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ABSTRACT

ROTATION-VIBRATION SPECTRA OF AXIALLY SYMMETRIC MOLECULES WITH LOCALIZED PERTURBATIONS

by William Errol Blass

The development of the molecular rotation-vibration Hamiltonian is reviewed especially as it applies to molecules belonging to the point group C_{3v}.

Problems involved in the analysis of the large number of observable transitions in one (or more) rotation-vibration bands are discussed. A generalized expression which simultaneously represents all observed unperturbed transitions of a particular molecule is given, and the application of this expression to the numerical analysis of rotation-vibration spectra is discussed in considerable detail. The generalized expression is applied in the analysis of a perpendicular band, $\nu_3 + \nu_4$, of CH_3F.

In addition, an expression is given which simultaneously represents all observable ground-state combination differences of a particular molecule. This expression was applied to $\nu_3 + \nu_4$ of CH_3F at 4058cm^{-1}, $\nu_1 + \nu_2$ of CHD_3 at 5134cm^{-1}, and $\nu_2 + \nu_3$ of CH_3D at 3500cm^{-1}, to obtain values of B_0, D_0^J and D_0^{JK}. Similar expressions for upper-state combination differences are also discussed.

The work of Dr. G. Amat of the University of Paris on an orderly semi-quantitative approach to perturbations in infrared spectra is reviewed. Additional considerations

which may facilitate the experimentalist's analysis of localized perturbations in the spectra of axially symmetric molecules are presented. Several well-substantiated perturbations were found in $\nu_3 + \nu_4$ of CH_3F. The most completely substantiated perturbations are a Coriolis resonance which lifts the degeneracy of the $K' = \ell = \pm 1$ levels, and an accidental resonance affecting the $K' = \pm 2$, $\ell = \pm 1$ and the $K' = \pm 2$, $\ell = \mp 1$ levels. The analysis of these perturbations was carried as far as currently possible.

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TO MY WIFE

ROSANNE

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INTRODUCTION

During the past ten years the spectroscopy of small molecules in the near infrared region has advanced to such an extent that smaller and smaller effects are being observed in ever-increasing detail. Attendant with this advance in the experimental aspect of the art, the number of anomalies which are observed in spectra has increased rapidly (1-11). In fact, many of the effects deemed unimportant or listed as unobserved by Herzberg (12) in 1951 are now of great interest or have at least by now been observed.

Furthermore, with the improvement of resolution and precision of infrared spectrometers a single rotation-vibration band may exhibit up to a thousand observed transitions. Meaningful values for many molecular parameters may be obtained. Together these two facts make the problem of data analysis in molecular spectroscopy quite formidable, and lead quite naturally to the use of an electronic computer in the analysis of spectra. We have written and regularly used programs which obtain values of the molecular parameters and also give statistical information on the accuracy of the molecular parameters obtained.

In Chapter 1 we review Amat and Nielsen's (13-21) development of the Hamiltonian of the molecular vibrating-rotor while attempting to cast the results into a form immediately usable by the experimentalist in the analysis of axially symmetric molecules.

In Chapter 2 we comment briefly on the symmetry of rotation-vibration wave functions, and set down several selection rules which are useful in the analysis of spectra.

The simultaneous representation of all infrared transitions of a particular molecule is discussed in Chapter 3 and some of the ramifications of such a representation are discussed.

Another data analysis consideration makes up Chapter 4, i.e., the simultaneous analysis of all observed ground state combination differences. This method, to our knowledge, has not specifically been used before, whereas it appears to be the method to use to obtain the statistically most favorable values of B_0, D_0^J and D_0^{JK} from infrared data. It is especially valuable when applied to the many molecules whose microwave pure rotation spectra has not been observed.

Chapter 5 contains a "how to do it" discussion of the data analysis problem.

In Chapter 6 we have gathered together much of the work of Dr. G. Amat on the orderly semi-quantitative analysis of perturbed spectra. We have attempted to embellish the discussion with several additions to extend its usefulness for the experimentalist.

The experimental details regarding the collection and calibration of the spectra of $\nu_3 + \nu_4$ of CH_3F, $\nu_1 + \nu_2$ of CHD_3 and $\nu_2 + \nu_3$ of CH_3D makes up Chapter 7.

The application of the first six chapters to $\nu_3 + \nu_4$ of CH_3F is presented in Chapter 8. This perpendicular band contains several interesting perturbations. Especially in-

teresting is an accidentally strong resonance affecting the +1 and -3 subbands and a Coriolis resonance which lifts the degeneracy of the $K' = \ell = \pm 1$ upper state levels. For both the Coriolis resonance and the accidentally strong resonance affecting the $K' = \pm 2$, $\ell = \pm 1$ levels, we believe that we have one of the most detailed and substantiated examples for both types of resonances since we have in almost every instance found the three individual transitions to each perturbed upper state level.

In Chapter 9 we have applied the results of Chapter 4 on ground state combination differences to a parallel band of CHD_3 and a parallel band of CH_3D to obtain values of B_0, D_0^J and D_0^{JK}. This is especially interesting since the microwave spectra of CH_3D and CHD_3 has not been observed and as a result our values of B_0, D_0^J and D_0^{JK} represent a valuable addition to the spectroscopic data on CH_3D and CHD_3.

In summary, existing theory and procedures for analysis are reviewed and original contributions are made to the analysis by line frequency, by combination differences and in the analysis of perturbed spectra. These methods are applied in the analysis of bands of CH_3F, CH_3D and CHD_3. Even so, the complexity of the situation, especially in the case of CH_3F, has not permitted a <u>complete</u> solution at this time.

CHAPTER 1

ROTATION-VIBRATION ENERGY OF THE AXIALLY SYMMETRIC MOLECULE

In this work, Amat and Nielsen's development of the rotation-vibration Hamiltonian is used. We have attempted to use this formalism especially as it applies to the analysis of rotation-vibration spectra of axially symmetric molecules belonging to the symmetry group C_{3v}.

Summary of the Development of the Rotation-Vibration Hamiltonian

Briefly, one begins with a classical Hamiltonian and converts it into a quantum mechanical Hamiltonian (22,23,24). Then, this Hamiltonian is expanded in a power series in the normal coordinates (13) and the resulting terms are grouped according to the estimated order of magnitude of the contribution to the energy of rotation-vibration. The expanded Hamiltonian is diagonal with respect to J and M but may contain terms off-diagonal with respect to v_s, ℓ_s, m_s, and K. [1]

---

[1] One defines the following symbols:
- J: quantum number associated with the total angular momentum.
- M: quantum number of the projection of the total angular momentum on a space-fixed axis.
- K: quantum number of the projection of the total angular momentum on the body-fixed symmetry axis of the molecule.
- v_s: quantum number of the s-th normal vibration.
- ℓ_s: second quantum number of doubly degenerate normal vibrations (associated with internal angular momentum)
- m_s: third quantum number of threefold degenerate normal vibrations (not needed for axially symmetric molecules).

At this point a contact transformation (25,26,27) is made on the Hamiltonian (14)

$$H = H_0 + H_1 + H_2 + \ldots \qquad (1.1)$$

such that the resulting Hamiltonian

$$h' = H_0 + h'_1 + h'_2 + h'_3 + \ldots \qquad (1.2)$$

is diagonal, through h'_1, with respect to all quantum numbers for axially symmetric molecules. (This is valid only in the absence of accidental resonances. In the event of such resonances a special transformation must be performed on H to preserve the contact transformation (19).) For axially symmetric molecules, since H_0 and h'_1 are diagonal, and as the first non-diagonal terms occur in h'_2, the energy of any particular level is given through third order by the diagonal elements of $H_0 + h'_1 + h'_2 + h'_3$ (21), i.e., in the absence of accidental resonances, off-diagonal terms of h'_2 will not contribute to the energy before fourth order.

Amat and Nielsen performed a second contact transformation (15) which diagonalized h' through second order with respect to the vibrational quantum number v_s. For axially symmetric molecules the twice transformed Hamiltonian

$$h_2^+ = H_0 + h'_1 + h_2^+ + h_3^+ + h_4^+ + \ldots$$

is diagonal with respect to the vibrational quantum numbers v_s through h_2^+. However, h_2^+ has off-diagonal terms with respect to K and ℓ_s. In addition h_3^+, h_4^+,... have terms off-diagonal with respect to v_s, ℓ_s and K.

For symmetric tops, i.e., axially symmetric molecules,

the twice transformed Hamiltonian, h^+, yields energies good through third order since the terms in h_2^+ which are off diagonal in K and ℓ_s do not in general contribute before the fourth order. Since h^+ is diagonal with respect to v_s through h_2^+, terms off-diagonal with respect to v_s in h_3^+ will not contribute to the energy before sixth order.

Rotation-Vibration Energy Through Fourth Order

The twice transformed Hamiltonian

$$h^+ = H_o + h'_1 + h_2^+ + h_3^+ + h_4^+ + \ldots \qquad (1.3)$$

may be used to obtain the rotation-vibration energy of axially symmetric molecules by solving the secular equation

$$\det \left[\langle JMK\ldots v_s,\ \ell_s\ldots | H_o + h'_1 + h_2^+ + h_3^+ + h_4^+ + \ldots | JMK,\ldots v'_s,\ \ell'_s\ldots \rangle - \delta_{KK'}\ldots \delta_{v_s v'_s}\ldots \delta_{\ell_s \ell'_s}\ldots E_{VR} \right] = 0 \qquad (1.4)$$

where $\delta_{ii'}$ is the Kronecker symbol and E_{VR} is the energy of rotation-vibration which we wish to obtain.

For energies through third order, in the absence of accidental resonances, the secular equation which must be solved is simple enough since h^+ is diagonal and the energy of rotation-vibration is given by the diagonal elements of $H_o + h'_1 + h_2^+ + h_3^+$. Table 1.1 presents the terms in the Hamiltonian and the resulting contribution to E_{VR} (28,29,30) in this case. In Table 1.1 the operators are taken from h' rather than from h^+ since the second transformation does not add any new quantum dependence to the energy through

Table I.I Symmetric top transformed Hamiltonians and energy.

Operator			Axial Molecule Energy
H_0		$\frac{1}{2}\sum_{\alpha}\frac{P_\alpha^2}{I_\alpha}$	$B_e J(J+1) + (A_e - B_e)K^2$
		$\frac{\hbar}{2}\sum_{s\sigma}\lambda_s^{\frac{1}{2}}\left(\frac{p_{s\sigma}^2}{\hbar^2}+q_{s\sigma}^2\right)$	$\sum_s \omega_s\left(v_s+\frac{g_s}{2}\right)$
h_1'		$\frac{1}{2}\sum_{\alpha}\sum_{ab}{}^{\alpha}{}_{(1)}Y_a{}^b\left(q_a p_b + p_b q_a\right)P_\alpha$	$-2A_e\sum_t \zeta_t^z \ell_t K$
h_2'	h_{21}'	$\sum_{\alpha\beta\gamma\delta}{}^{\alpha\beta\gamma\delta}{}_{(2)}Y\,P_\alpha P_\beta P_\gamma P_\delta$	$-D_e{}^J J^2(J+1)^2 - D_e{}^{JK}K^2 J(J+1) - D_e{}^K K^4$
	h_{22}'	$\sum_{\alpha\beta}\sum_{\substack{ab\\a\le b}}\left({}^{\alpha\beta}{}_{(2)}Y^{ab}p_a p_b + {}^{\alpha\beta}{}_{(2)}Y_{ab}\,q_a q_b\right)P_\alpha P_\beta$	$-\sum_s \alpha_s{}^B\left(v_s+\frac{g_s}{2}\right)J(J+1) - \sum_s(\alpha_s{}^A-\alpha_s{}^B)\left(v_s+\frac{g_s}{2}\right)K^2$
	h_{23}'	$\sum_{\substack{abcd\\a\le b;c\le d}}\left({}_{(2)}Y_{ab}{}^{cd}\right)\frac{1}{2}\left(q_a q_b p_c p_d + p_c p_d q_a q_b\right)$ $+\sum_{\substack{abcd\\a\le b\le c\le d}}\left({}_{(2)}Y_{abcd}\right)q_a q_b q_c q_d$	$\sum_{\substack{ss'\\s\le s'}}x_{ss'}\left(v_s+\frac{g_s}{2}\right)\left(v_{s'}+\frac{g_{s'}}{2}\right)$ $+\sum_{\substack{tt'\\t\le t'}}x_{\ell_t\ell_{t'}}\ell_t\ell_{t'}$

Table 1.1 continued.

	Operator	Axial Molecule Energy
	$\sum_{\alpha\beta\gamma} \sum_{ab} ({}^{\alpha\beta\gamma}{}_{(3)}Y_a{}^b) \frac{1}{2}(q_a p_b + p_b q_a) P_\alpha P_\beta P_\gamma$	$\sum_t \ell_t \eta_{t,J} J(J+1) K$
h_3'	$\sum_\alpha \sum_{\substack{abcd \\ b\le c\le d}} ({}^{\alpha}{}_{(3)}Y_a{}^{bcd}) \frac{1}{2}(q_a p_b p_c p_d + p_b p_c p_d q_a) P_\alpha$	$\sum_t \ell_t \eta_{t,K} K^3$
	$+\sum_\alpha \sum_{\substack{abcd \\ a\le b\le c}} ({}^{\alpha}{}_{(3)}Y_{abc}{}^{d}) \frac{1}{2}(q_a q_b q_c p_d + p_d q_a q_b q_c) P_\alpha$	$+\sum_t \ell_t \left[\eta_t + \sum_s \eta_{t,s}(v_s + \frac{g_s}{2})\right] K$

third order but, in so far as diagonal terms are concerned, it changes slightly the interpretation of spectroscopic constants in terms of the basic molecular constants I_{dd} $a_{s\sigma}^{\alpha\beta}$, $\zeta_{ss'}^{\alpha}$, and the force constants, the $k_{s_1 s_2 \cdots s_m}$ (14), of the molecule. Table 1.2 gives a list of symbols found in Table 1.1 with appropriate definitions.

From these tables the energy of rotation-vibration to any desired order through the third may be obtained. In addition, a partial fourth order correction to the energy is given in Table 1.3. However, it is necessary that one be cognizant of the fact that this is a partial correction and that an added correction may come from the off-diagonal terms of h_2^+, and also from other terms in h_4^+ which are diagonal in J, K, ℓ_s and v_s. Specifically, the off-diagonal lines (Table1.1) which can contribute to fourth order are: h_{21}', K-type resonance and doubling (31); h_{22}', rotational ℓ-type resonance and doubling (28); and h_{23}', vibrational ℓ-type doubling and resonance (28).

h_4^+ also contains operators which may contribute further to fourth order. No results of any study of these terms has been published for the case of an axially symmetric molecule.[2]

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[2] Chung and Parker (32) have studied the terms of h_{43}^+ for the asymmetric top case. In addition Benedict (33) found it useful to use a lumped sixth power correction of the form $-1.0 \times 10^{-6}\{[J(J+1)-K^2]^3 + J(J+1)K^2[J(J+1)-K^2]\}$ to fit an NH_3 overtone band. Ramadier and Amat (34) have studied the sixth power terms of h_{43}^+ in the special case of a linear molecule.

Table 1.2 List of symbols from Table 1.1 with description.

Symbol	Description
α	x,y,z (likewise for β and γ) (body-fixed)
s	index for the normal vibration
n	index for specifically non-degenerate normal vibration
t	index for specifically 2-fold degenerate vibration
a,b	dummy index for s
σ	ordering index for the two components of a degenerate vibration
Y Z	constant coefficients (generally complicated) of the transformed Hamiltonians
P_α	rotational angular momentum operator
q_s	normal coordinate operator
p_s	momentum operator conjugate to q_s
I_α	principal equilibrium moment of inertia about the α axis
B_e	$= h/(8\pi^2 c I_x)$, $I_x = I_y$
A_e	$= h/(8\pi^2 c I_z)$ I_z is unique $I_z \neq I_x = I_y$
ω_s	harmonic frequency (cm^{-1}) of sth normal mode
λ_s	$= (2\pi c \omega_s)^2$
g_s	degeneracy of the sth normal mode
ζ_t^z	Coriolis coupling constant - a function of molecular geometry
D_e^m	m = J,K,JK: equilibrium centrifugal distortion constant
d_s^B	correction to B_e due to vibration
d_s^A	correction to A_e due to vibration

Table 1.2 Continued.

Symbol	Description
$X_{ss'}, X_{\ell_t \ell_{t'}}$	anharmonic vibrational constants
$\eta t,m$	m = J,K,S or nothing: third order constants

Table 1.3 Contribution to symmetric top energy from h_4^+.

	Axial Molecule Energy
h_{41}^+	$\sum_s \beta_s^J \left[v_s + \frac{g_s}{2}\right] J^2 \left[J+1\right]^2 + \sum_s \beta_s^{JK} \left[v_s + \frac{g_s}{2}\right] J\left[J+1\right] K^2 + \sum_s \beta_s^K K^4$
h_{42}^+	$\left\{ \sum_{\substack{ss' \\ s \le s'}} \gamma_{ss'}^B \left[v_s + \frac{g_s}{2}\right]\left[v_s + \frac{g_{s'}}{2}\right] + \sum_{\substack{tt' \\ t \le t'}} \gamma^B{}_{l_t l_{t'} l_t l_{t'}} + \Delta B_e^{(a)} \right\} \left\{ J\left[J+1\right] - K^2 \right\} +$ $\left\{ \sum_{\substack{ss' \\ s \le s'}} \gamma_{ss'}^A \left[v_s + \frac{g_s}{2}\right]\left[v_s + \frac{g_{s'}}{2}\right] + \sum_{\substack{tt' \\ t \le t'}} \gamma^A{}_{l_t l_{t'} l_t l_{t'}} + \Delta A_e^{(a)} \right\} K^2$
h_{44}^+	$\sum_{\substack{ss's'' \\ s \le s' \le s''}} y_{ss's''} \left[v_s + \frac{g_s}{2}\right]\left[v_{s'} + \frac{g_{s'}}{2}\right]\left[v_{s''} + \frac{g_{s''}}{2}\right] + \sum_{\substack{stt' \\ t \le t'}} y_{s l_t l_{t'} l_t l_{t'}} \left[v_s + \frac{g_s}{2}\right] +$ $\sum_s \Delta\omega_s \left[v_s + \frac{g_s}{2}\right]$

(a) These constants also receive a contribution from h_{21}^+ (35).

However as Maes pointed out in his study of third order terms (29), from the point of view of spectral analysis, it is the quantum dependence which is important from third order on since there seems to be no simple connection between the constant coefficients of these high order terms and the molecular parameters. The constants are in general complicated combinations of molecular parameters and force constants.

Table 1.4 lists the operators found in h_4^+ (16) which we subdivide into five parts:

$$h_4^+ = h_{41}^+ + h_{42}^+ + h_{43}^+ + h_{44}^+ + h_4^{+*} \qquad (1.5)$$

such that h_4^{+*} contains only terms off-diagonal in v_s (16) and in the absence of accidental resonances is able to contribute to the energy only in the eighth or higher orders. Table 1.5 gives a description of the contribution of the various terms of h_4^+ to E_{VR}. Table 1.3 presents the contribution of h_{41}^+, h_{42}^+ and h_{44}^+ to E_{VR} (35). Table 1.6 is a description of the constants used in Table 1.3.

The contribution of h_{43}^+ cannot yet be given since no results of a systematic study of its contribution to E_{VR} have been published for the case of an axially symmetric molecule.

Discussion of the Orders of Magnitude of Contributions to E_{VR}

The expansion of the Hamiltonian is effected with an assumed expansion parameter on the order of 1/30. It is assumed that a zero order contribution to the energy is approximately $1000cm^{-1}$. One should realize that order of

Table 1.4 Fourth order transformed Hamiltonian.

