.1800	0.0899
13	15	7	7	2139.5207	2140.9445	-1.4238	7.7165
13	15	9	9	2082.7461	2082.8903	-0.1442	-15.7315
13	16	1	1	2203.5596	2203.7350	-0.1754	0.1237
13	16	9	9	2082.8036	2082.7657	0.0379	-16.4159
13	17	1	1	2203.5594	2203.7303	-0.1709	0.1592
13	17	9	9	2082.8641	2082.6233	0.2408	-17.1531
13	18	1	1	2203.5594	2203.7250	-0.1656	0.1964
13	18	9	9	2082.9246	2082.4611	0.4635	-17.9452

TABLE A-1 (continued)

K	J	S	S'	Obs.	Calc.	O-C	Total Shift
13	19	1	1	2203.5615	2203.7189	-0.1574	0.2352
13	19	9	9	2082.9828	2082.2767	0.7061	-18.7944
13	20	1	1	2203.5552	2203.7120	-0.1568	0.2756
13	20	9	9	2083.0358	2082.0677	0.9681	-19.7032
13	21	1	1	2203.5559	2203.7041	-0.1482	0.3173
13	21	9	9	2083.0798	2081.8315	1.2483	-20.6742
13	22	1	1	2203.5570	2203.6951	-0.1381	0.3604
13	22	9	9	2083.0945	2081.5653	1.5292	-21.7102
13	23	1	1	2203.5601	2203.6849	-0.1248	0.4046
13	23	9	9	2083.0701	2081.2661	1.8040	-22.8141
13	24	1	1	2203.5563	2203.6733	-0.1170	0.4497
13	25	1	1	2203.5558	2203.6601	-0.1043	0.4956
13	26	1	1	2203.5572	2203.6450	-0.0878	0.5419
13	27	1	1	2203.5590	2203.6277	-0.0687	0.5885
13	29	1	1	2203.5591	2203.5852	-0.0261	0.6806
13	30	1	1	2203.5670	2203.5588	0.0082	0.7252
13	31	1	1	2203.5622	2203.5282	0.0340	0.7679
13	32	1	1	2203.5620	2203.4925	0.0695	0.8078
14	14	1	1	2200.3507	2200.5961	-0.2454	0.0312
14	14	7	7	2138.1838	2139.9148	-1.7310	6.5231
14	14	9	9	2082.0866	2082.6392	-0.5526	-14.6658
14	15	1	1	2200.3514	2200.5944	-0.2430	0.0646
14	15	7	7	2138.4207	2140.3598	-1.9391	7.2299
14	15	9	9	2082.1451	2082.4289	-0.2838	-15.4009
14	16	1	1	2200.3491	2200.5925	-0.2434	0.1000
14	16	9	9	2082.1942	2082.2011	-0.0069	-16.1886
14	17	1	1	2200.3567	2200.5903	-0.2336	0.1376
14	17	7	7	2138.9360	2141.2536	-2.3176	8.6996
14	17	9	9	2082.1954	2081.9547	0.2407	-17.0298
14	18	1	1	2200.3521	2200.5879	-0.2358	0.1772
14	18	9	9	2082.4531	2081.6887	0.7644	-17.9256
14	19	1	1	2200.3530	2200.5852	-0.2322	0.2189
14	19	9	9	2082.4369	2081.4017	1.0352	-18.8774
14	20	1	1	2200.3529	2200.5822	-0.2293	0.2627
14	20	9	9	2082.4371	2081.0924	1.3447	-19.8865
14	21	1	1	2200.3554	2200.5789	-0.2235	0.3084
14	21	9	9	2082.5054	2080.7594	1.7460	-20.9543
14	22	1	1	2200.3582	2200.5752	-0.2170	0.3561
14	22	9	9	2082.5687	2080.4010	2.1677	-22.0824
14	23	1	1	2200.3597	2200.5711	-0.2114	0.4058
14	23	9	9	2082.6357	2080.0158	2.6199	-23.2724
14	24	1	1	2200.3620	2200.5666	-0.2046	0.4574
14	24	9	9	2082.6971	2079.6022	3.0949	-24.5258
14	25	1	1	2200.3627	2200.5617	-0.1990	0.5108
14	25	9	9	2082.7683	2079.1585	3.6098	-25.8442
14	26	1	1	2200.3560	2200.5562	-0.2002	0.5661
14	26	9	4	2082.8283	2078.6835	4.1448	7.4039
14	27	9	4	2082.9012	2078.1756	4.7256	7.2511
14	29	1	1	2200.3757	2200.5363	-0.1606	0.7425
14	30	1	1	2200.3809	2200.5282	-0.1473	0.8045
15	15	1	1	2197.1185	2197.4372	-0.3187	0.0345
15	15	9	9	2081.4986	2082.0773	-0.5787	-14.9018
15	16	1	1	2197.1180	2197.4371	-0.3191	0.0714
15	16	9	9	2081.5608	2081.6803	-0.1195	-15.8587
15	17	1	1	2197.1223	2197.4371	-0.3148	0.1106
15	17	9	9	2081.6263	2081.2722	0.3541	-16.8616
15	18	1	1	2197.1261	2197.4370	-0.3109	0.1521
15	18	9	9	2081.6941	2080.8523	0.8418	-17.9113
15	19	1	1	2197.1287	2197.4370	-0.3083	0.1960
15	19	9	9	2081.7620	2080.4197	1.3423	-19.0087
15	20	1	1	2197.1281	2197.4371	-0.3090	0.2422
15	20	9	9	2081.8331	2079.9736	1.8595	-20.1547
15	21	1	1	2197.1297	2197.4372	-0.3075	0.2908
15	21	9	9	2081.9034	2079.5126	2.3908	-21.3504
15	22	1	1	2197.1343	2197.4375	-0.3032	0.3419
15	22	9	9	2081.9748	2079.0358	2.9390	-22.5970
15	23	1	1	2197.1359	2197.4378	-0.3019	0.3954
15	23	9	9	2082.0527	2078.5419	3.5108	-23.8956
15	24	1	1	2197.1398	2197.4384	-0.2986	0.4513
15	24	9	9	2082.1342	2078.0297	4.1045	-25.2476
15	25	1	1	2197.1459	2197.4392	-0.2933	0.5098
15	25	9	9	2082.1983	2077.4979	4.7004	-26.6542
15	26	1	1	2197.1473	2197.4402	-0.2929	0.5709
15	26	9	9	2082.2793	2076.9453	5.3340	-28.1165
15	27	1	1	2197.1531	2197.4416	-0.2885	0.6346
15	27	9	4	2082.3355	2076.3708	5.9647	4.4996
15	28	1	1	2197.1643	2197.4433	-0.2790	0.7009
15	28	9	10	2082.3782	2087.8524	-5.4742	4.4818
15	29	1	1	2197.1690	2197.4455	-0.2765	0.7701
15	29	9	10	2082.3921	2087.3272	-4.9351	4.4483
15	30	1	1	2197.1767	2197.4482	-0.2715	0.8421
15	31	1	1	2197.1867	2197.4515	-0.2648	0.9170
15	32	1	1	2197.2025	2197.4556	-0.2531	0.9950
15	33	1	1	2197.2284	2197.4606	-0.2322	1.0761
15	34	1	1	2197.2887	2197.4665	-0.1778	1.1605
16	16	1	1	2193.8650	2194.2701	-0.4051	0.0380
16	16	9	9	2080.8624	2081.3229	-0.4605	-15.3067
16	17	1	1	2193.8682	2194.2719	-0.4037	0.0786
16	17	9	9	2080.9175	2080.6240	0.2935	-16.6004
16	18	1	1	2193.8722	2194.2739	-0.4017	0.1217
16	18	9	9	2080.9777	2079.9556	1.0221	-17.8987
16	19	1	1	2193.8757	2194.2762	-0.4005	0.1673
16	19	9	9	2081.0310	2079.3076	1.7234	-19.2115
16	20	1	1	2193.8732	2194.2789	-0.4057	0.2156
16	20	9	9	2081.0870	2078.6731	2.4139	-20.5458
16	21	1	1	2193.8860	2194.2819	-0.3959	0.2665
16	21	9	9	2081.1440	2078.0466	3.0974	-21.9071
16	22	1	1	2193.8880	2194.2854	-0.3974	0.3202
16	22	9	9	2081.1990	2077.4239	3.7751	-23.2996
16	23	1	1	2193.8975	2194.2894	-0.3919	0.3766

TABLE A-1 (continued)

K	J	S	S'	Obs.	Calc.	O-C	Total Shift
16	23	9	9	2081.2524	2076.8015	4.4509	-24.7267
16	24	1	1	2193.8977	2194.2939	-0.3962	0.4360
16	24	9	9	2081.3166	2076.1763	5.1403	-26.1917
16	25	9	9	2081.3700	2075.5458	5.8242	-27.6970
16	26	9	4	2081.4300	2074.9075	6.5225	1.7111
16	27	1	1	2193.9277	2194.3122	-0.3845	0.6322
16	28	1	1	2193.9268	2194.3201	-0.3933	0.7040
16	29	1	1	2193.9432	2194.3293	-0.3861	0.7793
16	30	1	1	2193.9633	2194.3397	-0.3764	0.8582

APPENDIX B

THE DISTRIBUTION OF ν_1 INTENSITY

The complexity of the 5 μm spectrum of $^{13}CD_3F$ can be further demonstrated by examining the intensity borrowing from the ν_1 band. The interactions between ν_1, $2\nu_5(\ell=0)$ and $2\nu_2$ probably give rise to nearly all of the intensity observed in $2\nu_5(\ell=0)$ and $2\nu_2$. The other fundamental in the 5 μm region, ν_4, does not produce such intensity sharing except for local interactions. The ν_1 intensity sharing for the twelve states considered in this work is calculated using the parameters found in Table X-3 (p. 111). The fractional intensities are plotted for K=4 through K=10 for $J \leq 30$. The numbers in these plots refer to the vibrational states using the same notation as in Appendix A.