	Operator
h_{41}^{+}	$\sum_{\alpha\beta\gamma\delta} \sum_{\substack{ab \\ a\le b}} \left({}^{\alpha\beta\gamma\delta}_{(4)}Z_{ab}\, q_a q_b + {}^{\alpha\beta\gamma\delta}_{(4)}Z^{ab}\, p_a p_b\right) P_\alpha P_\beta P_\gamma P_\delta$
h_{42}^{+}	$\sum_{\alpha\beta}\Bigg\{ \sum_{\substack{abcd \\ a\le b\le c\le d}} \left[{}^{\alpha\beta}_{(4)}Z_{abcd}\, q_a q_b q_c q_d + {}^{\alpha\beta}_{(4)}Z^{abcd}\, p_a p_b p_c p_d \right]$ $+ \sum_{\substack{abcd \\ a\le b;\, c\le d}} {}^{\alpha\beta}_{(4)}Z_{ab}{}^{cd}\, \frac{1}{2}(q_a q_b p_c p_d + p_c p_d q_a q_b) + {}^{\alpha\beta}_{(4)}Z \Bigg\} P_\alpha P_\beta$
h_{43}^{+}	$\sum^{\alpha\beta\gamma\delta\epsilon\eta}_{\alpha\beta\gamma\delta\epsilon\eta} {}_{(4)}Z\, P_\alpha P_\beta P_\gamma P_\delta P_\epsilon P_\eta$
h_{44}^{+}	$\sum_{\substack{abcdef \\ a\le b\le c\le d\le e\le f}} \left[{}_{(4)}Z_{abcdef}\, q_a q_b q_c q_d q_e q_f + {}_{(4)}Z^{abcdef}\, p_a p_b p_c p_d p_e p_f \right] + \sum_{\substack{abcdef \\ a\le b\le c\le d\le e\le f}} \Big[{}_{(4)}Z_{abcd}{}^{ef}\, \frac{1}{2}(q_a q_b q_c q_d p_e p_f + p_e p_f q_a q_b q_c q_d)$ $+ {}_{(4)}Z_{ef}{}^{abcd}\, \frac{1}{2}(p_a p_b p_c p_d q_e q_f + q_e q_f p_a p_b p_c p_d) \Big] + \sum_{\substack{ab \\ a\le b}} \left[{}_{(4)}Z_{ab}\, q_a q_b + {}_{(4)}Z^{ab}\, p_a p_b \right]$

Table 1.5 Description of contributions of terms in h_4^+ to E_{VR}.

	Diagonal Contribution to E_{VR}
h_{41}^+	correction to centrifugal distortion; due to vibration
h_{42}^+	second correction to inverse moments of inertia; due to vibration
h_{43}^+	correction to centrifugal distortion; due to rotation
h_{44}^+	additional anharmonic contributions to vibrational energy

Table 1.6 List of symbols from Table 1.3 with descriptions.

Symbol	Description
β_s^m	m = J,K,JK; correction to D_e^m due to vibration
$\gamma_{ss'}^B$	correction to B_e due to vibration
$\gamma_{ss'}^A$	correction to A_e due to vibration
$y_{ss's''}$, $y_{sl_t l_t'}$	anharmonic vibrational constants
ΔB_e, ΔA_e	"correction" to B_e and A_e which has exactly the same quantum dependence as B_e and A_e
ω_s	"correction" to ω_s which has exactly the same quantum dependence as ω_s

magnitude considerations are approximations and are not to be taken too literally, and therefore, they should serve as a helpful guide rather than as restrictions in the analysis of spectra. For convenience Table 1.7 lists the expected approximate magnitude of a contribution to the energy of terms of order m.

In the following, the orders of magnitude of only the diagonal contributions to the energy are discussed. For a further discussion of this case and of the order of magnitude of off-diagonal contributions the work of Amat and Nielsen (18) is fundamental.

At this point it is useful to use simpler notation by following the convention (18) that operators in the Hamiltonian having the forms $q_a q_b$, $p_a p_b$ or $q_a p_b$ be called r^2, etc., that $P_\alpha P_\beta P_\gamma$ be called P^3, etc., and that the sub- and superscripts on the Y's and Z's be dropped. Thus $h'_{22} = (2)Yr^2P^2$.

The order of magnitude expansion of the Hamiltonian is valid for $J \approx K \approx 30$. For other values of J and K a term may be demoted or promoted from its present formal order to a different order which we would then call the "true" order of magnitude of its contribution.

A relatively simple approach to the problem leads us to discuss first the order of magnitude of a given <u>constant</u> appearing in h_m^+. Consider the generic term

$$(m)Zr^nP^s$$

which is a term (from the m-th order transformed Hamiltonian)

Table 1.7 Approximate magnitude of the formal orders of magnitude.

Order m	Magnitude in cm^{-1}
0	1000
1	30
2	1
3	3×10^{-2}
4	1×10^{-3}
5	3×10^{-5}
6	1×10^{-6}
7	3×10^{-8}
8	1×10^{-9}
9	3×10^{-11}
10	1×10^{-12}

with the constant coefficient (m)Z, a product of n vibrational operators and s rotational operators. The order of magnitude of the constant (m)Z is m + s. For example D_e^J is of order 6 since m = 2 and s = 4. Table 1.8 lists the order of magnitude of the constants in h^+ from Tables 1.1 and 1.3.

The computation of the "true" order of magnitude of the contribution of a term in E_{VR} may be carried out with the aid of Tables 1.1, 1.3, 1.7, and 1.8 by substituting the values of J and K in question into the contribution of the term to E_{VR} in Tables 1.1 or 1.3 using the approximate magnitude of the constant from Table 1.8 and comparing the answer with the list in Table 1.7. For example, from Table 1.8, D_e^J is of order 6 but the term from Table 1.1, of which D_e^J is the constant coefficient, is of order 2 for $J \approx 20$, $K \approx 0$ or $K \approx 30$. At times a more meaningful order of magnitude of the contribution of a term to E_{VR} may be computed if one has available the actual value of the constant involved. Some applications of these concepts will be found in the following chapters.

Table 1.8 Order of magnitude of constants.

h_m^+	Operator	Constant	Order of Constant	Approximate Magnitude of Constant
H_0	$(0)Xr^2$	ω_s	0	1000 cm^{-1}
	$(0)XP^2$	A_e , B_e	2	1
h_1'	$(1)Yr^2P$	$2A_e\sum_t \zeta_t^z \ell_t$	2	1
h_{21}^+	$(2)ZP^4$	D_e^J , D_e^{JK}, D_e^K	6	1×10^{-6}
h_{22}^+	$(2)Zr^2P^2$	α_s^A , α_s^B	4	1×10^{-3}
h_{23}^+	$(2)Zr^4$	$x_{ss'}$, $x_{\ell_t\ell_{t'}}$	2	1
h_3^+	$(3)Zr^2P^3$	η_t^J	6	1×10^{-6}
	$(3)Zr^2P^3$	η_t^K	6	1×10^{-6}
	$(3)Zr^4P$	η_t , $\eta_{t,s}$	4	1×10^{-3}
h_{41}^+	$(4)Zr^2P^4$	β_s^J , β_s^{JK} , β_s^K	8	1×10^{-9}
h_{42}^+	$(4)Zr^4P^2$	$\gamma_{ss'}^A$, $\gamma_{ss'}^B$, $\gamma_{\ell_t\ell_{t'}}^A$, $\gamma_{\ell_t\ell_{t'}}^B$	6	1×10^{-6}
	$(4)ZP^2$	ΔA_e , ΔB_e	6	1×10^{-6}
h_{44}^+	$(4)Zr^6$	$y_{ss's''}$, $y_{s\ell_t\ell_{t'}}$	4	1×10^{-3}
	$(4)Zr^2$	$\Delta\omega_s$	4	1×10^{-3}

CHAPTER 2

SYMMETRY PROPERTIES AND SELECTION RULES

In this chapter we comment briefly on the symmetry species to which a given energy level may belong and tabulate selection rules on the quantum number l in infrared absorption spectra.

At the time this work was in progress no complete treatment of the symmetry species of the molecular wave functions was available. Scattered through the literature one finds numerous partial treatments of the problem (36-47). However, the problem has not been fully resolved and many subtle considerations enter into the full treatment (48). The specific problem applied to XYZ_3 molecules which belong to the point group C_{3v} is the problem of classifying the full molecular wave function including vibration, inversion, rotation and nuclear spin according the species A_1, A_2 or E_1. If the rotational functions only are considered, they may be classified according to the rotational subgroup C_3 which has species A or E.

For the work which we have done, it is sufficient to know the symmetry species of the levels according to the rotational subgroup C_3. These may be found for the rotational wave functions in reference 12. Very simply, the species in a pure rotational state or an A_1 vibrational state are given by

$$\begin{aligned} K = 3p &: \text{ species A} \\ K \neq 3p &: \text{ species E} \end{aligned} \qquad (2.1)$$

where p = 0,1,2, ...

In the case of degenerate vibrational states the problem is more complex. A very simple method of finding the result is given in Appendix I. We find that for all rotation-vibration levels of C_{3v} molecules, if

$$K - \Sigma \ell_t = \pm 3p \qquad (2.2)$$

the levels are of species A under the point group C_3 (i.e., an A_1A_2 pair according to the C_{3v} point group), whereas if

$$K - \Sigma \ell_t = \pm(3p \pm 1) \qquad (2.3)$$

the levels are of species E_1. In Eqs (2.2) and (2.3) p takes the values 0,1,2,...as in Eq (2.1).

We do know, however, that the total overall symmetry of the molecular wave function including the electronic, vibrational, rotational, and nuclear spin contribution must be A_2 for ZXH_3 molecules or A_1 for ZXD_3 molecules for those energy levels which can be populated (38,39,40).[3]

Due to the restrictions on the overall symmetry of the molecular wave functions, there is a well-known effect observed in the spectra of ZXY_3 molecules. For ZXH_3 molecules, the effect is the 2:1 intensity enhancement of transitions originating from ground states in which

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[3] These restrictions arise from the fact that the ZXH_3 molecules obey Fermi-Dirac statistics whereas the ZXD_3 molecules obey Bose-Einstein statistics.

$K = 3p$, $p = 0, 1, 2 \ldots$ over those which originate from states where $K \neq 3p$. For ZXY_3, the effect is the same but the enhancement is only 11:8 (12).

Selection Rules on Infrared Rotation-Vibration Transitions

There are a number of selection rules which are well known in the study of absorption spectra of axially symmetric molecules (12). These are the symmetry selection rules on molecular energy level symmetries apart from nuclear spin under the rotational subgroup C_3

$$A \leftrightarrow A, \quad E \leftrightarrow E, \quad A \not\leftrightarrow E, \tag{2.4}$$

the inversion symmetry selection rule

$$+ \leftrightarrow -, \quad - \not\leftrightarrow -, \quad + \not\leftrightarrow +, \tag{2.5}$$

the selection rule on J

$$\Delta J = \pm 1, 0; \tag{2.6}$$

and on K

$$\Delta K = 0 \qquad A \text{ or } \| \text{ bands} \tag{2.7}$$

$$\Delta K = \pm 1 \qquad E \text{ or } \perp \text{ bands} \tag{2.8}$$

with the restriction that $J = 0$, $\Delta J = 0$ is forbidden.

Selection Rules on $\sum_t \lambda_t$

Making use of Eq. (2.4) and Eq. (2.8) and the results of Appendix I, the selection rules on $\sum_t \lambda_t$ may be deduced for any case of interest. The selection rule on $\sum_t \lambda_t$ for several cases is given in Table 2.1 with the restriction that only $+|K|$ values be considered. This restriction is generally adhered to in spectroscopic work. This restriction

Table 2.1 Selection rules on ℓ_t.

Absorption Band	$\sum_t \ell_t$	Vibration	ℓ_t	$\ell_{t'}$	$\ell_{t''}$	Selection Rule
ν_n						
$\nu_n + \nu_{n'} + \nu_{n''}$	0	A_1	0	0	0	$\Delta\ell=\Delta K=0$
$2\nu_n, 3\nu_n$						
ν_t	±1	E_1	±1	0	0	$\Delta\ell=\Delta K=\pm1$
$\nu_t + \sum_n \nu_n$	±1	E_1	±1	0	0	$\Delta\ell=\Delta K=\pm1$
$2\nu_t$	0	A_1	0	0	0	$\Delta\ell=\Delta K=0$
$2\nu_t$	±2	E_1	±2	0	0	$\Delta\ell=-2\Delta K=\pm1$
$\nu_t + \nu_{t'}$	0	A_1	±1	∓1	0	$\Delta\ell=\Delta K=0$
$\nu_t + \nu_{t'}$	±2	E_1	±1	±1	0	$\Delta\ell=-2\Delta K=\pm1$
$\nu_t + \nu_{t'} + \nu_{t''}$	±3	A_1	±1	±1	±1	$\Delta\ell=\Delta K=0$
$\nu_t + \nu_{t'} + \nu_{t''}$	±1	E_1	±1	±1	∓1	$\Delta\ell=\Delta K=\pm1$
		E_1	±1	∓1	±1	
		E_1	∓1	±1	±1	

simplifies the selection rules without reducing generality. The selection rules of Table 2.1 are given for transitions from the ground state where all ℓ_t are identically zero. The subscript index n corresponds to a specifically non-degenerate normal vibration, while t corresponds to a two-fold degenerate vibration.

CHAPTER 3

GENERALIZED EXPRESSION FOR THE SIMULTANEOUS REPRESENTATION OF ALL TRANSITION FREQUENCIES OF AN AXIALLY SYMMETRIC MOLECULE

In this chapter we develop a single expression which simultaneously represents all allowed rotation-vibration transitions of a particular molecule. The generalized transition frequency expression is of special value to the spectroscopist since it enables him to perform a simultaneous least squares analysis of all unperturbed transitions, or any subset of transitions, of a particular molecule. This then results in a consistent set of molecular constants and accordingly, as more and more transitions are analyzed simultaneously, the statistics involved [4] become more and more favorable.

Consider the energy levels of an axially symmetric molecule with a negligible inversion probability. These energy levels are given by the energy expressions of Chapter 1 and are specified by the quantum numbers v_n, v_{n+1} ,...v_t, ℓ_t, v_{t+1} , $\ell_t + 1$,...J,K,M.[5]

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[4] cf. Boyd, (50).

[5] In the absence of external electric or magnetic fields we shall omit M since the energy E_{VR} is then independent of M.

Consider the transition

$$v_n+\Delta v_n,\ldots v_t+\Delta v_t,\ell_t+\Delta\ell_t,\ldots J+\Delta J,K+\Delta K \leftarrow v_n,\ldots v_t,\ell_t,\ldots J,K \tag{3.1}$$

which is a transition[6] between the lower state

$$E''_{VR}(v_n,v_{n+1},\ldots v_t,\ell_t,v_{t+1},\ell_{t+1},\ldots J,K) \tag{3.2}$$

and the upper state

$$E'_{VR}(v_n+\Delta v_n,\ldots v_t+\Delta v_t,\ell_t+\Delta\ell_t,\ldots J+\Delta J,K+\Delta K). \tag{3.3}$$

A generalized transition frequency expression is obtained in a straight-forward manner when the upper and lower levels are written as in Eq. (3.3) and Eq. (3.2) respectively. Alternate forms of the transition frequency corresponding to the transition given by Eq. (3.1) are

$$\begin{aligned}&(v_n,v_{n+1},\ldots v_t,\ell_t,\ldots\Delta v_n,\ldots\Delta v_t,\Delta\ell_t,\ldots\Delta K,\Delta J,K,J) = \\ &(v_n,v_{n+1},\ldots v_t,\ell_t\ldots\Delta v_n\ldots\Delta v_t,\Delta\ell_t\ldots)^{\Delta K}_{\Delta J}{}_{K}(J) = \\ &E'_{VR}(v_n+\Delta v_n,\ldots v_t+\Delta v_t,\ell_t+\Delta\ell_t,\ldots J+\Delta J,K+\Delta K)- \\ &\qquad E''_{VR}(v_n,\ldots v_t,\ell_t\ldots JK).\end{aligned} \tag{3.4}$$

Table 3.1 presents the generalized transition frequency expression[7] defined by Eq. (3.4) for the case $\sum_s |v_s| = 0$ in E''_{VR}

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[6] For each transition the set $\Delta v_n,\Delta v_{n+1},\ldots\Delta v_t,\Delta\ell_t,\ldots{}^{\Delta K,\Delta J}$ are determined by the selection rules for that particular transition.

[7] The terms in Table 3.1 are grouped according to the various molecular constants. However, special considerations found in Chapter 5 must be taken into account before using the expressions given in this chapter in the numerical analysis of spectra in order to avoid linear dependence or a poorly conditioned set of normal equations.

Table 3.1 Generalized transition frequency expression.

$(v_n, v_{n+1}, \ldots v_t, \ell_t, v_{t+1}, \ell_{t+1}, \ldots)^{\Delta K} \Delta J_K(J) =$	Index
$\sum_s v_s(\omega_s + \Delta\omega_s) +$	a
$\sum_{\substack{s \\ s \le s'}} \sum_{s'} x_{ss'}\left[(v_s + \frac{g_s}{2})(v_{s'} + \frac{g_{s'}}{2}) - \frac{g_s g_{s'}}{4}\right] +$	b
$\sum_{\substack{t \\ t \le t'}} \sum_{t'} x_{\ell_t \ell_{t'}} \ell_t \ell_{t'} +$	c
$\sum_{\substack{s \\ s \le s' \le s''}} \sum_{s'} \sum_{s''} y_{ss's''}\left[(v_s + \frac{g_s}{2})(v_{s'} + \frac{g_{s'}}{2})(v_{s''} + \frac{g_{s''}}{2}) - \frac{g_s g_{s'} g_{s''}}{8}\right] +$	d
$\sum_s \sum_{\substack{t \\ t \le t'}} \sum_{t'} y_{s \ell_t \ell_{t'}} (v_s + \frac{g_s}{2}) \ell_t \ell_{t'} +$	e
$A_o\left[(K+\Delta K)^2 - K^2\right] +$	f
$B_o\left[(J+\Delta J)(J+1+\Delta J) - J(J+1) - (K+\Delta K)^2 + K^2\right] +$	g
$\left[-2A_e \sum_t \zeta_t^z \ell_t + \sum_t \{\eta_t + \sum_s \eta_{t,s}(v_s + \frac{g_s}{2})\} \ell_t\right]\left[K + \Delta K\right] +$	h

Table 3.1 Continued.

$-D_o^J\left[(J+\Delta J)^2(J+1+\Delta J)^2-J^2(J+1)^2\right]+$		i
$-D_o^{JK}\left[(K+\Delta K)^2(J+\Delta J)(J+1+\Delta J)-K^2J(J+1)\right]+$		j
$-D_o^K\left[(K+\Delta K)^4-K^4\right]+$		k
$\left[-\sum_s \alpha_s^A v_s+\sum_{ss'}\gamma_{ss'}^A\left(v_s v_{s'}+\frac{v_s g_{s'}}{2}+\frac{v_{s'}g_s}{2}\right)+\sum_{\substack{tt'\\ t\le t'}}\gamma_{\ell_t\ell_{t'}}^A \ell_t\ell_{t'}\right]\left[(K+\Delta K)^2\right]+$		l
$\left[-\sum_s \alpha_s^B v_s+\sum_{ss'}\gamma_{ss'}^B\left(v_s v_{s'}+\frac{v_s g_{s'}}{2}+\frac{v_{s'}g_s}{2}\right)+\sum_{\substack{tt'\\ t\le t'}}\gamma_{\ell_t\ell_{t'}}^B \ell_t\ell_{t'}\right]\left[(J+\Delta J)(J+1+\Delta J)-(K+\Delta K)^2\right]+$		m
$\sum_t \eta_t^J \ell_t (K+\Delta K)(J+\Delta J)(J+1+\Delta J)+$		n
$\sum_t \eta_t^K \ell_t (K+\Delta K)^3+$		p
$\sum_s \beta_s^J v_s\left[(J+\Delta J)^2(J+1+\Delta J)^2\right]+$		q
$\sum_s \beta_s^{JK} v_s\left[(K+\Delta K)^2(J+\Delta J)(J+1+\Delta J)\right]+$	$\sum_s \beta_s^K v_s (K+\Delta K)^4$	r | s

complete (in the absence of accidental resonances) through the contributions of h_3^+ [8]; Table 3.1 also contains a partial contribution of h_4^+.[9]

The definitions given in Eqs. (3.5) identify some of the constants appearing in Table 3.1 with those found in the literature and in papers on analysis of spectra.

$$B_o=B''=B_e-\sum_s(g_s/2)\alpha_s^B+\sum_{s\leq s'}\sum_{s'}(g_s/4)\,\gamma_{ss'}^B+\Delta B_e$$

$$B_v=B'=B_o-\sum_s v_s\alpha_s^B+\sum_{s\leq s'}\sum_{s'}\left(v_sv_{s'}+\frac{v_sg_{s'}}{2}+\frac{v_{s'}g_s}{2}\right)\gamma_{ss'}^B+$$

$$\sum_{t\leq t'}\sum_{t'}\gamma_{l_tl_{t'},l_tl_{t'}}^B.$$

$$A_o=A''=A_e-\sum_s(g_s/2)\alpha_s^A+\sum_{s\leq s'}\sum_{s'}(g_s/4)\gamma_{ss'}^A+\Delta A_e \qquad (3.5)$$

$$A_v=A'=A_o-\sum_s v_s\alpha_s^A+\sum_{s\leq s'}\sum_{s'}\left(v_sv_{s'}+\frac{v_sg_{s'}}{2}+\frac{v_{s'}g_s}{2}\right)\gamma_{ss'}^A+$$

$$\sum_{t\leq t'}\sum_{t'}\gamma_{l_tl_{t'},l_tl_{t'}}^A$$

$$D_o^m=D_m''=D_e^m-\sum_s(g_s/2)\beta_s^m \qquad m=J,K,JK$$

$$D_v^m=D_m'=D_o^m-\sum_s v_s\beta_s^m \qquad m=J,K,JK$$

Table 3.2 contains descriptions of symbols found in Table 3.1 but not defined in Table 1.2 or Table 1.6.