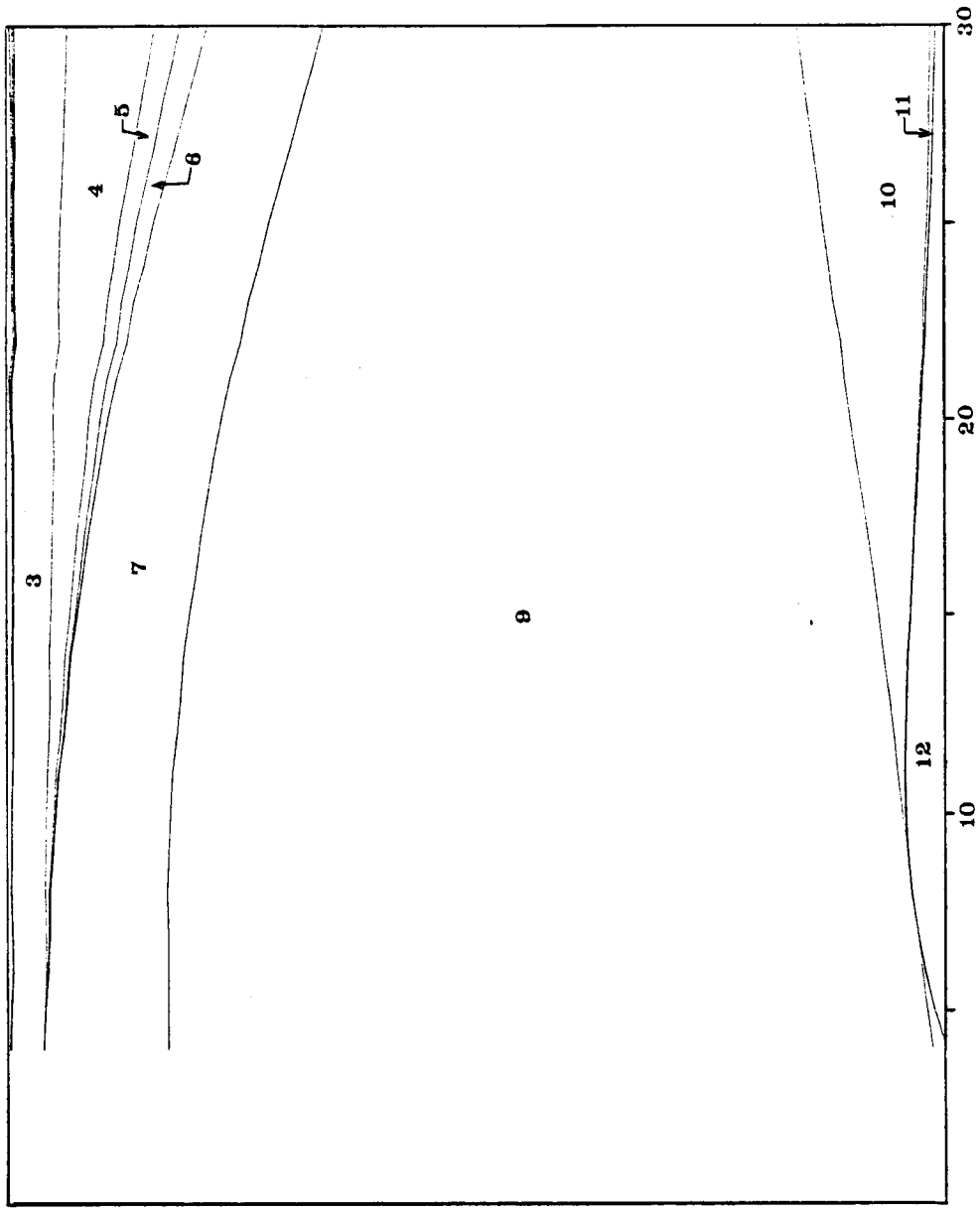


Figure B-1. Distribution of ν_1 intensity for K=4.

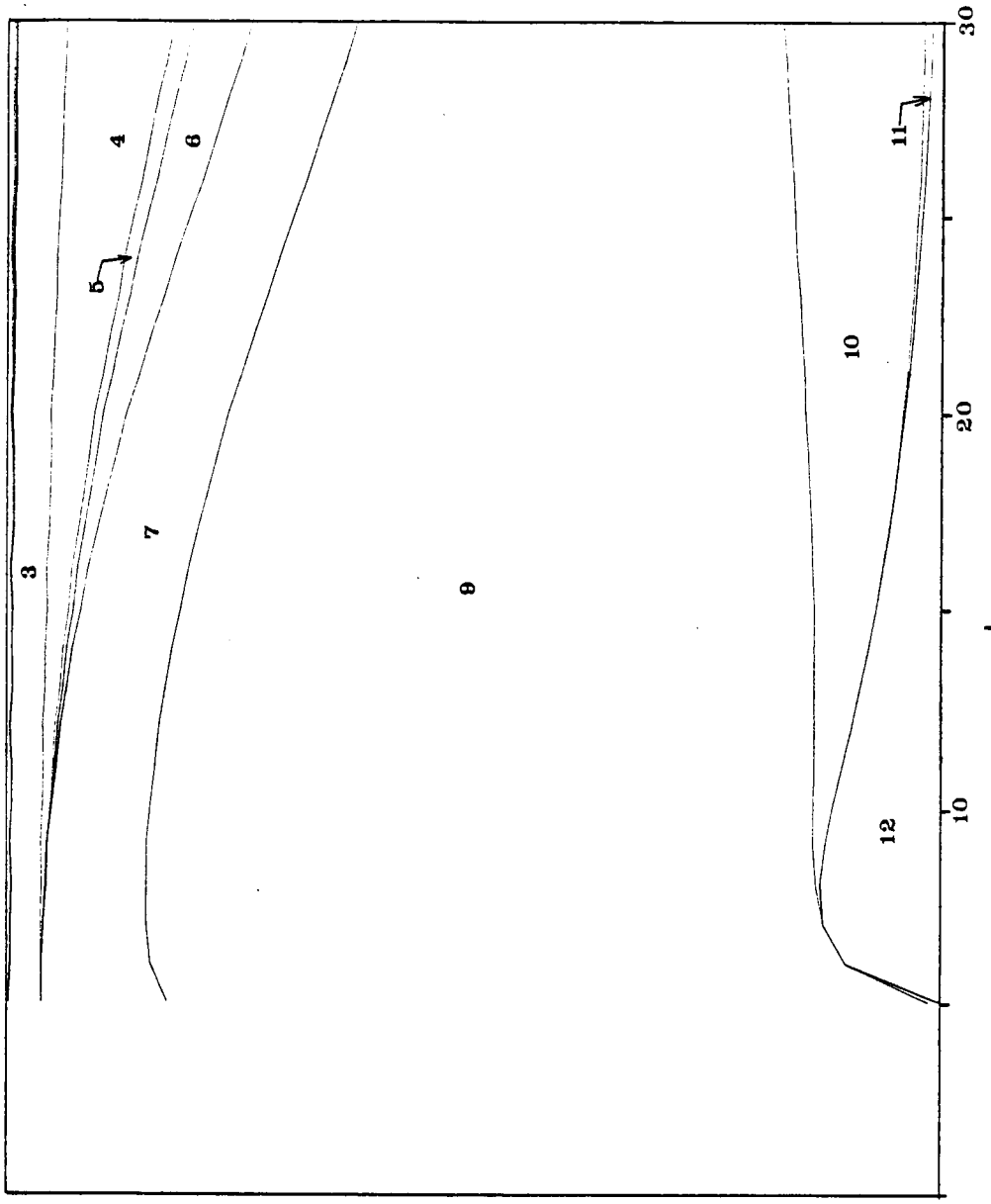


Figure B-2. Distribution of ν_1 intensity for K=5.