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[8] cf. Table 1.1.

[9] cf. Table 1.5.

Table 3.2 Description of symbols found in Table 3.1.

Symbol	Description
B_0	ground state constant corresponding to B_e
α_s^A, α_s^B	coefficients of the correction to A_e and B_e, respectively, due to vibration
D_0^J, D_0^{JK}, D_0^K	ground state centrifugal distortion constants
s	refers generically to any vibrational mode
n	refers specifically to non-degenerate vibrations
t	refers specifically to two-fold degenerate vibrations
v_s	vibrational quantum number for the sth mode, e.g., if three quanta of ν_4 are excited, $v_4 = 3$
ℓ_t	internal angular momentum quantum number associated with two-fold degenerate vibrations where ℓ_t may take on values $v_t, v_t-2, v_t-4, \ldots 0$ or 1
J	total angular momentum quantum number
K	quantum number associated with the projection of J on the symmetry axis of the molecule
ΔJ	change in J in the transition being considered, i.e., if $J_2 \leftarrow J_1$, then $\Delta J = J_2 - J_1$
ΔK	similarily, for $K_2 \leftarrow K_1$, $\Delta K = K_2 - K_1$

There is an important restriction to be observed regarding the expression in Table 3.1. The quantum number K may properly take the values $\pm|K|$. However, in Table 3.1, one need only take $+|K|$ values into account, and in fact, if one desires to retain simplicity in selection rules, only $+|K|$ should be used.

Returning to the significance of the general transition frequency expression of Table 3.1, it is important to note that simply by specifying, for a given transition, $v_1, v_2 \ldots v_n$, $v_t, v_{t+1}, \ldots \ell_t, \ell_{t+1}, \Delta v_1, \Delta v_2, \ldots \Delta v_n, \Delta v_t, \Delta \ell_t, \Delta v_{t+1}, \Delta \ell_{t+1} \ldots J$, $\Delta J, K$, and ΔK as independent variables, the transition frequency stands, in relation to these, as the dependent variable. Thus, a simultaneous least squares analysis of all unperturbed transitions of a given molecule may be obtained.

Quite often this is impractical especially if any of the levels involved are perturbed but the fact remains that it is otherwise possible. Of course, any subset of transitions believed to be unperturbed may be analyzed using an appropriate modification of the generalized expression of Table 3.1.[10] For example, the sum of the purely vibrational contributions in Table 3.1 may be called ν_0, and all the spectral lines of a given rotation-vibration band may be simultaneously analyzed. An example of this may be found in

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[10] One must of course be careful to avoid linear dependence in the expression used in the actual analysis. This is further discussed in Chapter 5.

Chapter 8. Another case, where both parallel and perpendicular components of a first overtone of an axially symmetric molecule were analyzed simultaneously, may be found in a thesis by Boyd (50). In the particular case of some diatomic molecules it appears quite feasible to analyze simultaneously all observed bands of a particular molecule since the addition of each band requires only the inclusion of a single new term, the vibrational frequency of the added band.[20]

Another consideration in the analysis of spectra involves the expected order of magnitude of the contribution of any particular term found in Table 1.1 and Table 1.3 to the vibration-rotation energy. However, since the transition frequency results from the difference of E'_{VR} and E''_{VR}, certain of the terms in the transition frequency expression are demoted to a higher order of magnitude than they had in the energy expression. Furthermore, as mentioned in Chapter 1, the formal order of magnitude of some contributions to the energy are "correct" only for $J \approx K \approx 30$. For $J \not\approx 30$ or $K \not\approx 30$ various terms are demoted or promoted from their formal order of magnitude to a higher order or lower order.

The importance of the order of magnitude of various terms in the transition frequency expression is discussed in Chapter 5. The basic idea is that one does not wish to exclude terms which should make larger contributions than

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[20] Olman, Hause, and McNellis (51) are simultaneously analyzing bands of $N^{15}O$ and $N^{14}O$ in this manner.

others which have been included.

Table 3.3 indicates the theoretical order of magnitude of the five terms in the transition frequency expression of Table 3.1 which are independent of J, K, ΔJ and ΔK. Tables 3.4 to 3.12 present the theoretical magnitude and order of magnitude of the terms in Table 3.1 which do depend on J, K, ΔJ and ΔK for the transition $\Delta K = 0$, $\Delta J = -1, 0, +1$; $\Delta K = +1$, $\Delta J = -1, 0, +1$; and $\Delta K = -1$, $\Delta J = -1, 0, +1$ for several values of J and K. These tables were constructed by substituting the theoretical magnitude of the molecular constants from Table 1.8 and the values of J and K indicated in Tables 3.4 to 3.12 into the individual terms in Table 3.1 and calculating the approximate magnitude of the contribution of that term to E_{VR}. The order for the various values of J and K was obtained using this calculated magnitude and Table 1.7.

These tables may be used by spectroscopists in determining which terms from Table 3.1 contribute sufficiently to the transition frequency to be used in an analysis. However, it is necessary to take two factors into account; it is necessary to consider the accuracy and reproducibility of the spectral data involved, and it should be noted that for a given band, promotion or demotion of one order of magnitude is not unusual. In this respect, we would expect that terms whose <u>largest</u> contribution to any of the transitions used in the analysis is less than the accuracy and reproducibility of the data would be statistically and

Table 3.3 Formal order of magnitude of the contribution to the transition frequency of terms a,b,c,d,e in Table 3.1 for $v_s \approx 1$.

Coefficient Descriptive of Term	Table 3.1 Index	Order J any K any	Approximate Magnitude (cm^{-1})
ω_s	a	1	30
$x_{ss'}$	b	2	1
$x_{\ell_t \ell_t'}$	c	2	1
$y_{ss's''}$	d	4	1×10^{-3}
$y_{s\ell_t\ell_t'}$	e	4	1×10^{-3}

Table 3.4 Order of magnitude of terms for $\Delta K=0$, $\Delta J=-1$, i.e., ${}^{Q}P_{K}(J)$.

Coefficient Descriptive of Term	Table 3.1 Index	Order $J\approx30$ $K\approx30$	Approximate Magnitude (cm^{-1})	Order $J\approx1$ $K\approx1$	Approximate Magnitude (cm^{-1})	Order $J\approx20$ $K\approx1$	Approximate Magnitude (cm^{-1})	Order $J\approx20$ $K\approx10$	Approximate Magnitude (cm^{-1})
A_0	f	∞	0	∞	0	∞	0	∞	0
B_0	g	1	60	2	2	1	40	1	40
$A_e\zeta$	h	∞	0	∞	0	∞	0	∞	0
D_0^J	i	3	1×10^{-1}	6	4×10^{-6}	3	4×10^{-2}	3	4×10^{-2}
D_0^{JK}	j	3	5×10^{-2}	6	2×10^{-6}	5	4×10^{-5}	4	4×10^{-3}
D_0^K	k	∞	0	∞	0	∞	0	∞	0
α_s^A	l	2	9×10^{-1}	4	1×10^{-3}	4	1×10^{-3}	3	1×10^{-1}
α_s^B	m	3	3×10^{-2}	4	1×10^{-3}	3	4×10^{-1}	3	3×10^{-1}
η_t^J	n	∞	0	∞	0	∞	0	∞	0
η_t^K	p	∞	0	∞	0	∞	0	∞	0
β_s^J	q	4	7×10^{-4}	∞	0	6	1×10^{-5}	6	1×10^{-5}
β_s^{JK}	r	4	8×10^{-4}	∞	0	7	4×10^{-7}	5	4×10^{-5}
β_s^K	s	4	6×10^{-4}	8	1×10^{-9}	8	1×10^{-9}	6	1×10^{-5}

Table 3.5 Order of magnitude of terms for $\Delta K=0$, $\Delta J=0$, i.e., ${}^{Q}Q_{K}(J)$.

Coefficient Descriptive of Term	Table 3.1 Index	Order $J\approx30$ $K\approx30$	Approximate Magnitude (cm^{-1})	Order $J\approx1$ $K\approx1$	Approximate Magnitude (cm^{-1})	Order $J\approx20$ $K\approx1$	Approximate Magnitude (cm^{-1})	Order $J\approx20$ $K\approx10$	Approximate Magnitude (cm^{-1})
A_o	f	∞	0	∞	0	∞	0	∞	0
B_o	g	∞	0	∞	0	∞	0	∞	0
$A_e\zeta$	h	∞	0	∞	0	∞	0	∞	0
D_o^J	i	∞	0	∞	0	∞	0	∞	0
D_o^{JK}	j	∞	0	∞	0	∞	0	∞	0
D_o^K	k	∞	0	∞	0	∞	0	∞	0
α_s^A	l	2	9×10^{-1}	4	1×10^{-3}	4	1×10^{-3}	3	1×10^{-1}
α_s^B	m	3	3×10^{-2}	4	3×10^{-3}	3	4×10^{-1}	3	3×10^{-1}
η_t^J	n	∞	0	∞	0	∞	0	∞	0
η_t^K	p	∞	0	∞	0	∞	0	∞	0
β_s^J	q	4	9×10^{-4}	8	8×10^{-9}	5	2×10^{-5}	5	2×10^{-5}
β_s^{JK}	r	4	8×10^{-4}	8	2×10^{-9}	7	4×10^{-7}	5	4×10^{-5}
β_s^K	s	4	6×10^{-4}	8	1×10^{-9}	8	1×10^{-9}	6	1×10^{-5}

Table 3.6 Order of magnitude of terms for $\Delta K=0$, $\Delta J=+1$, i.e., $^{Q}R_{K}(J)$.

Coefficient Descriptive of Term	Table 3.1 Index	Order $J\approx30$ $K\approx30$	Approximate Magnitude (cm^{-1})	Order $J\approx1$ $K\approx1$	Approximate Magnitude (cm^{-1})	Order $J\approx20$ $K\approx1$	Approximate Magnitude (cm^{-1})	Order $J\approx20$ $K\approx10$	Approximate Magnitude (cm^{-1})
A_o	f	∞	0	∞	0	∞	0	∞	0
B_o	g	1	62	2	4	1	42	1	42
$A_e\zeta$	h	∞	0	∞	0	∞	0	∞	0
D_o^J	i	3	1×10^{-1}	5	3×10^{-5}	3	4×10^{-2}	3	4×10^{-2}
D_o^{JK}	j	3	6×10^{-2}	6	4×10^{-6}	5	4×10^{-5}	4	4×10^{-3}
D_o^K	k	∞	0	∞	0	∞	0	∞	0
α_s^A	l	2	9×10^{-1}	4	1×10^{-3}	4	1×10^{-3}	3	1×10^{-1}
α_s^B	m	3	9×10^{-2}	4	5×10^{-3}	2	5×10^{-1}	3	4×10^{-1}
η_t^J	n	∞	0	∞	0	∞	0	∞	0
η_t^K	p	∞	0	∞	0	∞	0	∞	0
β_s^J	q	4	1×10^{-3}	7	4×10^{-8}	5	2×10^{-5}	5	2×10^{-5}
β_s^{JK}	r	4	9×10^{-4}	8	6×10^{-9}	6	5×10^{-7}	5	5×10^{-5}
β_s^K	s	4	6×10^{-4}	8	1×10^{-9}	8	1×10^{-9}	6	1×10^{-5}

Table 3.7 Order of magnitude of terms for $\Delta K=1$, $\Delta J=-1$, i.e., ${}^{R}P_{K}(J)$.

Coefficient Descriptive of Term	Table 3.1 Index	Order $J\approx30$ $K\approx30$	Approximate Magnitude (cm^{-1})	Order $J\approx1$ $K\approx1$	Approximate Magnitude (cm^{-1})	Order $J\approx20$ $K\approx1$	Approximate Magnitude (cm^{-1})	Order $J\approx20$ $K\approx10$	Approximate Magnitude (cm^{-1})
A_o	f	1	60	2	3	2	3	1	20
B_o	g	1	120	2	5	1	40	1	60
$A_e\zeta$	h	1	30	2	2	2	2	2	10
D_o^J	i	3	1×10^{-1}	6	4×10^{-6}	3	4×10^{-2}	3	4×10^{-2}
D_o^{JK}	j	4	1×10^{-3}	6	2×10^{-6}	4	1×10^{-3}	4	5×10^{-3}
D_o^K	k	3	1×10^{-1}	5	2×10^{-5}	5	2×10^{-5}	4	5×10^{-3}
α_s^A	l	2	1	4	4×10^{-3}	4	4×10^{-3}	3	1×10^{-1}
α_s^B	m	3	9×10^{-2}	4	4×10^{-3}	3	4×10^{-1}	3	3×10^{-1}
η_t^J	n	3	3×10^{-2}	∞	0	4	8×10^{-4}	4	4×10^{-3}
η_t^K	p	3	3×10^{-2}	6	8×10^{-6}	6	8×10^{-6}	4	1×10^{-3}
β_s^J	q	4	7×10^{-4}	∞	0	6	1×10^{-5}	6	1×10^{-5}
β_s^{JK}	r	4	8×10^{-4}	∞	0	6	2×10^{-6}	5	5×10^{-5}
β_s^K	s	4	7×10^{-4}	7	2×10^{-8}	7	2×10^{-8}	6	1×10^{-5}

Table 3.8 Order of magnitude of terms for $\Delta K=1$, $\Delta J=0$, i.e., $^{R}Q_{K}(J)$.

Coefficient Descriptive of Term	Table 3.1 Index	Order $J\approx30$ $K\approx30$	Approximate Magnitude (cm^{-1})	Order $J\approx1$ $K\approx1$	Approximate Magnitude (cm^{-1})	Order $J\approx20$ $K\approx1$	Approximate Magnitude (cm^{-1})	Order $J\approx20$ $K\approx10$	Approximate Magnitude (cm^{-1})
A_o	f	1	61	2	3	2	3	1	20
B_o	g	1	61	2	3	2	3	1	20
$A_e\zeta$	h	1	31	2	2	2	2	2	10
D_o^J	i	∞	0	∞	0	∞	0	∞	0
D_o^{JK}	j	3	6×10^{-2}	6	2×10^{-6}	4	1×10^{-3}	4	9×10^{-3}
D_o^K	k	3	1×10^{-1}	5	2×10^{-5}	5	2×10^{-5}	4	5×10^{-3}
α_s^A	l	2	1	4	4×10^{-3}	4	4×10^{-3}	3	1×10^{-1}
α_s^B	m	3	3×10^{-2}	4	2×10^{-3}	3	4×10^{-1}	3	3×10^{-1}
η_t^J	n	3	3×10^{-2}	6	4×10^{-6}	4	8×10^{-4}	4	5×10^{-3}
η_t^K	p	3	3×10^{-2}	6	8×10^{-6}	6	8×10^{-6}	4	1×10^{-3}
β_s^J	q	4	9×10^{-4}	8	8×10^{-9}	5	2×10^{-5}	5	2×10^{-5}
β_s^{JK}	r	4	9×10^{-4}	8	8×10^{-9}	6	2×10^{-6}	5	5×10^{-5}
β_s^K	s	4	7×10^{-4}	7	2×10^{-8}	7	2×10^{-8}	6	1×10^{-5}

Table 3.9 Order of magnitude of terms for $\Delta K=1$, $\Delta J=+1$, i.e., $^{R}R_{K}(J)$.

Coefficient Descriptive of Term	Table 3.1 Index	Order $J\approx30$ $K\approx30$	Approximate Magnitude (cm^{-1})	Order $J\approx1$ $K\approx1$	Approximate Magnitude (cm^{-1})	Order $J\approx20$ $K\approx1$	Approximate Magnitude (cm^{-1})	Order $J\approx20$ $K\approx10$	Approximate Magnitude (cm^{-1})
A_o	f	1	61	2	3	2	3	1	20
B_o	g	2	1	2	1	1	40	1	20
$A_e\zeta$	h	1	31	2	2	2	2	2	10
D_o^J	i	3	1×10^{-1}	5	3×10^{-5}	3	4×10^{-1}	3	4×10^{-2}
D_o^{JK}	j	3	1×10^{-1}	6	1×10^{-5}	4	1×10^{-3}	4	1×10^{-2}
D_o^K	k	3	1×10^{-1}	5	2×10^{-5}	5	2×10^{-5}	4	5×10^{-3}
α_s^A	l	2	1	4	4×10^{-3}	4	4×10^{-3}	3	1×10^{-1}
α_s^B	m	3	3×10^{-2}	4	2×10^{-3}	2	5×10^{-1}	3	3×10^{-1}
η_t^J	n	3	3×10^{-2}	6	1×10^{-5}	4	9×10^{-4}	4	5×10^{-3}
η_t^K	p	3	3×10^{-2}	6	8×10^{-6}	6	8×10^{-6}	4	1×10^{-3}
β_s^J	q	4	1×10^{-3}	7	4×10^{-8}	5	2×10^{-5}	5	2×10^{-5}
β_s^{JK}	r	4	1×10^{-3}	7	2×10^{-8}	6	2×10^{-6}	5	6×10^{-5}
β_s^K	s	4	7×10^{-4}	7	2×10^{-8}	7	2×10^{-8}	6	1×10^{-5}

Table 3.10 Order of magnitude of terms for $\Delta K=-1, \Delta J=-1$, i.e., $^{P}P_{K}(J)$.

Coefficient Descriptive of Term	Table 3.1 Index	Order $J\approx30$ $K\approx30$	Approximate Magnitude (cm^{-1})	Order $J\approx1$ $K\approx1$	Approximate Magnitude (cm^{-1})	Order $J\approx20$ $K\approx1$	Approximate Magnitude (cm^{-1})	Order $J\approx20$ $K\approx10$	Approximate Magnitude (cm^{-1})
A_o	f	1	60	2	1	2	1	1	20
B_o	g	1	120	2	1	1	40	1	20
$A_e\zeta$	h	1	30	∞	0	∞	0	2	10
D_o^J	i	3	1×10^{-1}	6	4×10^{-6}	3	4×10^{-2}	3	4×10^{-2}
D_o^{JK}	j	3	1×10^{-1}	6	2×10^{-6}	5	4×10^{-4}	3	2×10^{-2}
D_o^K	k	3	1×10^{-1}	6	1×10^{-6}	6	1×10^{-6}	4	4×10^{-3}
α_s^A	l	2	8×10^{-1}	∞	0	∞	0	3	8×10^{-2}
α_s^B	m	3	3×10^{-2}	∞	0	3	4×10^{-1}	3	3×10^{-1}
η_t^J	n	3	3×10^{-2}	∞	0	∞	0	4	3×10^{-3}
η_t^K	p	3	2×10^{-2}	∞	0	∞	0	4	8×10^{-4}
β_s^J	q	4	8×10^{-4}	∞	0	5	2×10^{-5}	6	1×10^{-5}
β_s^{JK}	r	4	7×10^{-4}	∞	0	∞	0	5	3×10^{-5}
β_s^K	s	4	6×10^{-4}	∞	0	∞	0	6	8×10^{-6}

Table 3.11 Order of magnitude of terms for $\Delta K=-1$, $\Delta J=0$, i.e., $^{P}Q_{K}(J)$.

Coefficient Descriptive of Term	Table 3.1 Index	Order $J\approx30$ $K\approx30$	Approximate Magnitude (cm^{-1})	Order $J\approx1$ $K\approx1$	Approximate Magnitude (cm^{-1})	Order $J\approx20$ $K\approx1$	Approximate Magnitude (cm^{-1})	Order $J\approx20$ $K\approx10$	Approximate Magnitude (cm^{-1})
A_o	f	1	60	2	1	2	1	1	20
B_o	g	1	60	2	1	2	1	1	20
$A_e\zeta$	h	1	30	∞	0	∞	0	2	10
D_o^J	i	∞	0	∞	0	∞	0	∞	0
D_o^{JK}	j	3	6×10^{-2}	6	2×10^{-6}	5	4×10^{-4}	4	6×10^{-3}
D_o^K	k	3	1×10^{-1}	6	1×10^{-6}	6	1×10^{-6}	4	4×10^{-3}
α_s^A	l	2	8×10^{-1}	∞	0	∞	0	3	8×10^{-2}
α_s^B	m	3	9×10^{-2}	4	4×10^{-3}	3	4×10^{-1}	3	4×10^{-1}
η_t^J	n	3	3×10^{-2}	∞	0	∞	0	4	4×10^{-3}
η_t^K	p	3	2×10^{-2}	∞	0	∞	0	4	8×10^{-4}
β_s^J	q	4	9×10^{-4}	8	8×10^{-9}	5	2×10^{-5}	5	2×10^{-5}
β_s^{JK}	r	4	8×10^{-4}	∞	0	∞	0	5	3×10^{-5}
β_s^K	s	4	6×10^{-4}	∞	0	∞	0	6	8×10^{-6}

Table 3.12 Order of magnitude of terms for $\Delta K=-1$, $\Delta J=+1$, i.e., $^{P}R_{K}(J)$.