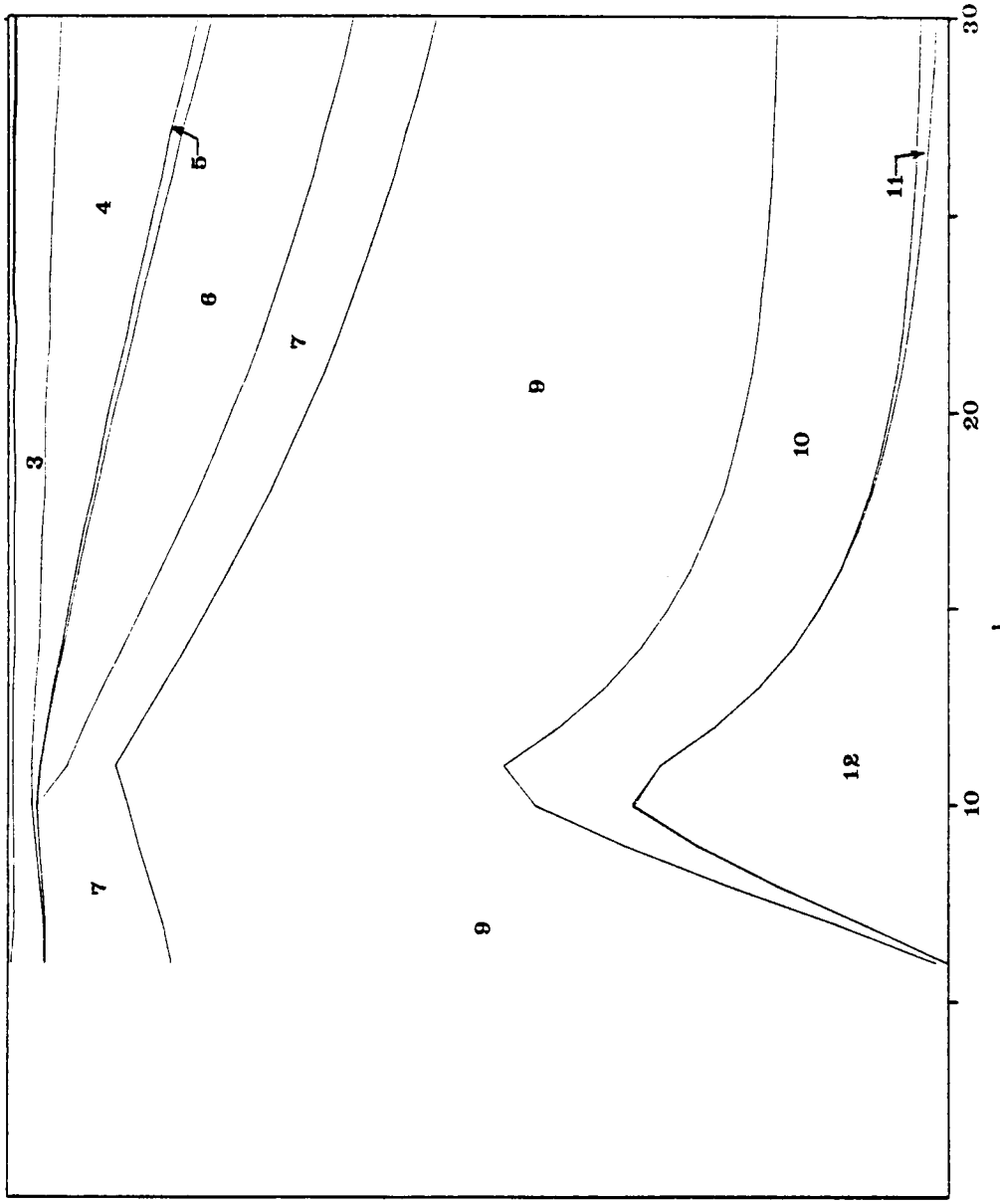


Figure B-3. Distribution of ν_1 intensity for K=6.