Coefficient Descriptive of Term	Table 3.1 Index	Order $J\approx30$ $K\approx30$	Approximate Magnitude (cm^{-1})	Order $J\approx1$ $K\approx1$	Approximate Magnitude (cm^{-1})	Order $J\approx20$ $K\approx1$	Approximate Magnitude (cm^{-1})	Order $J\approx20$ $K\approx10$	Approximate Magnitude (cm^{-1})
A_o	f	1	60	2	1	2	1	1	20
B_o	g	1	120	2	5	1	40	1	60
$A_e\zeta$	h	1	30	∞	0	∞	0	2	10
D_o^J	i	3	1×10^{-1}	5	3×10^{-5}	3	4×10^{-2}	3	4×10^{-2}
D_o^{JK}	j	4	3×10^{-3}	6	2×10^{-6}	5	4×10^{-4}	3	5×10^{-2}
D_o^K	k	3	1×10^{-1}	6	1×10^{-6}	6	1×10^{-6}	4	4×10^{-3}
α_s^A	l	2	8×10^{-1}	∞	0	∞	0	3	8×10^{-2}
α_s^B	m	3	2×10^{-1}	4	6×10^{-3}	2	5×10^{-1}	3	4×10^{-1}
η_t^J	n	3	3×10^{-2}	∞	0	∞	0	4	4×10^{-3}
η_t^K	p	3	2×10^{-2}	∞	0	∞	0	4	8×10^{-4}
β_s^J	q	4	1×10^{-3}	7	4×10^{-8}	5	2×10^{-5}	5	2×10^{-5}
β_s^{JK}	r	4	8×10^{-4}	∞	0	∞	0	5	4×10^{-5}
β_s^K	s	4	6×10^{-4}	∞	0	∞	0	6	8×10^{-6}

perhaps physically insignificant or meaningless. One should remember especially that order of magnitude considerations are a guide, and at times only a rather approximate guide. None the less, order of magnitude considerations serve as a starting point and often can be time and effort saving if properly applied. In Chapter 5 some of these considerations are discussed in more detail.

CHAPTER 4

COMBINATION DIFFERENCES

Combination differences are a powerful analytical tool available to the spectroscopist (12). In this chapter various uses of combination differences in the analysis of axially symmetric molecules (symmetric due to a three-fold or higher axis of symmetry) are considered. Perhaps the most significant development is that all ground state combination differences can be described by a single analytical function of the ground state quantum numbers and the changes in the quantum numbers for the transition involved, i.e., in terms of J, K, ΔJ and ΔK. As a result, a relatively simple least squares analysis of all observed ground state combination differences for a given molecule provides statistically favorable values of B_o, D_o^J and D_o^{JK} for the molecule. However, in so far as the other ground state constants A_o, D_o^K,... are concerned, the spectroscopist must still rely on analysis of spectral lines or other means in order to obtain values of these constants as they cannot be obtained from "true" combination differences.

In the event that good values of B_o, D_o^J and D_o^{JK} are already available from analysis of microwave spectra of pure rotation transitions, or from a good analysis of infrared data, numerical values of the ground state combination differences can be calculated and used as an invaluable aid in the assignment or verification of assignment of transitions

in infrared spectra.

Where a molecule has only at best a small permanent dipole moment, and the pure rotation spectra is not observed, the method of simultaneous analysis of all available ground state combination differences can provide the statistically most favorable values of B_0, D_0^J and D^{JK} available. CH_3D and CD_3H fall into this category, and application of the method of this chapter to these molecules is discussed in Chapter 9.

It is also possible to represent simultaneously all observed upper state combination differences from an individual parallel band or from a perpendicular band.[11] However, the expressions obtained are applicable only in the absence of perturbations.

Definition of Ground State Combination Differences

Consider a generic binary combination of transitions with a common upper state:

$$^{\Delta K_1}\Delta J_{1_{K_1}}(J_1-\Delta J_1)-{}^{\Delta K_2}\Delta J_{2_{K_2}}(J_2-\Delta J_2)$$

where in order that the two transitions have a common upper state it is necessary that $K_1 = K_2$, $\Delta K_1 = \Delta K_2$, with $J_1 = J_2$, and with ΔJ_1 and ΔJ_2 standing in relation to each other

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[11] For a parallel band the expression is simple and quite similar to the ground state combination difference expression. For a perpendicular band the expression is more complicated.

as (+1,-1), (0,-1), (+1,0). That these provide the conditions required for a common upperstate in the absence of perturbation is evident since:

$$ {}^{\Delta K}\Delta J_{1_K}(J-J_1) - {}^{\Delta K}\Delta J_{2_K}(J-J_2) = $$

$$F'(K+\Delta K,J)-F''(K,J-\Delta J_1)-F'(K+\Delta K,J)+F''(K,J-\Delta J_2) = \qquad (4.1)$$

$$F''(K,J-\Delta J_2)-F''(K,J-\Delta J_1),$$

where F'' is the ground state term value and F' is the upper state term value. If one refers to Fig. 4.1 where examples of each type of allowed transition for parallel and perpendicular bands are shown, one can see that the conditions given above insure that the binary combination of Eq. (4.1) does have a common upper state and is therefore a true ground state combination difference.

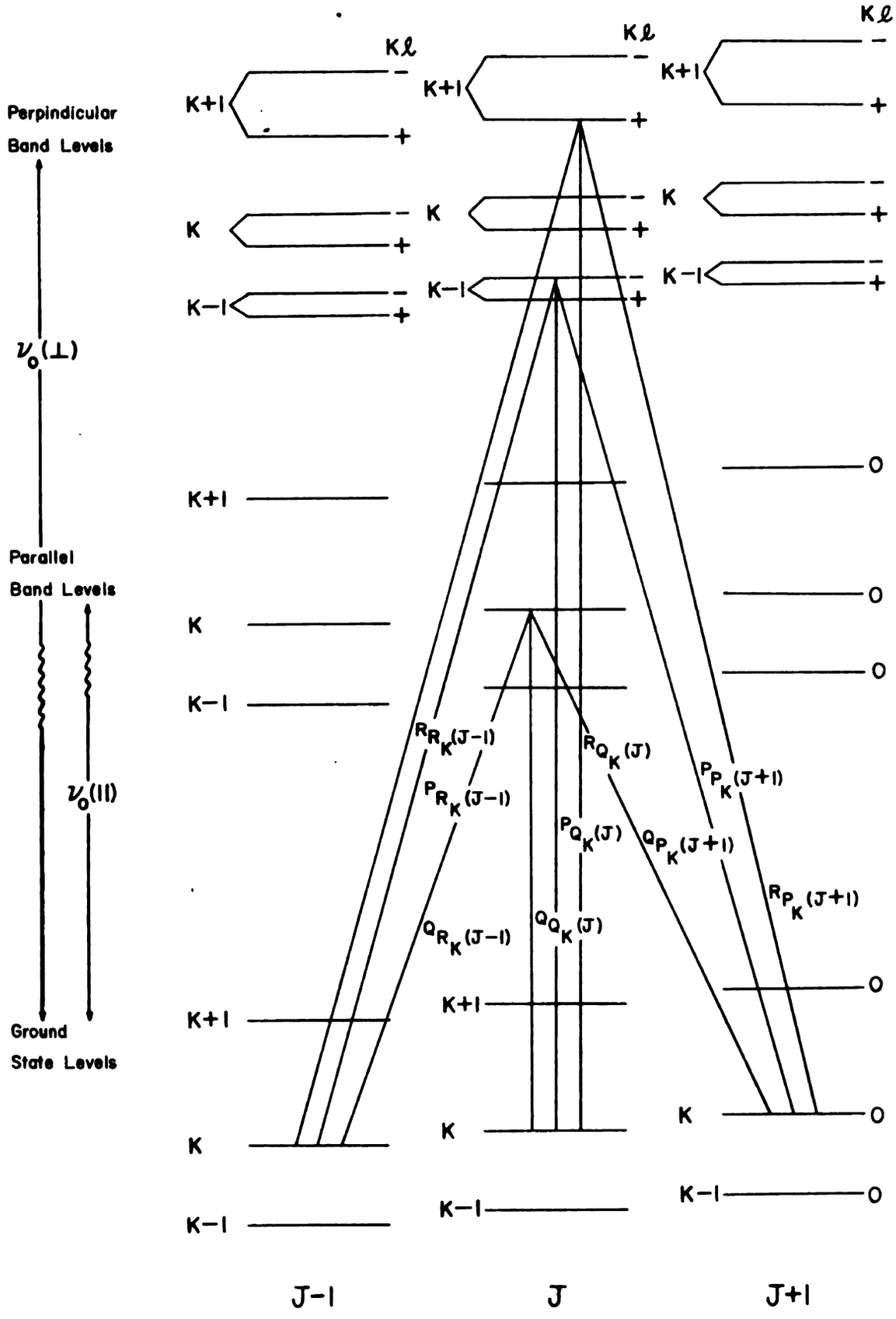
Some care must be exercised in the event that the transition terminates on an (A_1A_2) degenerate upper level. Since it is possible that a perturbation may split the upper level, the various transitions terminating on the degenerate (A_1A_2) level might now terminate on two different (energy-wise) levels.[12] An example of this occurrence is found in Chapter 8 where a Coriolis resonance splits the $K=\ell=\pm1$ upper levels.[13]

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[12] When possible one modifies the expression for the ground state combination differences to take such a perturbation of known form into account.

[13] For details in this instance refer to Chapter 8.

Fig. 4.1 Ground state combination differences.



Furthermore, when a molecule has a non-zero inversion splitting, the ground state combination differences associated with the + inversion vibrational ground state only (or the - inversion ground state), should be fit simultaneously since effectively the B_o, D_o^J and D_o^{JK} are different in the + and - inversion ground states.

In the event that the "ground state" is the lower level of a hot band (12), care must be exercised since the expressions relative to ground state combination differences in this chapter apply, strictly, only to the case where the ground state is the vibrational ground state, the so called "zero vibrational state".

Simultaneous Representation of All "Nine" Types of Ground State Combination Differences

In the literature one generally finds distinct individual expressions for the "different" ground state combination differences given, e.g. as

$$\Delta K_{R_K}(J) - \Delta K_{Q_K}(J+1) = 2(B_o - K^2 D_o^{JK})(J+1) - 4D_o^J(J+1)^3 \qquad (4.2a)$$

$$\Delta K_{Q_K}(J) - \Delta K_{P_K}(J+1) = 2(B_o - K^2 D_o^{JK})(J+1) - 4D_o^J(J+1)^3 \qquad (4.2b)$$

$$\Delta K_{P_K}(J-1) - \Delta K_{P_K}(J+1) = \left[4(B_o - K^2 D_o^{JK}) - 6D_o^J\right](J+\tfrac{1}{2}) - 8D_o^J(J+\tfrac{1}{2})^3 \qquad (4.2c)$$

On the surface it appears that one has at least two irreconcilable expressions, and that if one had, for example, ten combination differences represented by Eq. (4.2a) and

two represented by Eq. (4.2c), the two represented by Eq. (4.2c) could not be combined with the other ten. Or in another instance, if one had data for ground state combination differences from two bands, one of which yields data represented by Eq. (4.2a) and the other represented by Eq. (4.2c) it would seem that there was no way, other than by averaging the resulting values for the constants, of combining the data to get the best ground state constants. A different mistake is sometimes made regarding ground state combination differences, i.e., one might think that since

$$(R-P) = (R-Q) + (Q-P)$$

(for appropriate J values), no new information is contained in the third possible difference (e.g. Q-P, where R-P and R-Q are also known). This neglects to take into account the manner in which the data is fit, i.e., the way in which the three members enter into the normal equations involved in the least squares fitting of the data.

We have been able to write a single expression which represents simultaneously all possible ground state combination differences. This relation is given by:

$$\Delta''(K,\Delta K,J,\Delta J_1,\Delta J_2) = {}^{\Delta K}\Delta J_{1_K}(J-\Delta J_1) - {}^{\Delta K}\Delta J_{2_K}(J-\Delta J_2) =$$

$$\left\{B_o - K^2 D_o^{JK} - D_o^J \left[2J(J+1) - \delta_1 - \delta_2\right]\right\}(\delta_1 - \delta_2) \qquad (4.3)$$

where $$\delta_i = (2J+1-\Delta J_i)\Delta J_i\,, \qquad i = 1 \text{ or } 2. \qquad (4.3a)$$

This expression simultaneously represents all "nine" types of ground state combination differences; this

expression allows the simultaneous least squares analysis of <u>all</u> ground state combination differences of a particular molecule thus leading to the statistically most favorable results available from a particular set of data.

In making use of Eq. (4.3) it is necessary that the values of J given below in Eq. (4.5) and Eq. (4.6) be used; i.e., calling the combination difference

$$\begin{aligned}\Delta''(K,\Delta K,J,\Delta J_1,\Delta J_2) &= {}^{\Delta K}\Delta J_{1_K}(J-\Delta J_1) - {}^{\Delta K}\Delta J_{2_K}(J-\Delta J_2) \\ &= \Delta J_1,\Delta J_2,K,J\end{aligned} \tag{4.4}$$

we have from parallel bands

$$\begin{aligned}
{}^{Q}R_K(J-1) - {}^{Q}Q_K(J) &= RQK,J && a \\
{}^{Q}Q_K(J) - {}^{Q}P_K(J+1) &= QPK,J && b \\
{}^{Q}R_K(J-1) - {}^{Q}P_K(J+1) &= RPK,J && c
\end{aligned} \tag{4.5}$$

and from perpendicular bands

$$\begin{aligned}
{}^{R}Q_K(J) - {}^{R}P_K(J+1) &= QPK,J && a \\
{}^{R}R_K(J-1) - {}^{R}Q_K(J) &= RQK,J && b \\
{}^{R}R_K(J-1) - {}^{R}P_K(J+1) &= RPK,J && c \\
{}^{P}Q_K(J) - {}^{P}P_K(J+1) &= QPK,J && d \\
{}^{P}R_K(J-1) - {}^{P}Q_K(J) &= RQK,J && e \\
{}^{P}R_K(J-1) - {}^{P}P_K(J+1) &= RPK,J. && f
\end{aligned} \tag{4.6}$$

It should be noted that these differ from Eq. (4.2a) in the J value used relative to Eq. (4.2b) and Eq. (4.2c); also, we point out that Δ" is independent of ΔK except that both transitions used in the binary combination must have the same ΔK. [14]

Equation (4.3) then allows one to make full use of each ground state combination difference obtainable for a particular molecule and leads thereby to the statistically most favorable set of molecular constants B_0, D_0^J, D_0^{JK} which can be obtained from a given set of infrared spectral data. In Chapter 8 the methods described in this chapter are applied to a perpendicular band of CH_3F. In this case however, good values of the constants B_0, D_0^J and D_0^{JK} are already available from the microwave spectra of pure rotation transitions. However, if the pure rotation spectra is not observable in the microwave region as is the case for CHD_3 and CH_3D (which have a very small permanent dipole moment), we can obtain statistically favorable values of B_0, D_0^J and D_0^{JK} following the method outlined in this chapter. This was done for two parallel bands, $\nu_2 + \nu_3$ of CH_3D and $\nu_1 + \nu_2$ of CHD_3, and is discussed in Chapter 9.

Calculated Ground State Combination Differences for Use in the Assignment of Transitions

In the case of axially symmetric molecules which possess

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[14] That is, both transitions in a given combination difference must come from the same subband.

a permanent electric dipole moment, analysis of the pure rotation spectra in the microwave region yields very accurate values of some of the molecular parameters for the ground state, i.e., B_o, D_o^J, D_o^{JK}. The methyl halides, a family of molecules of particular interest in this work, have been thoroughly investigated by microwave spectroscopists (52-59), and accurate ground state constants are available. In these cases, as well as in cases where good values of B_o, D_o^J, and D_o^{JK} are available from infrared data, the ground state combination differences may be computed and the numerical values used as a valuable aid in the assignment of transitions in complex spectra. This was done in the case of the perturbed band $\nu_3 + \nu_4$ of CH_3F discussed in Chapter 8 and proved to be very valuable in assignment and analysis. Any modest size computer may be programmed to perform this computation so that complete tables of $\Delta''(K, J, \Delta J_1, \Delta J_2)$ may be obtained. Appendix II contains such a table for CH_3F, Appendix III, for CHD_3, and Appendix IV, for CH_3D.[15]

Simultaneous Representation of Upper State Combination Differences

In the event that one has an unperturbed band or bands of an axially symmetric molecule which allows one to obtain a number of upper state combination differences, one can perform a simultaneous least squares analysis. The appropriate

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[15] For CH_3F, B_o, D_o^J, and D_o^{JK} were taken from the results of microwave spectral analysis (58). For CH_3D and CHD_3 the values of B_o, D_o^J, and D_o^{JK} were obtained from our analysis (cf. Chapter 9).

combination differences are

$$\Delta'(K,\Delta K,J,\Delta J,\Delta J_2)={}^{\Delta K}\Delta J_{1_K}(J)-{}^{\Delta K}\Delta J_{2_K}(J)=\Delta J_1,\Delta J_2,K,J \qquad (4.7)$$

and the resulting expression for the upper state combination differences may be written as

$$\begin{aligned}
&{}^{\Delta K}(\Delta J_1)_K(J_1)-{}^{\Delta K}(\Delta J_2)_K(J_2)= \\
&\Big\{\Big[B_o-\textstyle\sum_s \alpha_s^B v_s\Big]+\Big[\sum_t \eta_t^J \ell_t\Big]\,[K+\Delta K]+ \qquad (4.8)\\
&\Big[-D_o^{JK}+\textstyle\sum_s \beta_s{}^{JK} v_s\Big]\,[(K+\Delta K)^2]+ \\
&\Big[-D_o^{J}+\textstyle\sum_s \beta_s{}^{J} v_s\Big]\,[2J(J+1)+\delta_1+\delta_2]\Big\}\,(\delta_1-\delta_2)
\end{aligned}$$

with

$$\delta_i=(2J+1+\Delta J_i)\Delta J_i\,, \qquad i=1 \text{ or } 2. \qquad (4.9)$$

Thus, using Eq. (4.8) one may analyze simultaneously the three "types" of upper state combination differences from a parallel band, i.e.,

$$\begin{aligned}
&{}^{Q}R_K(J)-{}^{Q}Q_K(J)=RQK,J && \text{a}\\
&{}^{Q}Q_K(J)-{}^{Q}P_K(J)=QPK,J && \text{b} \qquad (4.10)\\
&{}^{Q}R_K(J)-{}^{Q}P_K(J)=RPK,J && \text{c}
\end{aligned}$$

or the six from a perpendicular band

$$\begin{aligned}
&{}^{R}Q_K(J)-{}^{R}P_K(J)=QPK,J && \text{a}\\
&{}^{R}R_K(J)-{}^{R}Q_K(J)=RQK,J && \text{b}\\
&{}^{R}R_K(J)-{}^{R}P_K(J)=RPK,J && \text{c}
\end{aligned}$$

$$^{P}Q_{K}(J)-{}^{P}P_{K}(J)=QPK,J \qquad d \qquad (4.11)$$

$$^{P}R_{K}(J)-{}^{P}Q_{K}(J)=RQK,J \qquad e$$

$$^{P}R_{K}(J)-{}^{P}P_{K}(J)=RPK.J \qquad f$$

One must of course realize that due to the difference of the various upper state constants from band to band, upper state combination differences from only one band may be fit simultaneously.

In the case of a parallel band with all $l_t = 0$ in the upper state [16] the term containing η_t^J is identically zero and must not be included in an analysis of parallel band upper state combination differences.

In the event that a band is perturbed by a perturbation of known form, it may sometimes be possible to modify Eq. (4.8) to include the effect of the perturbation and still carry out the upper state combination difference analysis.

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[16] An exception to this is the case of a parallel band which is one component of the band $\nu_t + \nu_t$, for example. Here the η_t^J term must be retained.

CHAPTER 5

ANALYSIS OF ROTATION-VIBRATION SPECTRA OF AXIALLY SYMMETRIC MOLECULES USING A COMPUTER PROGRAMMED ANALYSIS SCHEME

The analysis of rotation-vibration spectra is facilitated by the use of electronic computers. We use a computer in our analysis scheme because of the ease, speed, precision, and accuracy with which the computer can carry out the varied and often quite complicated numerical calculations required. However, many of the considerations discussed in this chapter should also be useful for an analysis carried out with a desk calculator. None of the computations are impossible to perform on a desk calculator, although it would be a rather Herculean task in some cases.

Before one begins to make use of the computer it is necessary to identify the observed transitions in the spectrum, i.e., to assign the quantum numbers of the ground state, and the changes in the quantum numbers for the transition being considered. The discussion which follows is based on the assumption that one uses only transitions which have been correctly identified and that the numerical values of the frequencies of the observed transitions are

available.[17]

In order to perform an analysis it is necessary to set down an expression for the transition frequencies which will be used in the analysis of the spectrum; the analysis is then carried out by the method of least squares (50,60,61) which gives the best unbiased linear estimator of the transition frequency expression (50).[18] From the analysis we can also determine certain statistical information about the molecular constants which are determined.

The description which follows is divided into two parts; the first concerns the computer analysis scheme, the second concerns the transition frequency expression to be used.

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[17]In the process of assignment, several specific aids (apart from experience) are available. The absence of transitions for which $K > J$ in either the lower or upper state is an aid to unequivocal assignment of the quantum numbers of the observed transitions (12). Relative intensities also provide an aid to assignment (12); however, they cannot be considered to be of the same quality as considerations relative to missing lines since intensity anomalies are not a rarity. A great aid to assignment is the use of ground state combination differences. If good values for B_o, D_o^{JK} and D_o^J are available, the various ground state combination differences can be calculated. Then, if one transition of the binary pairs in Eqs. (4.5) and (4.6) has been identified, the frequency of the second member of the pair may be calculated.

[18]The transition frequency is assumed to be a linear function of the molecular parameters, an assumption borne out in all the expressions we have used.

Analysis Scheme and Computer Program

In this section we assume that a specific transition frequency has been selected, e.g.,

$$\nu = a + b(J\Delta J) + c(J+\Delta J)^2 + d(K\Delta K) \qquad (5.1)$$

where a, b, c, and d are molecular constants (such as B_0, D_0^J, etc.) or combination of molecular constants. Furthermore, we have n sets of data labeled

$$\{K_i, J_i, \Delta K_i, \Delta J_i, \nu_i\} \qquad (5.2)$$

for the n observed transitions of frequency ν_i.

The mechanics of the analysis scheme involves computing the normal equations (50) given in Table 5.1 for a least squares analysis based on Eq. (5.1) (or whatever equation is to be used). Then, the normal equations must be solved [19] for the numerical values of the constant coefficients (e.g., a, b, c, d in Eq. (5.1)). In the process of the solution of the normal equations it is valuable to find the inverse of the normal equation matrix (50) since the inverse is utilized in the statistical interpretation of the results. The numerical values of the constants obtained from the least squares analysis (e.g., a, b, c, d in Eq. (5.1)) are used in the line frequency expression (e.g., Eq. (5.1)) to calculate a value for each observation, $\nu_{i_{obs}}$. The calculated value is called $\nu_{i_{calc}}$, and the difference

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[19] The normal equations for a frequency expression used to find p constants (e.g., a, b, c, d in Eq. (5.1)) form a set of p simultaneous linear equations.

Table 5.1 Normal equations for Eq. (5.1), (all sums over i from 1 to n).

$$
\begin{array}{llll}
a\sum 1 & + b\sum J_i\Delta J_i & + c\sum (J_i+\Delta J_i)^2 & + d\sum K_i\Delta K_i = \sum \nu_i \\
a\sum J_i\Delta J_i & + b\sum (J_i\Delta J_i)^2 & + c\sum (J_i\Delta J_i)(J_i+\Delta J_i)^2 & + d\sum (J_i\Delta J_i)(K_i\Delta K_i) = \sum \nu_i J_i\Delta J_i \\
a\sum (J_i+\Delta J_i)^2 & + b\sum (J_i\Delta J_i)(J_i+\Delta J_i)^2 & + c\sum (J_i+\Delta J_i)^4 & + d\sum (J_i+\Delta J_i)^2(K_i\Delta K_i) = \sum \nu_i (J_i+\Delta J_i)^2 \\
a\sum K_i\Delta K_i & + b\sum J_i\Delta J_i K_i\Delta K_i & + c\sum (J_i+\Delta J_i)^2(K_i\Delta K_i) & + d\sum (K_i\Delta K_i)^2 = \sum \nu_i (K_i\Delta K_i)
\end{array}
$$

$$\Delta_i(o-c) = \nu_{i_{obs}} - \nu_{i_{calc}} \tag{5.3}$$

is computed. The sum of the squares of the $\Delta_i(o-c)$ is also formed for use in statistical analysis.[20] If n observations ν_i are used, and p constants determined, then

$$s^2 = \frac{\sum_{i=1}^{n} \left[\Delta_i(o-c)\right]^2}{n-p} \tag{5.4}$$

is an unbiased estimator of the variance of the parent statistical distribution of the errors in the observations (50). We call

$$s = \left[\frac{\sum_{i=1}^{n} \left[\Delta_i(o-c)\right]^2}{n-p}\right]^{\frac{1}{2}} \tag{5.5}$$

the standard deviation of the points, i.e., of the observations ν_i.

In addition, if the generic constant determined is b_j, then the corresponding diagonal element of the inverse of the normal equation matrix, N_{jj}^{-1}, is related to the standard deviation of the constants determined as (50)

$$s_{b_j} = s^2 N_{jj}^{-1} \tag{5.6}$$

and the simultaneous confidence interval (50) for the "true" value β_j of the constant estimated by b_j with a

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[20] The statistical considerations described in this chapter have been taken from a recent Doctoral thesis by J.W. Boyd (50).

confidence coefficient (50) of $(1-\alpha)$ is given by

$$b_j \pm S\Delta_{b_j} \tag{5.7}$$

where

$$S = pF_\alpha(p,n-p) \tag{5.8}$$

p is the number of constants determined, n is the number of observations used, and $F_\alpha(p,n-p)$ are tabulated values of the F distribution (62, 63, 64). One interpretation which may be made regarding the confidence interval $b_j \pm S\Delta_{b_j}$ is that if we consider the data used, i.e. a particular spectrum, to be a sampling of an infinite sample population, i.e., all conceivable records of the spectrum obtained by whatever observer, wherever, whenever, the probability that $b_j \pm S\Delta_{b_j}$ will contain the "true" value of the constant β_j for our data is $(1-\alpha)$.[21]

Furthermore, Boyd (50) points out that the test to determine whether a particular b_j is significant in the fit of the data, i.e., whether the data depends significantly upon the term of which a particular b_j is the coefficient, is performed by comparing the ratio $|b_j|/\Delta_{b_j}$ with S. If

$$\begin{aligned} \frac{|b_j|}{\Delta_{b_j}} > S &\Rightarrow \text{significant} \\ \frac{|b_j|}{\Delta_{b_j}} < S &\Rightarrow \text{not significant} \end{aligned} \tag{5.9}$$

---

[21] Boyd (50) presents a more detailed discussion of the use of simultaneous confidence intervals in the analysis of spectral data.

When a term is found to be significant it is of course retained in the fit. If it is insignificant it should be dropped from the fit.[22] In this case there are two possible interpretations. They are, that no such term should be in the expression used or that the data used is not sufficient to determine the constant coefficient of the term.

The foregoing analysis scheme has been programmed for the Michigan State University digital computer, MISTIC (65). The program DAEA embodies a flexible symmetric top analysis scheme patterned after the above discussion. Data is punched on IBM cards as

ΔK	ΔJ	K,J	frequency	Δν	weight
F	Q	0,5	0000.0000	.0000	00.00

where weighting (50) may be effected using either the weight or the Δν taken, of course, from the appropriate card columns. The latter is assumed to be related to the weight w as

$$w = \frac{(\mathrm{NORM})^2}{(\Delta\nu)^2} \qquad (5.10)$$

Equation (5.10) implies the assumption that the errors in the observations, i.e., in the ν_i, are statistically randomly distributed and all removable or known biases removed. The Norm simply allows one to obtain an average weight of 1 regardless of the quality of observations used in a least squares fit.

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[22] For a derivation of these results as well as a more detailed discussion, cf. Boyd (50).

The polynomial to which the data is to be fit is specified by the program user. For example, Eq.(5.1) may be specified with punched tape input to the computer as

$$\begin{aligned} &F0. = 1. \\ &F1 = 3x5. \\ &F2 = 3x3+3x5+3x5+5x5. \qquad (5.11) \\ &F3 = 2x4. \\ &N = 6. \end{aligned}$$

where the indices 1,2,3,4,5,6 refer to 1,K,J,ΔK,ΔJ,ν, respectively.

Upon input of the polynomial specification tape and the data cards, the computer executes a least squares fit of the data, and outputs the least squares estimators of the constant coefficients,[23] the standard deviations of the constants, i.e., the λ_{b_j}'s, the calculated ν and the observed ν for each point fit, the Δ_i(o-c) for each point fit, and the standard deviation of the points, i.e., the λ.

In addition, provision is made to compare other observations not included in the least squares fit and also to calculate additional transition frequencies.

The use of the computer programmed analysis scheme allows the spectroscopist to take advantage of the generalized

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[23] The program employs double-precision floating point arithmetic which is equivalent to approximately 20 decimal digits. Solution of the normal equations is accomplished by a Crout reduction (66) and round-off error for a well conditioned set of equations has been found to be insignificant for a 13x13 normal equation matrix.



transition frequency expression in Table 3.1 to analyze simultaneously, for example, all transitions observed in a single perpendicular band. In general, if one were forced to rely on a desk calculator, it would not be feasible to attempt to simultaneously analyze all transitions of a given band, determining for example nine constants from 315 transitions as was done by Boyd (50) in a simultaneous analysis of both the parallel and perpendicular components of $2\nu_4$ of CD_3I. In addition, as was pointed out in Chapter 3, simultaneous analysis insures consistency of analysis since it prevents one from obtaining and using several values (however nearly equal these may be) for the same constant, as happens when one analyzes one subband at a time (4).

Method of Analysis and Generalized Transition Frequency Expression Suitable for Analysis

We shall outline the approach we use in the analysis of a perpendicular band $\nu_n + \nu_t$ of an axially symmetric molecule of the form ZXY_3. The very same approach may be used for a parallel band or a combination of bands.

The first point to consider is the question of linear independence of the terms to be fit to the data.[24] Essentially, linear dependence, which makes the solution of the normal equations impossible or meaningless, results when

[24] For a detailed discussion of linear independence in reference to $2V_4$ $\parallel$ and $\perp$ of CD_3I cf. Boyd (50).

a given quantum dependence of a constant to be determined is a linear combination of any of the quantum dependences of the other constants to be determined. For example, because of linear dependence it is not possible to determine individually A_o, α^A, ζ_t^Z, ν_o, η_t^K and D_o^K from a single perpendicular band of the type $\nu_n + \nu_t$. One can only obtain linear combinations of these constants from such an analysis.

Using the generalized transition frequency expression from Table 3.1, taking care to avoid linear dependence, the most general transition frequency expression suitable for analysis of $\nu_n + \nu_t$ is given in Table 5.2. The selection rule $\Delta\ell = \Delta K$, from Table 2.1, is incorporated in the expression given in Table 5.2. In addition, all sums appearing in Table 3.1 except the one involving $\eta_{t,s}$ are written out explicitly.

Using the expression in Table 5.2 it is possible to perform a least squares analysis of the assigned transitions and frequencies of the band $\nu_n + \nu_t$. We have found that an efficient way to proceed is to fit the data to a first approximation to the expression of Table 5.2 to check assignments and measurements of frequencies. The reasoning is that a "low order fit" of the data will indicate errors of this sort since there are only a few variables available to the least squares fit to be adjusted to best represent the data. On the other hand, if the full expression of Table 5.2 is used in preliminary analyses, there are so many variables to be adjusted that errors in assignment or measure-

Table 5.2 Generalized transition frequency expression suitable for the least squares analysis of $\nu_n + \nu_t$.

$^{\Delta K}\Delta J_K(J) =$	Index
$\left[\nu_o - A_e\zeta_t^z + \frac{1}{2}\eta_t + \frac{1}{2}\sum_s \eta_{t,s}(v_s + \frac{g_s}{2}) - \frac{1}{4}\eta_t^K\right] +$	a
$\left[A_o - A_e\zeta_t^z + \frac{1}{2}\eta_t + \frac{1}{2}\sum_s \eta_{t,s}(v_s + \frac{g_s}{2}) - \frac{1}{2}\eta_t^K\right]\left[2K\Delta K + \Delta K^2\right] +$	b
$\left[\alpha_n^A + \alpha_t^A - \frac{5}{2}\gamma_{tn}^A - 3\gamma_{tt}^A - 2\gamma_{nn}^A - \gamma_{(g)tt}^A - \alpha_n^B - \alpha_t^B + \frac{5}{2}\gamma_{tn}^B + 3\gamma_{tt}^B + 2\gamma_{nn}^B + \gamma_{(g)tt}^B - \frac{3}{2}\eta_t^K\right]\left[-(K+\Delta K)^2\right] +$	c
$\left[D_o^K - \frac{1}{4}\eta_t^K\right]\left[-(K+\Delta K)^4 + K^4\right] +$	d
$\left[\beta_n^K + \beta_t^K\right]\left[(K+\Delta K)^4\right] +$	e
$\left[B_o\right]\left[(J+\Delta J)(J+1+\Delta J) - (2K\Delta K + \Delta K^2)\right] +$	f
$\left[\alpha_n^B + \alpha_t^B - \frac{5}{2}\gamma_{tn}^B - 3\gamma_{tt}^B - 2\gamma_{nn}^B - \gamma_{(g)tt}^B\right]\left[-(J+\Delta J)(J+1+\Delta J)\right] +$	g
$\left[D_o^{JK}\right]\left[-(K+\Delta K)^2(J+\Delta J)(J+1+\Delta J) + K^2J(J+1)\right] +$	h
$\left[D_o^J\right]\left[-(J+\Delta J)^2(J+1+\Delta J)^2 + J^2(J+1)^2\right] +$	i

Table 5.2 Continued.

$\left[\eta_t^J\right]\left[(J+\Delta J)(J+1+\Delta J)(K+\Delta K)\Delta K\right] +$	j
$\left[\beta_n^{JK}+\beta_t^{JK}\right]\left[(K+\Delta K)^2(J+\Delta J)(J+1+\Delta J)\right] +$	k
$\left[\beta_n^J+\beta_t^J\right]\left[(J+\Delta J)^2(J+1+\Delta J)^2\right]$	l

ment may easily be concealed.[25]

Using the theoretical order of magnitude Tables 3.1 - 3.12 for the appropriate types of transitions involved, it is a straightforward process to obtain a first approximation to the expression in Table 5.2. Assume that we have transitions up to $K \approx 10$ and $J \approx 20$ and of the type ${}^{R}R_{K}(J)$ and ${}^{P}P_{K}(J)$. Then, from Tables 3.3, 3.9 and 3.10, taking terms through third order,[26] the appropriate expression to begin with would be the sum of the terms a,b,c,f,g,h,i from Table 5.2.

If as mentioned in Chapter 4, good values of the constants B_o, D_o^J, D_o^{JK} are available from microwave spectroscopy studies, these values should be substituted into the expression from Table 5.2 which is used and the value of the terms for each transition subtracted from the observed frequencies.[27]

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[25] Admittedly, the value of the constants obtained from such an erroneous high order fit could indicate the presence of errors. Even so, the deviations of the observed and the calculated transition frequencies would not indicate which transitions were in error as readily as in low order fit.

[26] These are expected to make a contribution to some transitions of approximately $0.02 cm^{-1}$ or greater on the basis of the theoretical magnitude of the constants in Table 1.8.

[27] In the event that one uses a desk calculator to carry out an analysis, the observed frequencies can be modified in this manner one time only, and the resulting modified frequencies used in all subsequent calculations.

Whenever, as for many molecules of the C_{3v} family, B_o, D_o^J and D_o^{JK} are known from microwave work, we shall assume that the dependence of the observed frequencies on these constants can be eliminated. Thus, as a first approximation in the analysis of $\nu_n + \nu_t$ the expression given in Table 5.3 would be suitable.

Since we assume B_o, D_o^J and D_o^{JK} to be available, the first approximation used contains only four variables which may be adjusted to obtain the best fit, i.e., $\nu_o - A_e\zeta_t^Z$, $A_o - A_e\zeta_t^Z$, $\alpha_n^A + \alpha_t^A$, and $\alpha_n^B + \alpha_t^B$. Under these conditions errors in assignment and measurement have been found to be readily located by scanning the Δ_1(obs-calc) results.

After all obvious errors have been eliminated, and the results of a fit to the expression of Table 5.3 have been obtained, the constants determined should be tested for significance as indicated by Eqs.(5.9). We shall assume, as is usually the case, that all constants from the fit based on the expression of Table 5.3 are significant. (If any are insignificant, they should be dropped and the data refit to the remaining expression.)

At this point, one proceeds by fitting the data to the expression of Table 5.3 plus each of the remaining terms in Table 5.2, one term at a time. That is, we would fit the expression of Table 5.3 plus d from Table 5.2, then Table 5.3 plus e, then plus j, then plus k, then plus l. The significance of d,e,j,k, and l is then tested with

Table 5.3 *First approximation of the expression in Table 5.2 for the preliminary analysis of* $\nu_n + \nu_t$.

$\left[{}^{\Delta K}\Delta J_K(J) \right]_{OBS} +$	Index
$B_o\left[-(J+\Delta J)(J+1+\Delta J)+(2K\Delta K+\Delta K^2)\right] +$	f
$D_o^{JK}\left[-(K+\Delta K)^2(J+\Delta J)(J+1+\Delta J)+K^2J(J+1)\right] +$	h
$D_o^{J}\left[-(J+\Delta J)^2(J+1+\Delta J)^2+J^2(J+1)^2\right] =$	i
$\left[\nu_o - A_e\zeta_t^z\right] +$	a
$\left[A_o - A_e\zeta_t^z\right]\left[2K\Delta K+\Delta K^2\right] +$	b
$\left[\alpha_n^A + \alpha_t^A - \alpha_n^B - \alpha_t^B\right]\left[-(K+\Delta K)^2\right] +$	c
$\left[\alpha_n^B + \alpha_t^B\right]\left[-(J+\Delta J)(J+1+\Delta J)\right]$	g

Eqs.(5.9)[28] and the most significant term (largest $|b_j| / \Delta_{b_j}$) added to the expression of Table 5.3. Assume that d was the most significant new term and call the expression of Table 5.3 plus d from Table 5.2, Eq.(x). The process is now repeated fitting Eq.(x) plus e, Eq.(x) plus j, etc. Then e,j,k,l are tested for significance, adding the most significant term to Eq.(x), and repeat the process until no new significant terms remain after the last fit performed.

When all significant terms have been included in the analysis, we may assume that we have gone as far as we can if the spectrum is unperturbed. In the case of perturbations, the best procedure to follow is not as straightforward and will be discussed in the following chapters.

At the termination of the analysis one has the estimators of the molecular constants, their simultaneous confidence intervals, the standard deviation of the points included in the analysis, and a table of the calculated and observed frequencies and the difference Δ_i(obs-calc).

One of the advantages of proceeding as outlined lies in the fact that a consistent analysis will be obtained in a systematic fashion and that the confidence intervals for the molecular parameters are obtained in a systematic, statistically based, reproducible manner.

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[28] Note that as each new term is added to the fit, p in Eq.(5.8) increases by 1 and thus the value of S changes.

CHAPTER 6

PERTURBATIONS IN THE SPECTRA OF AXIALLY SYMMETRIC MOLECULES

With the advent of higher and higher resolution of infrared spectrometers, more and more anomalies have been noticed in the near infrared spectra of small molecules. Particularly in the region from about 3000cm^{-1} up, in which overtone and combination bands normally occur (12), many perturbations giving rise to anomalous spectra have been seen (1). A major cause of these anomalies appears to be accidental resonances between overtone and combination levels. Since, for the most part, accurate anharmonic constants are not available for ZXY_3 molecules, and since in general each of these molecules have several low lying fundamentals on the order of 1000cm^{-1} or less, the a priori calculations needed to sort out unambiguously the possible resonances, are at best difficult to perform satisfactorily.

As a result, one desires a systematic approach to the problem of anomalous spectra which will allow the maximum information about the form and cause of the perturbation which has to be obtained from the meager amount of a priori information which is available.

In this chapter a brief review of rigorous perturbation treatments applied to axially symmetric molecules is presented, followed by a description of the method due to Amat (7) of systematically treating the anomalous, i.e., perturbed, spectra which are observed.

Origin of Anomalies in Observed Spectra

These anomalies are due in general to essential or accidental resonances between energy levels of the molecule. An essential resonance is a resonance between energy levels of a molecule due to the symmetry of the molecule. Essential resonances only occur within a single rotation-vibration band, i.e., $\sum_s \Delta v_s = 0$ for the matrix element causing the perturbation. For example, ℓ-type rotational resonance [29] between the $K'=\pm 1$, $\ell=\pm 1$ levels of a doubly-degenerate fundamental of a ZXY_3 molecule is an essential resonance. This resonance can exist for all ZXY_3 molecules due to symmetry, independent of the character of the constituent atoms. An accidental resonance, on the other hand, is a resonance between energy levels of the molecule due to the fortuitous combination of molecular parameters. For example, the Fermi resonance between ν_1 and $2\nu_5$ of some ZXY_3 molecules is an accidental resonance. Accidental resonance may occur within a single rotation-vibration band or more commonly between two or more different rotation-vibration bands.