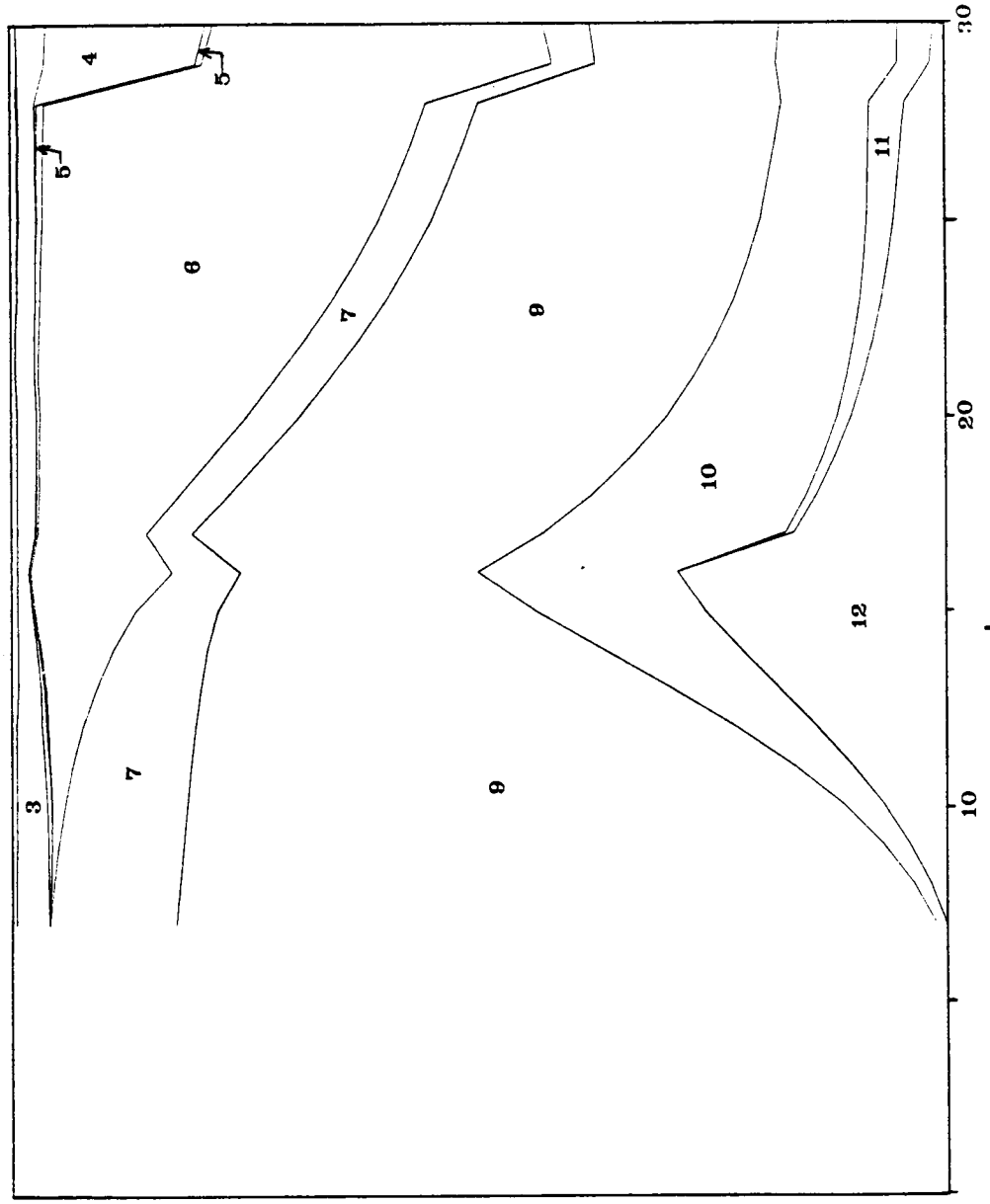


Figure B-4. Distribution of ν_1 intensity for K=7.