Previous Work on Perturbed Spectra

There have been many perturbed spectra found and some have been analyzed in the past. In the spectra of C_{3v} molecules, one of the more striking perturbations, due to a Coriolis resonance, has been illustrated by the work of

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[29] This is generally called ℓ-type doubling.

Nielsen and his co-workers on XY_3 molecules (8-11,67-69). Nielsen and co-workers have lately referred to this effect as giant ℓ-type doubling since it is similar to ℓ-type doubling observed for linear molecules. The effect manifests itself in a shift of the $^{R}R_0(J)$ and $^{R}P_0(J)$ lines relative to the $^{R}Q_0(J)$ lines. An example of this splitting in the $K'=\ell=\pm1$ levels of $\nu_3 + \nu_4$ of CH_3F is discussed in Chapter 8.

Other work on rotational resonances has been done by Benedict and co-workers on the NH_3 molecule (33,70,71,72). In addition, considerable other work has been done on perturbations both theoretical and in the interpretation of spectra (7,18-21,24,28-31,73-84).

Review of the Approach to Analysis of Perturbed Spectra

The general problem of perturbed spectra is complex and, although the theory is relatively straightforward, the application in particular cases is often discouragingly difficult. At this point we review the general problem of molecular spectra and show in general how one arrives at and treats perturbations in spectra. Recall that we began with a classical Hamiltonian (22,23) of the non-rigid vibrating rotor developed from a model of nuclear point masses in an anharmonic potential field due to the atomic electrons.

The classical Hamiltonian was then transformed into a quantum mechanical Hamiltonian and subsequently expanded in a power series of the normal coordinates of the harmonic vibrator (13).

Then, after collecting terms of the same order of magnitude, the Hamiltonian of Eq.(1.1) results. As pointed out in Chapter 1, this Hamiltonian is diagonal with respect to J and M but may have elements which are off-diagonal in v_s, ℓ_s, m_s, and K. However, H_o in Eq.(1.1) is diagonal with respect to all quantum numbers. The first contact transformation performed on Eq.(1.1) results in Eq.(1.2) such that the first order Hamiltonian is now diagonal with respect to v_s. The second contact transformation performed on Eq.(1.2) results in Eq.(1.3) such that the twice transformed Hamiltonian h^+ is diagonal with respect to v_s through terms of the second order of magnitude. As pointed out in Chapter 1, terms in h_3^+ which are off-diagonal will not be expected to contribute before sixth order, etc. Thus in the absence of essential or accidental resonances, the diagonal elements of the twice transformed Hamiltonian give a good representation of E_{VR} through third order.

For axially symmetric molecules, h_o^+ and h_1^+ are diagonal with respect to all quantum numbers. h_2^+, however, may have elements which are off-diagonal with respect to K and ℓ_s (16) while higher order Hamiltonians h_n^+ may have elements which are off-diagonal with respect to v_s, ℓ_s and K. Since the first part of the twice transformed Hamiltonian in which off-diagonal elements occur is h_2^+ (as indicated in Chapter 1), the lowest order to which these may contribute in the absence of essential or accidental resonances is the fourth order (21). Thus, in the unperturbed case, i.e., in the absence of

essential or accidental resonances, the diagonal elements of h^+ are a good representation of E_{VR} through third order. However in the event of essential or accidental resonances this is no longer the case, so that the secular equation given by Eq.(1.5) must be solved.

There is, however, an important point to consider. In performing the contact transformation, certain resonance denominators appear in the transformed Hamiltonian (19,20,24). These are of the form $1/(\omega_s - \omega_{s'})$ and in the event that any $\omega_s \approx \omega_{s'}$, the transformed Hamiltonian "becomes infinite". In these instances, Nielsen has shown (19,20,24) that the transformation function used in the contact transformation may be modified to eliminate the resonance denominator and preserve the contact transformation. In many other instances however, these resonance denominators are not the problem and a resonance results not from $\omega_s \approx \omega_{s'}$ but from

$$E_{VR}(v_s, \ell_s, \ldots J, K) \approx E_{VR}(v_{s'}, \ell_{s'}, \ldots J, K+\Delta K). \qquad (6.1)$$

In the latter instance, the secular equation of Eq.(1.5) may be solved without using a special transformation function to preserve the contact transformation.

A detailed résumé of the exact treatment of accidental or essential resonances is beyond the scope of this work and reference is made to the work of Nielsen, Amat and co-workers (8,11,18-20,24,28-31,67-69,73-77). The exact treatment is very complex and quite often requires the solution of secular equations of order three and higher.

In these instances it is not generally possible to solve the secular equation in closed form. One may either substitute approximate (or "guessed") values of the required constant coefficients into the secular equation and solve it numerically, and then perform iterative solutions, or as is possible in some cases, obtain approximate solutions in closed form by neglecting certain terms in the secular equation which are assumed to be small. In general, the best that can be done is to demonstrate that a given off-diagonal element(s) could produce the effect seen, and an approximate form of the perturbation may sometimes be found. One notable exception is the case of a first order Coriolis resonance which will be discussed in detail in Chapter 8.

Systematic Approach to the Analysis of Perturbed Spectra

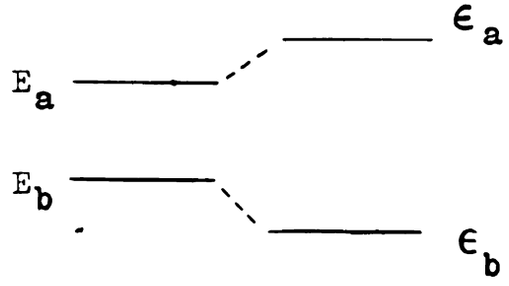
In 1962 at the Symposium on Molecular Structure and Spectra, Professor G. Amat presented a systematized approach to the treatment of perturbed spectra (7) which, while not possessing the complete rigor of some approaches, makes it possible to attack the problem of anomalies in the observed spectra of axially symmetric molecules [30] in an orderly manner. However, while approaching the problem in this orderly manner does not guarantee a complete solution of a perturbed spectrum, it does provide a good method which will

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[30] Parts of the following discussion are the result of several discussions with G. Amat, and much of this chapter follows rather closely an invited paper by G. Amat. (7)

enable an investigator to proceed as far as the available data will allow. For ZXY_3 molecules, the lack of good anharmonic constants makes a complete solution of a perturbed spectrum at best a very difficult task.

Consider two energy levels which perturb each other, viz.



where E_a and E_b are the unperturbed energies, and ϵ_a and ϵ_b are the resulting energies of levels a and b when the perturbation is taken into account. In order for a perturbation to exist, there must be some matrix element of h^+ coupling the two states a and b such that

$$E = \langle a \,|h^+|\, b\rangle \neq 0. \tag{6.2}$$

Thus, the resulting secular equation, giving the perturbed energies is

$$\begin{vmatrix} E_a - \epsilon & W \\ W & E_b - \epsilon \end{vmatrix} = 0 \tag{6.3}$$

which has the solution in closed form.

$$\epsilon = \frac{E_a + E_b}{2} \pm \sqrt{\left(\frac{E_a - E_b}{2}\right)^2 + W^2}. \tag{6.4}$$

As yet unexplored are considerations regarding the possible

states a,b,c... which may be coupled by a perturbation, as well as the form of W as a function of the quantum numbers of the levels coupled by the perturbation, and any possible analytical expression for E_a-E_b as a function of the molecular constants and the quantum numbers of levels E_a and E_b.

In the following, it will be found that from a knowledge of the form of the unperturbed energy levels, as presented in Chapter 1, a relatively simple expression, as a function of the relevant quantum numbers, can be given for the separation of the unperturbed energy levels, i.e., E_a-E_b. A practical problem arises, even though the expression is relatively simple, since at the present time, very often the molecular constants involved in the expression E_a-E_b are not known with sufficient accuracy. Furthermore, the large number of accidental resonances possible in the 3000-6000cm^{-1} region complicates the matter further since this means that we do not know the position of the unperturbed levels and makes the extraction of the "unperturbed" molecular constants difficult if not impossible.

The possible couplings of levels which may enter into a perturbation will be explored so that all those disallowed by symmetry considerations may be eliminated. This is especially helpful since without these rules many couplings would also be considered which in fact are identically zero due to the symmetry of the molecule. The possible forms of W as a function of the quantum numbers are also presented according to the scheme of Amat (7), and an orderly approach

for obtaining information about perturbed spectra is indicated. It should be noted, however, that the problem is so complex, and so many considerations are involved, that each perturbed spectrum is somewhat of a special case, and that proceeding in the manner outlined in this chapter does not guarantee a complete solution.

If $|E_a - E_b| \ll |W|$, the resonance is said to be a strong resonance, whereas if $|E_a - E_b| \gg |W|$, the resonance is said to be a weak resonance. The order of magnitude of W is said to be the order of the resonance. However, the order of magnitude of W is not necessarily the order of the Hamiltonian h_n^+ in which the perturbation matrix element occurs (7). Considerations regarding the order of magnitude of a perturbation are rather intricate and reference is made to the paper of Amat and Nielsen (18) for a clear presentation of these considerations. As mentioned above however, an estimate of the magnitude of the perturbation may be obtained by considering the magnitudes of $|E_a - E_b|$ and $|W|$ in Eq.(6.4).

In the event that three energy levels perturb one another, the secular equation is more complex, with no simple solution. Let the levels a,b,c be involved in the perturbation. Then, it is possible that the coupling elements are

$$W_1 = \langle a | h^+ | b \rangle$$

$$W_2 = \langle a | h^+ | c \rangle \qquad (6.5)$$

$$W_3 = \langle b | h^+ | c \rangle$$

which results in the secular equation

$$\begin{vmatrix} E_a - \epsilon & W_1 & W_2 \\ W_1 & E_b - \epsilon & W_3 \\ W_2 & W_3 & E_c - \epsilon \end{vmatrix} = 0. \qquad (6.6)$$

This case will not be pursued further at this time.

Rules That Determine Which Levels May Perturb One Another

An important consideration is the question of a particular coupling of energy levels. For example, if E_a and E_b are the two levels in question, under what conditions is a perturbation possible? First, only levels of the same J value may perturb each other, since h^+ (and in fact H and h') is diagonal in J, i.e., $\langle J_a | h^+ | J_b \rangle = W \delta_{J_a J_b}$ where $\delta_{J_a J_b}$ is the Kronecker symbol. Second, Amat's rule (49) indicates specifically which matrix elements of h^+ are identically zero due to the symmetry of the molecule, so that the matrix elements of h^+ which may result in a perturbation are indicated. When applied to a given symmetry group Amat's rule establishes the conditions on K_a, K_b, ℓ_a, ℓ_b in order that a perturbing matrix element $\langle a | h^+ | b \rangle$ may exist. Amat's rule applied to C_{3v} molecules [31] may be written as

$$\Delta K - \sum_{\ell_t} \Delta \ell_t = \pm 3p \qquad (6.7)$$

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[31] Care must be exercised here since the rule takes on a different form for different point group symmetries.

where $\Delta K = K_a - K_b$ and $\Delta \ell_t = \ell_{t_a} - \ell_{t_b}$ and where $p = 0,1,2,3,\ldots$

Thus the conditions on the levels E_a and E_b under which a perturbation is possible are:

$$J_a = J_b \tag{6.8}$$

and for C_{3v} molecules

$$(K_a - K_b) - \sum_t (\ell_{t_a} - \ell_{t_b}) = \pm 3p \tag{6.9}$$

or equivalently

$$\Delta K - \sum_t \Delta \ell_t = \pm 3p . \tag{6.9a}$$

In addition, there must be a term in h^+ which has matrix elements corresponding to the coupling conditions.

Method of Determining if a Particular Perturbation Element Exists in h^+

In order to ascertain the possibility of a given coupling in so far as the terms of h^+ are concerned, it is necessary to have tables of the matrix elements of q_s, p_s and P_α as well as tables of the terms in h^+. Table 6.1 contains the matrix elements of q_s and p_s for the one-dimensional (non-degenerate) harmonic oscillator (85,86), Table 6.2 contains the matrix elements of q_s and p_s for the two-dimensional (doubly-degenerate) harmonic oscillator (86). Table 6.3 contains the matrix elements of P_α and $P_\alpha P_\beta$ (86). From Table 6.3 higher order matrix elements of P_α may be found directly by multiplication.

Chapter 1 contains a partial list of elements in h^+. Many additional elements which have only off-diagonal elements are available in the literature (13-17). A list of

Table 6.1 Matrix elements for the one-dimensional harmonic oscillator.[a,b]

v'	operator f	element $(v \mid f \mid v')$
v-1	$q, p/i\hbar$	$[v/2]^{\frac{1}{2}}$
v+1	$q, -p/i\hbar$	$[(v+1)/2]^{\frac{1}{2}}$
v	$q^2, p^2/\hbar^2$	$(v+\frac{1}{2})$
v-2	$q^2, -p^2/\hbar^2$	$[v(v-1)]^{\frac{1}{2}}/2$
v+2	$q^2, -p^2/\hbar^2$	$[(v+1)(v+2)]^{\frac{1}{2}}/2$
v	$pq, -qp$	$-i\hbar/2$
v-2	pq, qp	$i\hbar[v(v-1)]^{\frac{1}{2}}/2$
v+2	pq, qp	$-i\hbar[(v+1)(v+2)]^{\frac{1}{2}}/2$
v-3	$q^3, -p^3/i\hbar^3$	$[v(v-1)(v-2)/8]^{\frac{1}{2}}$
v-1	$q^3, p^3/i\hbar^3$	$3[v/2]^{3/2}$
v+1	$q^3, -p^3/i\hbar^3$	$3[(v+1)/2]^{3/2}$
v+3	$q^3, p^3/i\hbar^3$	$[(v+1)(v+2)(v+3)/8]^{\frac{1}{2}}$
v	$q^4, p^4/\hbar^4$	$[3/2(v+\frac{1}{2})^2+3/8]$
v	p^2q^2, q^2p^2	$[\frac{1}{2}(v+\frac{1}{2})^2-3/8]\hbar^2$

[a] From W. Shaeffer, Revs. Mod. Phys. 16, 245 (1944).

[b] For simplicity the index s (from v_s) is omitted throughout the table.

Table 6.2 Matrix elements $(v,l|f|v',l')$ for the two-dimensional harmonic oscillator.[a]

		Operator f			
v'	l'	q_1	q_2	$p_1/\hbar$	$p_2/\hbar$
$v+1$	$l+1$	$-\frac{1}{2}\left(\frac{v+l+2}{2}\right)^{\frac{1}{2}}$	$-\frac{1}{2}\left(\frac{v+l+2}{2}\right)^{\frac{1}{2}}$	$+\frac{1}{2}\left(\frac{v+l+2}{2}\right)^{\frac{1}{2}}$	$-\frac{1}{2}\left(\frac{v+l+2}{2}\right)^{\frac{1}{2}}$
$v+1$	$l-1$	$+\frac{1}{2}\left(\frac{v-l+2}{2}\right)^{\frac{1}{2}}$	$-\frac{1}{2}\left(\frac{v-l+2}{2}\right)^{\frac{1}{2}}$	$-\frac{1}{2}\left(\frac{v-l+2}{2}\right)^{\frac{1}{2}}$	$-\frac{1}{2}\left(\frac{v-l+2}{2}\right)^{\frac{1}{2}}$
$v-1$	$l+1$	$+\frac{1}{2}\left(\frac{v-l}{2}\right)^{\frac{1}{2}}$	$+\frac{1}{2}\left(\frac{v-l}{2}\right)^{\frac{1}{2}}$	$+\frac{1}{2}\left(\frac{v-l}{2}\right)^{\frac{1}{2}}$	$-\frac{1}{2}\left(\frac{v-l}{2}\right)^{\frac{1}{2}}$
$v-1$	$l-1$	$-\frac{1}{2}\left(\frac{v+l}{2}\right)^{\frac{1}{2}}$	$+\frac{1}{2}\left(\frac{v+l}{2}\right)^{\frac{1}{2}}$	$-\frac{1}{2}\left(\frac{v+l}{2}\right)^{\frac{1}{2}}$	$-\frac{1}{2}\left(\frac{v+l}{2}\right)^{\frac{1}{2}}$

		Operator f					
v'	l'	q_1^2	q_2^2	q_1q_2	$p_1^2/\hbar^2$	$p_2^2/\hbar^2$	$p_2p_2/\hbar^2$
v	l	$\frac{1}{2}(v+1)$	$\frac{1}{2}(v+1)$	0	$\frac{1}{2}(v+1)$	$\frac{1}{2}(v+1)$	0
v	$l+2$	$-B$	$+B$	$-iB$	$-B$	$+B$	$-iB$
v	$l-2$	$-C$	$+C$	$+iC$	$-C$	$+C$	$+iC$
$v+2$	l	$-D$	$-D$	0	$+D$	$+D$	0
$v+2$	$l+2$	$+E$	$-E$	$+iE$	$-E$	$+E$	$-iE$
$v+2$	$l-2$	$+F$	$-F$	$-iF$	$-F$	$+F$	$+iF$
$v-2$	l	$-G$	$-G$	0	$+G$	$+G$	0
$v-2$	$l+2$	$+H$	$-H$	$+iH$	$-H$	$+H$	$-iH$
$v-2$	$l-2$	$+J$	$-J$	$-iJ$	$-J$	$+J$	$+iJ$

[a]For simplicity the index s has been omitted throughout the table.

Table 6.2 Continued.

		Operator f					
v'	ℓ'	$q_2p_2/\hbar$	$q_2p_2/\hbar$	$q_1p_1/\hbar$	$p_1q_1/\hbar$	$p_1q_1/\hbar$	$p_2q_2/\hbar$
v	ℓ	$+\frac{1}{2}\ell$	$-\frac{1}{2}\ell$	$\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$
v	$\ell+2$	0	0	0	0	0	0
v	$\ell-2$	0	0	0	0	0	0
$v+2$	ℓ	0	0	$+iD$	$+iD$	$+iD$	$+iD$
$v+2$	$\ell+2$	$+E$	$+E$	$-iE$	$-iE$	$+iE$	$+iE$
$v+2$	$\ell-2$	$-F$	$-F$	$-iF$	$-iF$	$+iF$	$+iF$
$v-2$	ℓ	0	0	$-iG$	$-iG$	$-iG$	$-iG$
$v-2$	$\ell+2$	$-H$	$-H$	$+iH$	$+iH$	$-iH$	$-iH$
$v-2$	$\ell-2$	$+J$	$+J$	$+iJ$	$+iJ$	$-iJ$	$-iJ$

where

$$B = \tfrac{1}{4}\left[(v+\ell+2)(v-\ell)\right]^{\frac{1}{2}}$$

$$C = \tfrac{1}{4}\left[(v-\ell+2)(v+\ell)\right]^{\frac{1}{2}}$$

$$D = \tfrac{1}{4}\left[(v+\ell+2)(v-\ell+2)\right]^{\frac{1}{2}}$$

$$E = 1/8\left[(v+\ell+2)(v+\ell+4)\right]^{\frac{1}{2}}$$

$$F = 1/8\left[(v-\ell+2)(v-\ell+4)\right]^{\frac{1}{2}}$$

$$G = \tfrac{1}{4}\left[(v+\ell)(v-\ell)\right]^{\frac{1}{2}}$$

$$H = 1/8\left[(v-\ell-2)(v-\ell)\right]^{\frac{1}{2}}$$

$$J = 1/8\left[(v+\ell-2)(v+\ell)\right]^{\frac{1}{2}}$$

Table 6.3 Matrix elements of P_α and $P_{\alpha\beta}$.[a]

$$(K \mid P_x \mid K\pm1) = \frac{h}{4\pi} \sqrt{f-K(K\pm1)}$$

$$(K \mid P_y \mid K\pm1) = \mp i\frac{h}{4\pi} \sqrt{f-K(K\pm1)}$$

$$(K \mid P_z \mid K) = \frac{h}{2\pi} K$$

$$(K \mid P_x^2 \mid K) = \frac{h^2}{8\pi^2} (f-K^2)$$

$$(K \mid P_y^2 \mid K) = \frac{h^2}{8\pi^2} (f-K^2)$$

$$(K \mid P_z^2 \mid K) = \frac{h^2}{4\pi^2} K^2$$

$$(K \mid P_x^2 \mid K\pm2) = \frac{h^2}{16\pi^2} \sqrt{f-K(K\pm1)} \sqrt{f-(K\pm1)(K\pm2)}$$

$$(K \mid P_y^2 \mid K\pm2) = \frac{h^2}{16\pi^2} \sqrt{f-K(K\pm1)} \sqrt{f-(K\pm1)(K\pm2)}$$

$$(K \mid P_xP_y \mid K\pm2) = \mp i\frac{h^2}{16\pi^2} \sqrt{f-K(K\pm1)} \sqrt{f-(K\pm1)(K\pm2)}$$

$$(K \mid P_yP_x \mid K\pm2) = \mp i\frac{h}{16\pi^2} \sqrt{f-K(K\pm1)} \sqrt{f-(K\pm1)(K\pm2)}$$

$$(K \mid P_xP_y \mid K) = -i\frac{h^2}{8\pi^2} K$$

$$(K \mid P_yP_x \mid K) = +i\frac{h^2}{8\pi^2} K$$

[a] For simplicity, $f \equiv J(J+1)$.