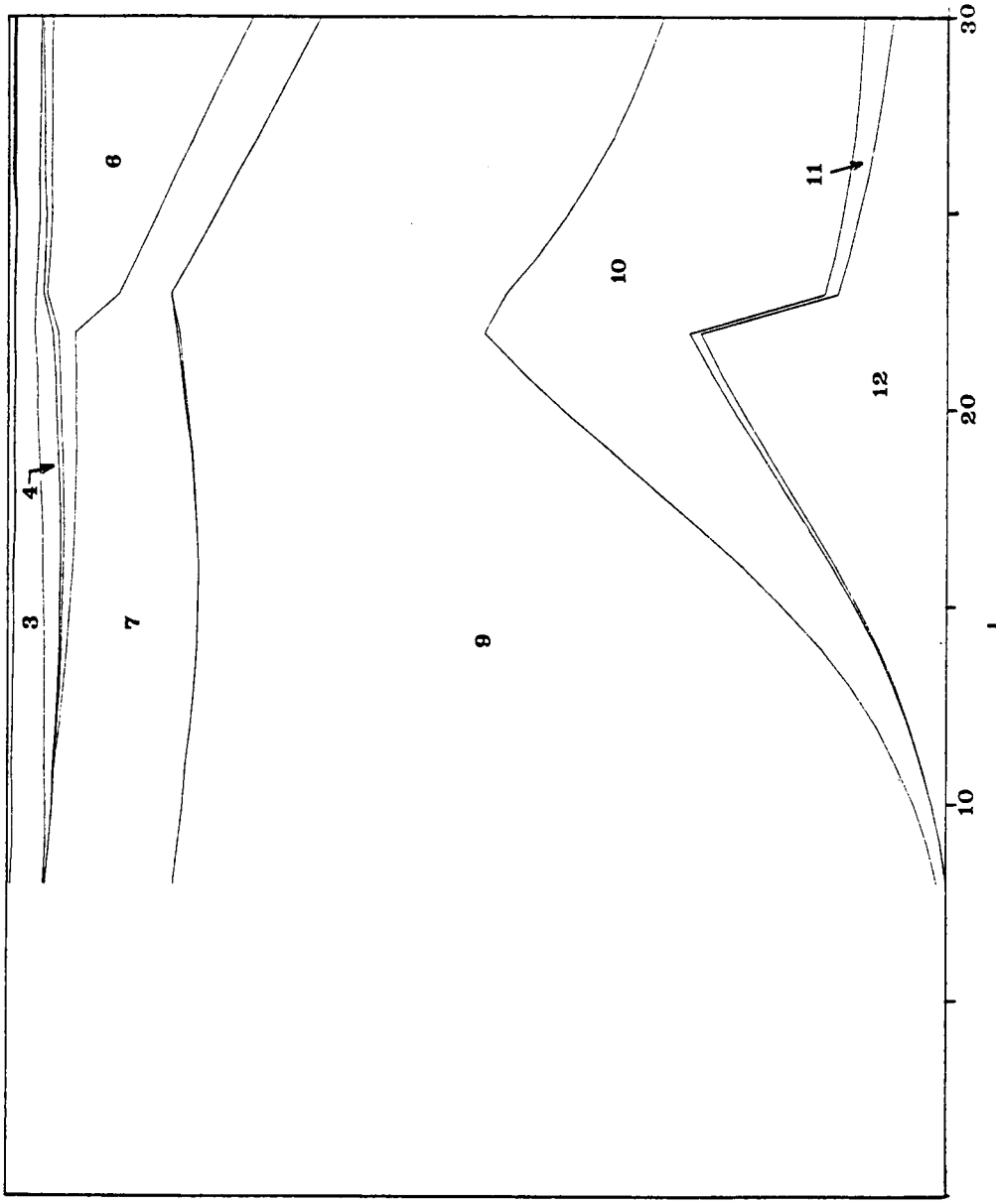


Figure B-5. Distribution of ν_1 intensity for K=8.

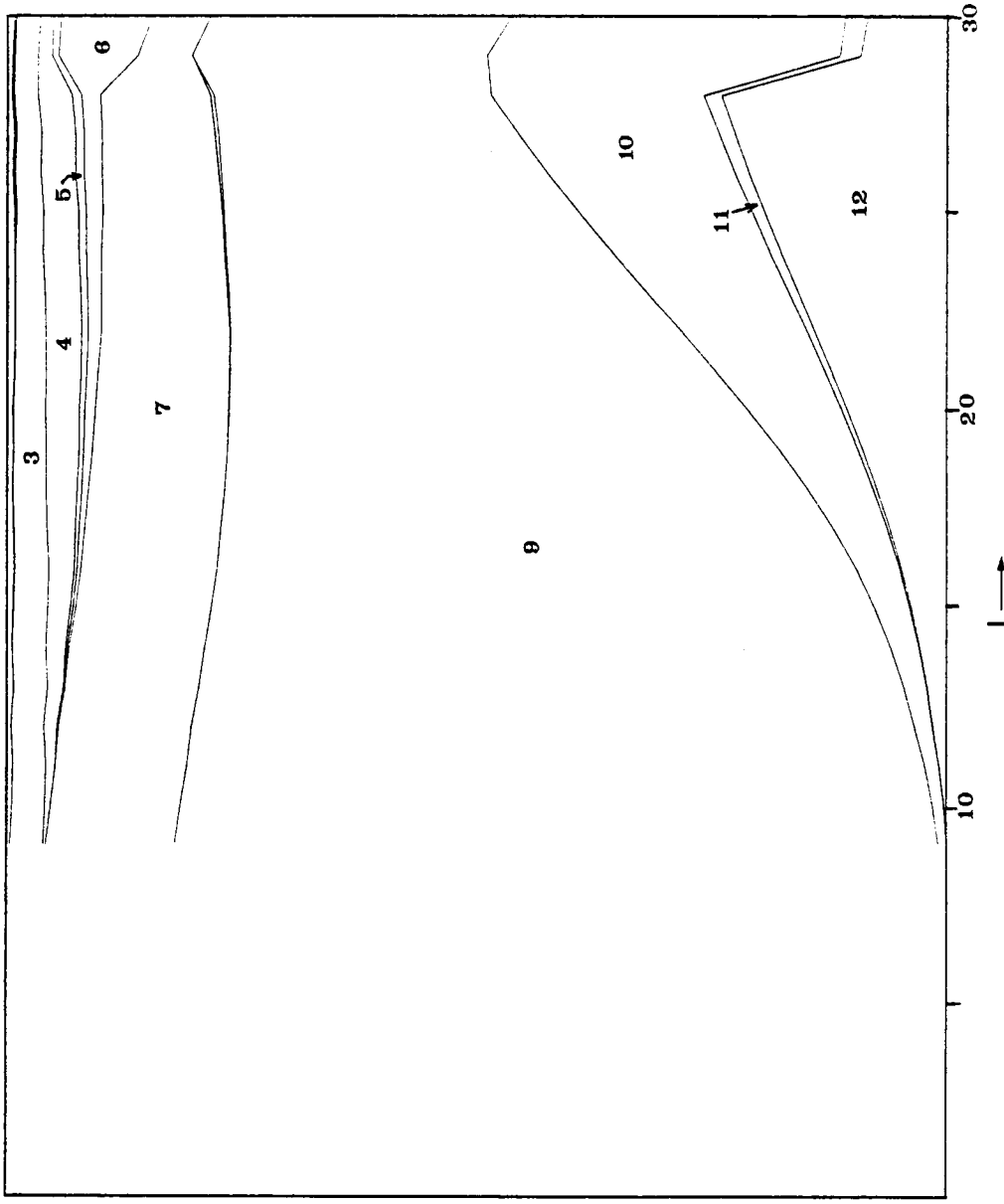


Figure B-6. Distribution of ν_1 intensity for K=9.

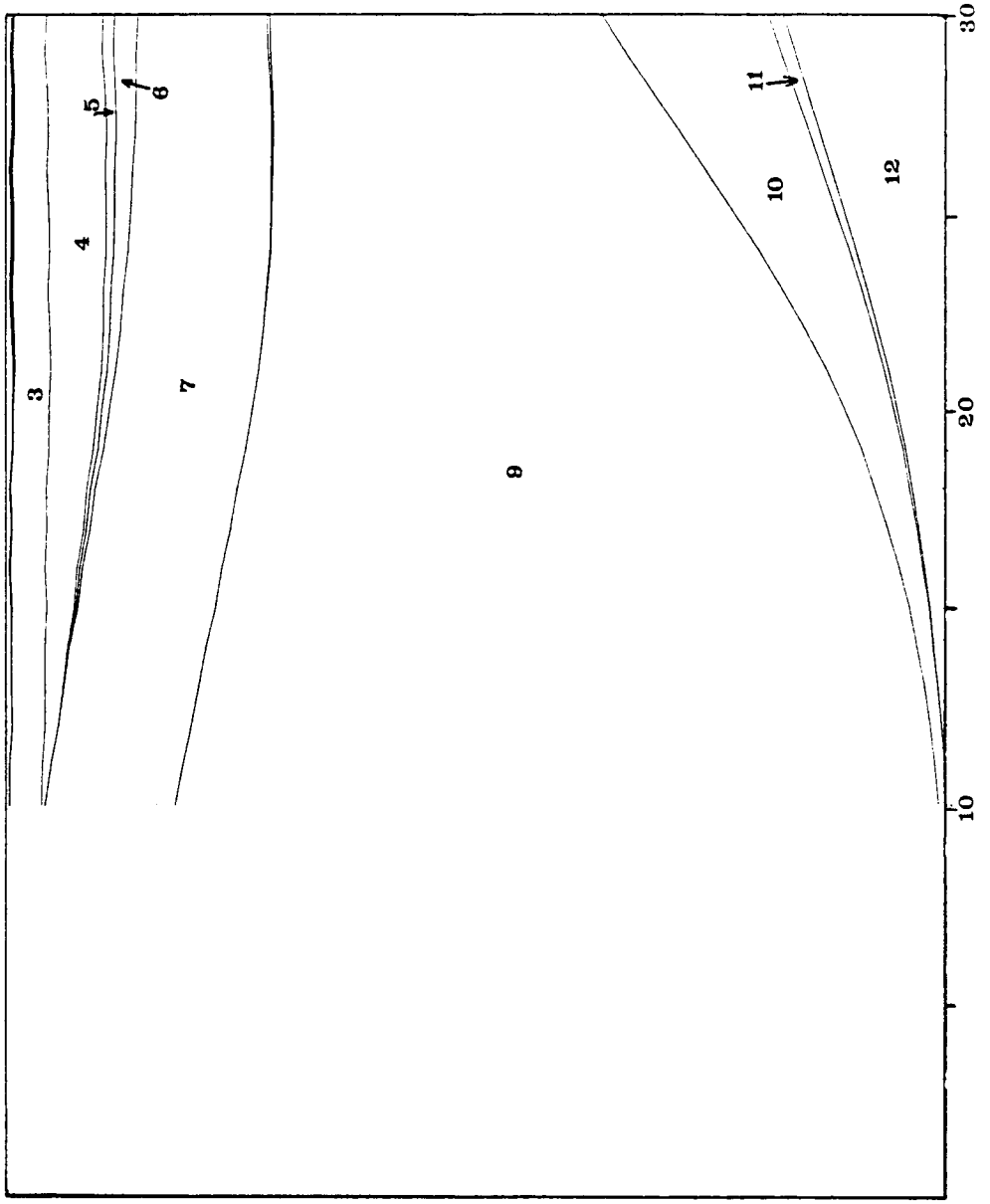


Figure B-7. Distribution of ν_1 intensity for K=10.

VITA

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He began his research at The University of Tennessee Molecular Spectroscopy Group in July 1973. He received the Doctor of Philosophy degree in Physics in June 1983. He is a member of the Coblenz Society and the Southeastern Section of the American Physical Society.