Table 6.3 Continued.

$$(K \mid P_y P_z \mid K\pm1) = \mp i \frac{h^2}{8\pi^2} (K\pm1) \sqrt{f-K(K\pm1)}$$

$$(K \mid P_z P_y \mid K\pm1) = \mp i \frac{h^2}{8\pi^2} K \sqrt{f-K(K\pm1)}$$

$$(K \mid P_z P_x \mid K\pm1) = \frac{h^2}{8\pi^2} K \sqrt{f-K(K\pm1)}$$

$$(K \mid P_x P_y \mid K\pm1) = \frac{h^2}{8\pi^2} (K\pm1) \sqrt{f-K(K\pm1)}$$

$$(K \mid P_x P_y + P_y P_x \mid K\pm2) = \mp i \frac{h^2}{8\pi^2} \sqrt{f-K(K\pm1)} \sqrt{f-(K\pm1)(K\pm2)}$$

$$(K \mid P_y P_z + P_z P_y \mid K\pm1) = \mp i \frac{h^2}{8\pi^2} (2K\pm1) \sqrt{f-K(K\pm1)}$$

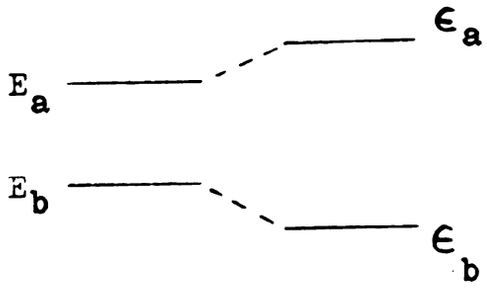
$$(K \mid P_y P_z + P_z P_y \mid K\pm1) = \frac{h^2}{8\pi^2} (2K\pm1) \sqrt{f-K(K\pm1)}$$

the elements of h^+ in the generic form used in Chapter 1 is given in Table 6.4.

From Tables 6.1-6.4 it is possible to ascertain whether a given coupling is possible as regards the existence of an appropriate element in h^+. Thus, combining the information contained in Eqs.(6.8) and (6.9) and the information contained in Tables 6.1-6.4, it is possible to determine whether a given coupling may possibly produce a perturbation in the spectra.

Expression for the Separation of Unperturbed Energy Levels

Recall again the case of two levels E_a and E_b coupled by some matrix element $\langle a | h^+ | b \rangle = W$ such that



where the secular equation, Eq.(6.3), has roots

$$\epsilon = \frac{E_a+E_b}{2} \pm \sqrt{\frac{\delta^2}{4} + W^2} \qquad (6.10)$$

where ϵ^a is ϵ using the + sign, ϵ^b is ϵ using the - sign and

$$\delta \equiv E_a - E_b \qquad (6.11)$$

is the separation of the unperturbed levels. Fig. 6.1 illustrates the effect of the perturbation W on the levels E_a and E_b and indicates certain magnitudes of shifts which

Table 6.4 Generic form of elements in h^+ capable of producing an accidental resonance.

h_m^+	Operator				
h_0^+					
h_1^+	r^3	r^2p			
h_2^+	r^4	r^3p	r^2p^2		
h_3^+	r^5	r^4p	r^3p^2	r^2p^3	
h_4^+	r^6	r^5p	r^4p^2	r^3p^3	r^2p^4

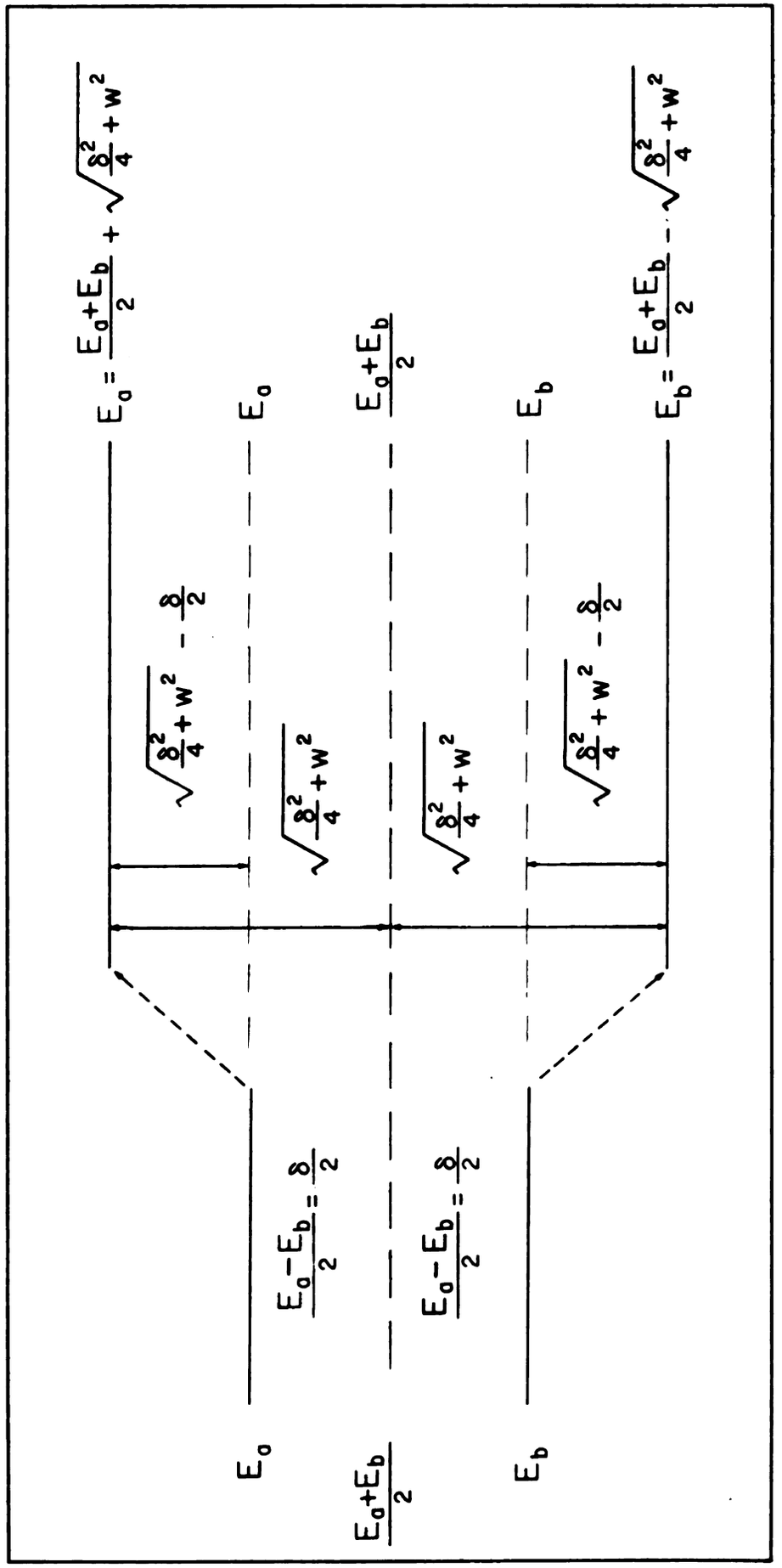


Fig. 6.1 Two level perturbation relations.

will prove useful in the following.

It may be shown by considering the differences of the unperturbed energy levels given (in Chapter 1) as a function of the several quantum numbers, that through third order contributions, for $J \approx 20$, $K \approx 10$, δ may be expressed as

$$\delta = a+bK+cK^2+dJ(J+1) \qquad (6.12)$$

where, for most cases which we will consider, the term cK^2 may be neglected.[32] The term $dJ(J+1)$ may be important especially in cases where $(\alpha_a^B - \alpha_b^B)$ is of the same order of magnitude as the resolution of the spectrometer used. This will become apparent in Chapter 8 where the term $dJ(J+1)$ plays an important role in the perturbations observed. As mentioned above, Eq.(6.12) may be obtained as the difference between the two levels in question, i.e.,

$$\delta = E_a(v_s \ell_s \ldots J, K_a) - E_b(v_s' \ell_s' \ldots J, K_b) \qquad (6.13)$$

for which a particular example is given in Chapter 8. Note however that since E_a and E_b are functions of the molecular constants and the quantum numbers K and J, the differences will obviously be a function of K,J and the molecular constants. A practical difficulty arises however, because the molecular constants involved in δ are often not known with

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[32] For a $\Delta K = 0$ coupling, the term CK^2 is negligible in nearly all cases. For a $\Delta K = \pm 1$ or greater coupling, CK^2 may occassionally be important.

sufficient accuracy to be useful, so that the required a priori calculations are very difficult (if not impossible) to perform effectively. At this time we shall consider only the form of Eq.(6.12) simplified by neglecting the term CK^2, i.e.,

$$\delta = a + bK + dJ(J+1). \qquad (6.14)$$

Up to this point we have given the rules needed to ascertain the possible existence of a given perturbation coupling, the method of ascertaining whether an appropriate term exists in h^+ to provide the perturbation element(s), and the form of the separation of two levels involved in a perturbation.

Accidental Resonances

First, we consider the problem of accidental resonances between the energy levels of two different vibration-rotation bands. Subsequently we shall consider the problem of essential resonances, since in so far as the approach used is concerned, essential resonances appear as a special case.

If we again consider two levels E_a and E_b, belonging to the same J value, with E_a having $\nu_s, \nu_s' \ldots$ excited whereas E_b has $\nu_s'', \nu_s''' \ldots$ excited, and seek to ascertain what possible couplings exist between E_a and E_b, we find the answer given by Amat (7).

Considering only the vibrational portion of the problem, if the vibrational coupling is expressed as

$$\langle v_n, \ldots v_t, \ldots \mid h^+ \mid v_n+\Delta v_n, \ldots v_t+\Delta v_t, \ldots \rangle \qquad (6.15)$$

let us call

$$\sum_n |\Delta v_n| = p_n \tag{6.16}$$

and

$$\sum_t |\Delta v_t| = p_t \tag{6.17}$$

and

$$p_t + p_n = p \tag{6.18}$$

so that p is the total number of (differences of) vibrational quanta involved in the resonance, p_n the total number of non-degenerate quanta, and p_t the total number of doubly-degenerate quanta involved in the resonance. For example, if we are considering a resonance between $\nu_1 + 2\nu_3 + \nu_4$ and $\nu_2 + \nu_3 + \nu_5 + \nu_6$ of CH_3F [33] then $|\Delta v_1| = 1$, $|\Delta v_2| = 1$, $|\Delta v_3| = 1$, $|\Delta v_4| = 1$, $|\Delta v_5| = 1$ and $|\Delta v_6| = 1$ so that $p = 6$, $p_n = 3$, $p_t = 3$.

Systematic Approach to Perturbation Couplings

Using the approach discussed in the beginning of this chapter, Tarrago and Amat (87) have found the possible couplings for several values of p, p_n and p_t. The possible types of couplings are (7,87):

I	W
I'	$W + W'J(J+1) + W''K^2$
II	$W\sqrt{J(J+1)-K(K\pm1)}$

[33] For the numbering of the fundamentals of XYZ_3 molecules we follow Herzberg (12) where ν_1, ν_2, and ν_3 are non-degenerate and ν_4, ν_5 and ν_6 two-fold degenerate, each in order of decreasing frequency.

III $\quad WK$

IV $\quad W\sqrt{J(J+1)-K(K\pm1)}\ \sqrt{J(J+1)-(K\pm1)(K\pm2)}$

V $\quad W\sqrt{J(J+1)-K(K\pm1)}\ \sqrt{J(J+1)-(K\pm1)(K\pm2)}\ \times$
$\sqrt{J(J+1)-(K\pm2)(K\pm3)}$

where W is a constant coefficient for terms in h^+ through $r^n p^3$ terms. These include all terms through those contained in h_3^+ (14-17). Tables 6.5-6.8 give the principal coupling[34] of each type for several values of p, p_n, p_t (87). The tables are self-explanatory except for the subscript on the W, i.e., $W_{(n)}$, which indicates the estimated order of the perturbation for $J \approx K \approx 1$. The column entitled "Order of Magnitude" gives the order of the perturbation for $J \approx K \approx 30$ unless otherwise indicated. ΔK is simply the required difference in K values between the perturbing levels; $\sum_t \Delta \ell_t$ is the sum of $\Delta \ell_t$ for the degenerate modes involved in the perturbation, i.e., for those modes which have a $\Delta v_t \neq 0$; the $\sum_{t'} \Delta \ell_{t'}$ is the sum of $\Delta \ell_t$ for those degenerate modes not involved in the perturbation, i.e., those for which $\Delta v_t = 0$. In those instances for which $\sum_t \Delta \ell_t$ or $\sum_{t'} \Delta \ell_{t'}$ is given as 0*, the notation indicates that the $\sum_t |\Delta \ell_t|$ or $\sum_t |\Delta \ell_{t'}| \neq 0$ but the $\sum_t \Delta \ell_t$ or $\sum_{t'} \Delta \ell_{t'} = 0$. The heavy box lines enclose the largest effects.

In summary, up to this point we have found how to determine whether or not a particular perturbation coupling is a

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[34]The author is indebted to G. Tarrago and G. Amat for these tables. (87)

Table 6.5 Perturbation couplings for $p \geq 3$, $p_t \neq 1$.

p_t	Matrix elements	ΔK	$\sum_t \Delta l_t$	$\sum_{t'} \Delta l_{t'}$	Cplng	Order of Magnitude		
						p=3	p=4	p=5
0	$W_{(1,2,3)}$	0		0	I	1	2	3
2	$W_{(1,2,3)}$	0	0*	0	I	1	2	3
	$W_{(3,4)}\sqrt{J(J+1)-K(K\pm1)}$	±1	∓2	0	II	2←	3←	
	$W_{(3)}$	0	±2	∓2	I	3		
	$W_{(5)}\sqrt{J(J+1)-K(K\pm1)}\times$ $\sqrt{J(J+1)-(K\pm1)(K\pm2)}$	±2	±2	0	IV	3←		
3	$W_{(1,2,3)}$	0	±3	0	I	1	2	3
	$W_{(3,4)}\sqrt{J(J+1)-K(K\pm1)}$	±1	±1	0	II	2↔3	3←	
	$W_{(3,4)}$	0	±1	±2	I	3		
	$W_{(5)}\sqrt{J(J+1)-K(K\pm1)}\times$ $\sqrt{J(J+1)-(K\pm1)(K\pm2)}$	±2	±1	0	IV	3←		
4	$W_{(2,3)}$	0	0*	0	I		2	3
	$W_{(4)}\sqrt{J(J+1)-K(K\pm1)}$	±1	±4	0	II		3←	
5	$W_{(3)}$	0	±3	0	I			3

Table 6.6 Perturbation couplings for $p \geq 2$, $p_f = 1$.

Matrix elements	ΔK	$\Delta \ell_f$	$\sum_{f'} \Delta \ell_{f'}$	Cplng	Order of Magnitude		
					p=2	p=3	p=4
$W_{(2,3,4)} \sqrt{J(J+1)-K(K+1)}$	± 1	± 1	0	II	1 ⟷ 2	2 ⟷ 3	3 ←
$W_{(2,3)}$	0	± 3	0	I	2	3	
	0	± 1	± 2				
$W_{(4,5)} \sqrt{J(J+1)-K(K\pm 1)} \times \sqrt{J(J+1)-(K\pm 1)(K\pm 2)}$	± 2	± 1	0	IV	2 ←	3 ←	

Table 6.7 Perturbation couplings for $p=2$, $p_t=2$.

Matrix elements	ΔK	$\sum_t \Delta \ell_t$	$\sum_{t'} \Delta \ell_{t'}$	Cpling	Order of Magnitude
$W_{(2)}\sqrt{J(J+1)-K(K\pm1)}$	±1	∓2	0	II	$1 \leftarrow\!\!\rightarrow 2$
$W_{(2)}K$	0	0^*	0	III	$1 \leftarrow\!\!\rightarrow 2$ $(K\approx30)(K\approx1)$
$W_{(2)}$	0	0^*	0	I	2
	0	±2	∓2		
$W_{(4)}\sqrt{J(J+1)-K(K\pm1)}\times$ $\sqrt{J(J+1)-(K\pm1)(K\pm2)}$	±2	±2	0	IV	$2 \leftarrow$
$W_{(6)}\sqrt{J(J+1)-K(K\pm1)}\times$ $\sqrt{J(J+1)-(K\pm1)(K\pm2)}\times$ $\sqrt{J(J+1)-(K\pm2)(K\pm3)}$	±3	0^*	0	V	$3 \leftarrow$

Table 6.8 Perturbation couplings for $p=2$, $p_t=0$.

Matrix elements	ΔK	$\sum_{t'} \Delta \ell_{t'}$	Coupling	Order of Magnitude
$W_{(2)}$ $W_{(4)} J(J+1) + W'_{(4)} K^2$	0	0	I	2 2 ← ($J \approx 30$)
$W_{(4)} \sqrt{J(J+1) - K(K \pm 1)}$	± 1	∓ 2	II	3 ←
$W_{(6)} \sqrt{J(J+1) - K(K \pm 1)} \times$ $\sqrt{J(J+1) - (K \pm 1)(K \pm 2)} \times$ $\sqrt{J(J+1) - (K \pm 2)(K \pm 3)}$	± 3	0	V	3 ←

possible coupling. We have also discussed the form of the analytical expression, δ, for the separation of two unperturbed levels as a function of molecular constants and J and K. Additionally, Tables 6.5-6.8 contain the principal perturbation couplings and their functional form due to terms contained in h^+ through h_3^+.

Hypothetical Example of an Accidental Resonance

At this point we shall consider a hypothetical example to indicate the relevance of the foregoing. Assume that $\nu_2 + \nu_5$ and ν_4 of CH_3X, where X is a halogen, perturb each other. Here, $p = 3$, $p_n = 1$, $p_t = 2$, and from Table 6.5 we see that the principal coupling is of type I, i.e., of the form W, and of first order of magnitude.

The separation of the unperturbed energy levels is given by

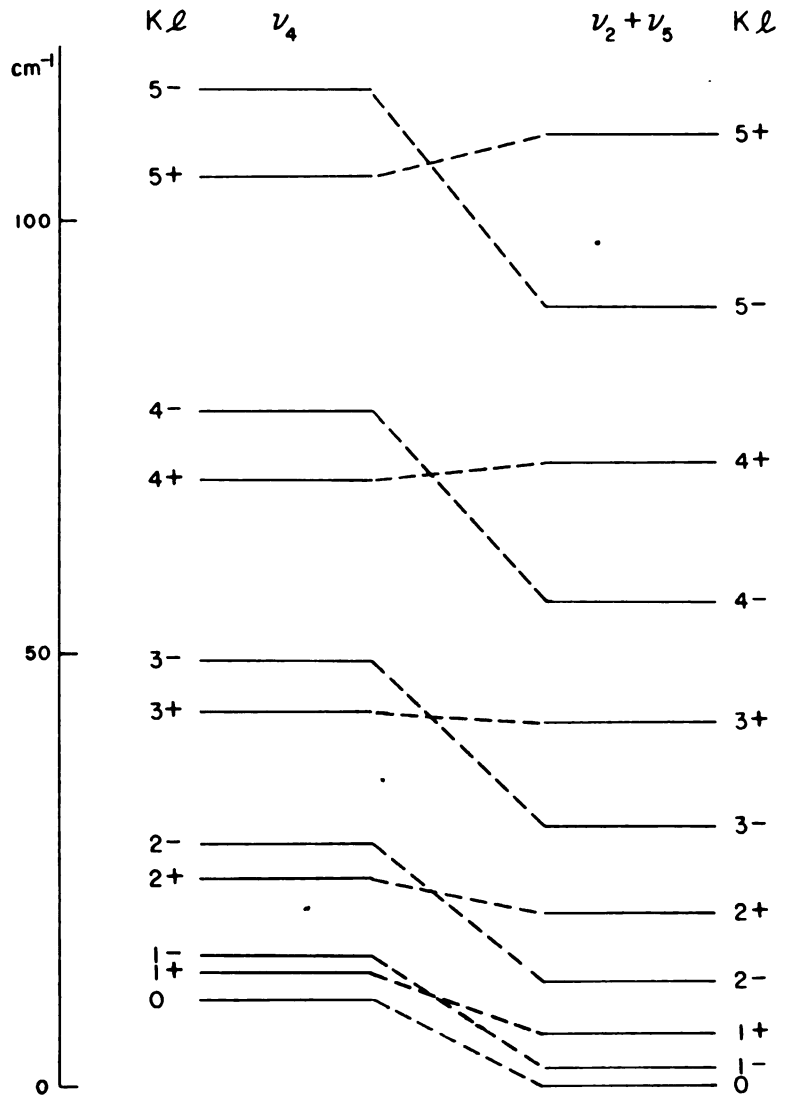
$$\delta = (\nu_2+\nu_5)-\nu_4+2A_e(\zeta_4^z-\zeta_5^z)K-(\alpha_2^B+\alpha_5^B-\alpha_4^B)J(J+1) \qquad (6.19)$$

which is obtained by finding the difference between E_{VR} for $\nu_2 + \nu_5$ and ν_4 (neglecting small terms). If in addition, $(\alpha_2^B + \alpha_5^B - \alpha_4^B)$ is negligible, then

$$\delta = (\nu_2+\nu_5)-\nu_4+2A_e(\zeta_4^z-\zeta_5^z)K \qquad (6.20)$$

which leads to a level scheme given in Fig. 6.2 for $(\nu_2 + \nu_5) - \nu_4 \approx -10\text{cm}^{-1}$ and $2A_e(\zeta_4^z - \zeta_5^z) \approx 3\text{cm}^{-1}$. We further assume $\nu_2+\nu_5$ is of such a low intensity as to be normally unobserved, and that, in the absence of the perturbation, only ν_4 would be observed. From Table 6.5 we note that the

Fig. 6.2 Hypothetical perturbation with coupled levels indicated by dashed lines.

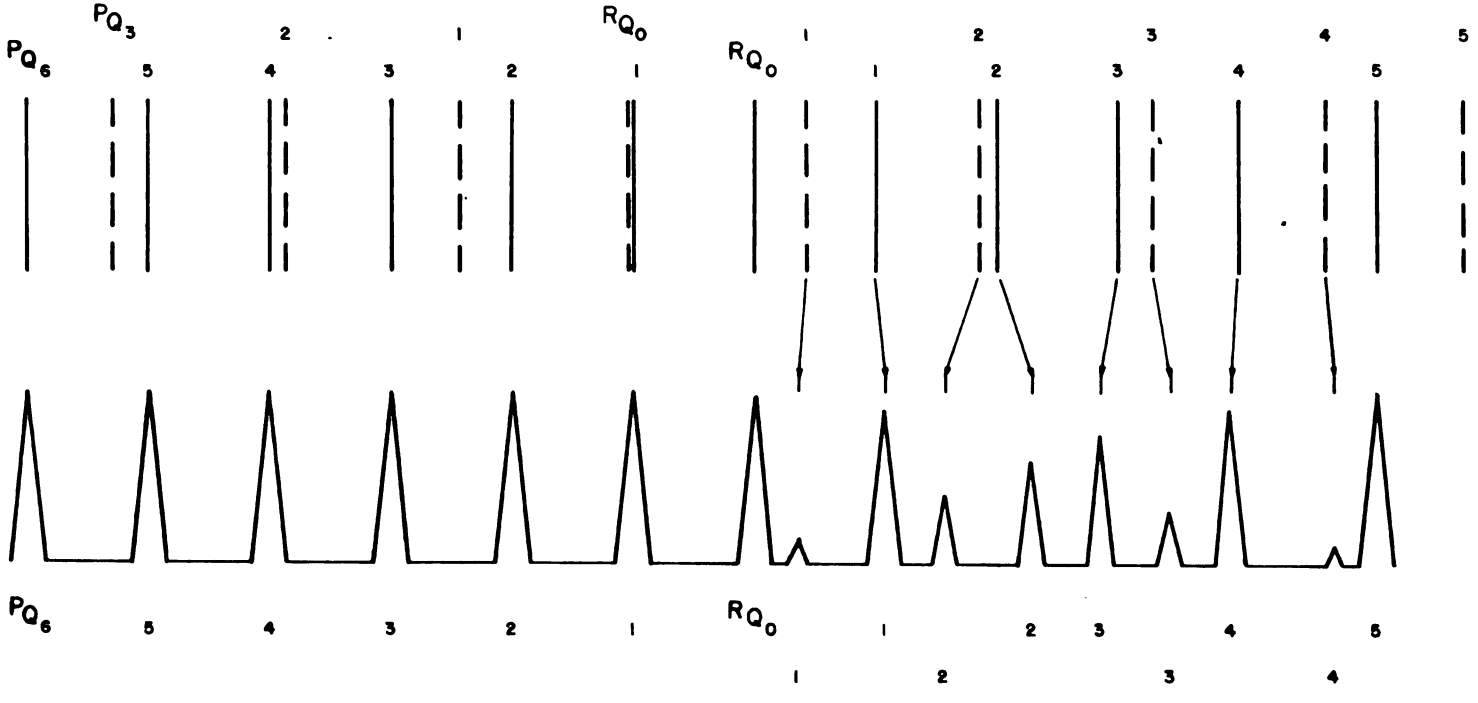


coupling is a $\Delta K = 0$, $\sum_t \Delta \ell_t = 0$ case so that the $K\ell^+$ levels of ν_4 couple to the $K\ell^+$ levels of $\nu_2 + \nu_5$ and the $K\ell^-$ to the $K\ell^-$. It is apparent from Fig. 6.2 that the separation of the unperturbed levels is smallest near the K = 3 levels of these upper states and the perturbation should be the strongest here. These levels correspond, for the case considered, to the ${}^{R}Q_2(J)$ lines of ν_4. Fig. 6.3 presents in the top row the position of the Q lines for ν_4 (solid lines) and $\nu_2 + \nu_5$ (dashed lines) in the absence of a perturbation. The second row shows the resulting spectrum which would be observed (drawn for an arbitrary W). Notice that in the vicinity of the maximum perturbation, the lines of ν_4 are not only shifted, but several additional lines appear due to the mixing of wave functions of ν_4 and $\nu_2 + \nu_5$ when the perturbation is a maximum. The relevant theory involved in the intensity considerations and the "borrowed" intensity of the extra lines will be discussed below. Chapter 8 contains an actual example of the effect of a perturbation of type II and is discussed in detail.

Intensities in Perturbations-- "Borrowed Intensity"

When a perturbation is observed, intensities are an important factor to consider. Assume that two levels are resonating, a and b, with zero order (unperturbed) wave functions Ψ_a^o and Ψ_b^a. Let the matrix element of the perturbation be W. Then in the notation used in this chapter, the new wave functions are

Fig. 6.3 Position of the Q branches for unperturbed ν_4 (solid lines) and $\nu_2 + \nu_5$ (dashed lines) and the resulting spectrum observed (hypothetical) due to a perturbation of type I.



$$\Psi_a = \alpha \Psi_a^o + \beta \Psi_b^o \tag{6.20}$$

$$\Psi_b = -\beta \Psi_a^o + \alpha \Psi_b^o \tag{6.21}$$

where

$$\alpha = \left[\frac{\Delta + \delta/2}{2\Delta}\right]^{\frac{1}{2}}$$

$$\beta = \left[\frac{\Delta - \delta/2}{2\Delta}\right]^{\frac{1}{2}} \tag{6.23}$$

and

$$\Delta .\equiv. \sqrt{\delta^2/4 + W^2} \tag{6.24}$$

$$\delta .\equiv. E_a - E_b. \tag{6.25}$$

It has been shown (88) that for the transitions $\nu_a \leftarrow \nu''$ and $\nu_b \leftarrow \nu''$ where a perturbation W exists, the intensity of two perturbing transitions in the perturbed absorption bands may be given by

$$I_{\nu_a} = \left[\alpha (I^o_{\nu_a})^{\frac{1}{2}} + \beta (I^o_{\nu_b})^{\frac{1}{2}}\right]^2 \tag{6.26}$$

$$I_{\nu_b} = \left[-\beta (I^o_{\nu_a})^{\frac{1}{2}} + \alpha (I^o_{\nu_b})^{\frac{1}{2}}\right]^2 \tag{6.27}$$

where $I^o_{\nu_i}$ is the unperturbed intensity of a ν_i transition.

Thus the intensities in a perturbation may be calculated, given the information required by Eqs.(6.26) and (6.27). However, even if all of the information needed to calculate the intensities is not available, some information may be extracted.

Considering the case where the rotation-vibration band belonging to level b is not normally observed, i.e., $I^o_{\nu_b} = 0$,

$$\frac{I_{\nu_b}}{I_{\nu_a}} = \frac{\beta^2}{\alpha^2} = \frac{\Delta - \delta/2}{\Delta + \delta/2}$$
$$= 1 - \delta\left[\sqrt{\delta^2/4 + W^2} + \delta/2\right]^{-1}. \qquad (6.28)$$

Thus if W = 0, $(I_{\nu_b}/I_{\nu_a}) = 0$, whereas $(I_{\nu_b}/I_{\nu_a}) = 1$ if $\delta = 0$), i.e., at the position of exact resonance.

Another view is also interesting. From Fig. 6.1 the magnitude of the shift of the perturbed level from its unperturbed position is

$$\gamma \equiv -\frac{\delta}{2} + \sqrt{\delta^2/4 + W^2} \qquad (6.29)$$

which when substituted into Eq.(6.28) results in the expression

$$\frac{I_{\nu_b}}{I_{\nu_a}} = 1 - \left[\frac{1}{1 + \gamma/\delta}\right] \qquad (6.30)$$

which proves to be helpful in the analysis of perturbed spectra.

Eq.(6.30) implies that when the shift of the observed line from its unperturbed position is the greatest, the intensity sharing by the transitions of the unobserved level is the greatest. This is seen in the hypothetical example illustrated by Fig. 6.3 for the $^{R}Q_2(J)$ levels. The intensities of extra lines is proportional to the shift from the unperturbed positions. Eq.(6.30) also indicates that as the shift goes to zero, so does the intensity sharing.

It is apparent then that in a perturbation, transitions normally not observed may borrow intensity from the transitions which they perturb. In Chapter 8 an example of this intensity borrowing will be seen in several instances.

In the event that both levels involved in the perturbation have non-zero intensities in the unperturbed case, the problem is even more complex and the intensity sharing is not easily described. However, when applicable, the calculations using Eqs.(6.16) and (6.17) are straight-forward.

Essential Resonances

Although essential resonances have not been treated in detail in this chapter, they can be important in the interpretation of spectra.

In an essential resonance, the resonance occurs between levels in the same rotation-vibration band. It is necessary to be clear about the term "same rotation-vibration band" since it is used here in a broad sense. By the same rotation-vibration band we mean the entire band which has the same vibrational quantum numbers. For example, for ZXY_3 molecules, the same rotation-vibration band is taken to mean the entire complex for which $v_1, v_2, \ldots v_6$ are identical. However, ℓ_4, ℓ_5 and ℓ_6 may be different, e.g., an essential resonance may occur between the parallel and perpendicular components of $2\nu_4$ of a ZXY_3 molecule.

In treating essential resonances the same considerations of this chapter apply with the restriction that the perturbation matrix elements satisfy the rule $\sum_s |\Delta v_s| \equiv 0$.

Summary

In general, there are several points which should be systematically considered when analysing perturbed spectra. These are:

1) the order of magnitude of W
2) the type of coupling (I,II...)
3) the number of quanta involved in the resonance, i.e., p, p_n, p_t
4) the order of magnitude of a,b,c,d (Eq.(6.12))
5) the number of resonating levels
6) observed intensities.

The appearance of the perturbation is governed by considerations 1,2,4,5, and 6 while 3 presents a systematic approach to the consideration of the couplings possible. In Chapter 8, these considerations are applied to $\nu_3 + \nu_4$ of CH_3F.

CHAPTER 7

EXPERIMENTAL DETAILS AND CALIBRATION OF RECORDS

Spectrometer

The spectra of CH_3F, CHD_3 and CH_3D were obtained with a high resolution vacuum recording spectrometer employing an f/ 5 Pfund-Littrow monochromator of focal length 1 meter (89-91) and one of two Bausch and Lomb "certified precision" echelette gratings, a 600 line/mm, 212x158mm, grating blazed at 1.6μ and a 300 line/mm, 254x128mm, grating blazed at 5μ. The gas samples were contained in a White type multiple traverse cell (92,93). Two entrance optics arrangements were used, one employing three calcium fluoride lenses and several front surface aluminized mirrors, the other employing an all mirror system.

The infrared energy was detected using Eastman-Kodak lead sulfide detectors, type P and type N. The detectors were cooled to one of two temperatures, -50°C by a circulating dry ice-acetone mixture and -175°C by a pressure driven liquid air cooling system. The infrared beam was chopped at 90 cycles per second and the lead sulfide detector outputs amplified by a Tektronix Type 122 preamplifier followed by a phase sensitive amplifier. The amplifier output was recorded by a Leeds and Northrup Model G two-pen recorder.

Calibration was effected by interpolation between the visible fringes from a Fabry-Perot interferometer following the method of Douglas and Sharma (94). The Fabry-Perot

fringes which are equally spaced on the chart with respect to frequency are calibrated by a least squares fit of the fringe position of well known standard lines versus their frequency in cm^{-1}. The standard lines are normally recorded simultaneously with the infrared absorption record. Several types of standard lines are used in the calibration of the fringes. The best standards available for calibration of infrared absorption spectra are the carefully measured absorption lines of CO, NO_2, HCl and HCN measured by Rank and co-workers (95-97). These standards are recorded simultaneously with the spectra by including the calibration gas with the sample gas in the multiple traverse cell. In addition, well known Argon emission lines (98) due to the Argon carrier gas in the 300 watt Zirconium arc, which we use as an infrared source, provide another source of standards; and an end-on Neon lamp inserted in the entrance optic train by a movable mirror also provides a source of standard lines (98).

Calibration of CH_3F Bands

The $\nu_3 + \nu_4$ band of CH_3F discussed in Chapter 8 was calibrated using secondary infrared standards as follows. Seven CO lines (95), one Argon emission line (98) and one Neon emission line (98) were recorded simultaneously with the best infrared absorption lines of $\nu_3 + \nu_4$. Subsequently the Fabry-Perot fringes of the record CH_3F Chart I were calibrated using these standard lines. The results of this linear least squares fit are given in Table 7.1. Table 7.1

Table 7.1 Calibration of Fabry-Perot fringes of $\nu_3 + \nu_4$ CH_3F Chart I.

Std.	Fringe Position of Standard	Frequency cm^{-1}	Calculated Frequency cm^{-1}	Wt.	Δ_1(o-c) cm^{-1}
Ne	-134.1973	3903.8008	.7992	2	+0.0016
A	222.2884	4018.4135	.4148	4	-0.0013
P(22)	661.2890	4159.5609	.5603	1	+0.0006
P(21)	677.7175	4164.8423	.8423	1	0.0000
P(18)	725.7604	4180.2843	.2889	1	-0.0046
P(17)	741.3288	4185.2971	.2943	1	+0.0028
P(16)	756.7080	4190.2424	.2390	1	+0.0034
P(14)	786.8532	4199.9298	.9311	1	-0.0013
P(12)	816.1305	4209.3454	.3442	1	+0.0013

$\nu = a + b(f\#)$
$a = 3946.94567 cm^{-1}$
$b = 0.3215154 cm^{-1}$
$s = \pm 0.0026 cm^{-1}$ Std. dev. of points

Table 7.2 Calibration of CH_3F Chart II vs frequencies of absorption lines from Chart 1.

Fringe Position Chart II	Standard Freq. Chart I cm^{-1}	Calculated Freq. Chart II cm^{-1}	$\Delta_i(c-c)$ cm^{-1}
211.503	4014.9496	.9480	+0.0016
212.112	4015.1423	.1438	-0.0015
278.657	4036.5384	.5416	-0.0032
279.522	4036.8182	.8198	-0.0016
280.302	4037.0704	.0706	-0.0002
301.133	4043.7727	.7689	+0.0038
302.053	4044.0705	.0647	+0.0058
305.445	4045.1620	.1554	+0.0066
305.921	4045.3114	.3085	+0.0029
306.272	4045.4187	.4214	-0.0027
347.422	4058.6532	.6533	-0.0001
348.453	4058.9814	.9848	-0.0034
349.378	4059.2782	.2823	-0.0041
350.230	4059.5523	.5562	-0.0039
352.275	4060.2131	.2138	-0.0007
352.826	4060.3869	.3910	-0.0041
416.372	4080.8260	.8245	+0.0015
419.225	4081.7442	.7419	+0.0023
420.075	4082.0153	.0152	+0.0001
514.786	4112.4689	.4699	-0.0010
515.324	4112.6414	.6429	-0.0015
516.995	4113.1838	.1803	+ .0035

$\nu = a + b(f\#)$
$a = 3946.93827 cm^{-1}$
$b = 0.3215543 cm^{-1}$
$s = \pm 0.0032 cm^{-1}$ Std. dev. of points

presents the internal calibration of CH_3F Chart II against the frequencies of infrared absorption lines obtained from CH_3F Chart I.

The initial analysis was carried out using Chart II. Subsequently, the resolution of the spectrometer was improved by cooling the PbS detectors to -175°C. The CH_3F was rerun in the double pass configuration of the Pfund-Littrow monochromator. A difficulty arose, however, since the Fabry-Perot fringes were single passed. As a result of the different dispersion at which the infrared and fringes were obtained on Chart III, it was found that a quadratic fit of the fringe position of the best lines on Chart III vs the frequencies of these same lines from Chart II was required to obtain a good calibration of Chart III. The results are given in Table 7.3.

Secondary internal calibration was used on these records due to the difficulty of using primary standards in this region. As is apparent from Table 7.1, there is a lack of accurate and observable standards in this region and since the internal calibration fits were as good as they turned out to be, secondary internal calibration was used. The principal effect of this approach would be to introduce a small error in absolute accuracy of frequencies. However, the relative accuracy should be extremely good.

Table 7.4 presents a summary of experimental conditions for all usable records of $\nu_3 + \nu_4$ for CH_3F which were run. Unfortunately, the last three records listed in Table 7.4

Table 7.3 Calibration of CH_3F Chart III vs. frequencies of absorption lines from Chart I.

Fringe Position Chart III	Standard Freq. Chart II cm^{-1}	Calculated Freq. Chart III cm^{-1}	Δ.(o-c) cm^{-1}
188.219	3989.8449	.8437	+0.0012
200.099	3995.5406	.5437	-0.0031
215.684	4003.0261	.0223	+0.0038
231.132	4010.4369	.4362	+0.0007
251.128	4010.0350	.0343	+0.0007
265.710	4027.0310	.0348	-0.0038
277.953	4032.9120	.9131	-0.0011
291.014	4039.1807	.1848	-0.0041
300.564	4043.7696	.7711	-0.0015
315.877	4051.1280	.1258	+0.0022
326.836	4056.3899	.3900	-0.0001
335.160	4060.3946	.3887	+0.0059
345.477	4065.3513	.3453	+0.0060
366.376	4075.3857	.3872	-0.0015
372.535	4078.3466	.3470	-0.0004
416.574	4099.5142	.5150	-0.0008
442.455	4111.9603	.9590	+0.0013
453.489	4117.2560	.2652	+0.0008
459.746	4120.2699	.2744	-0.0045
474.552	4127.4023	.3957	+0.0066
485.544	4132.6861	.6833	+0.0028

$\nu = a + b(f\#) + c(f\#)^2$
$a = 3899.61773 cm^{-1}$
$b. = 0.4789606 cm^{-1}$
$c = 0.000002159 cm^{-1}$
$s = \pm .0040 cm^{-1}$ Std. dev. of points

Table 7.4 Experimental conditions for records of $\nu_3 + \nu_4$ of CH_3F at 2.5μ.

Record Number	Pressure mm Hg	Path Length (meters)	Traversals	Grating Lines/mm	Order IR	Double or Single Pass	Detector	Detector Temperature	Spectral Slit Width (cm^{-1})	Comments
I	9	12.8	16	600	1	Single	PbS-P	−50 °C	0.04	Primary calibration
IIa	9	8	24	600	1	Single	PbS-P	−50 °C	0.04	Measured and used
IIb	7	12.8	16	600	1	Single	PbS-P	−50 °C	0.04	
III	6	6.4	8	600	1	Double	PbS-N	−175 °C	0.02	Measured and used
	6	6.4	8	600	1	Single	PbS-N	−175 °C	0.02	No Fabry-Perot fringes, used for detail
	7	6.4	8	300	2	Single	PbS-N	−175 °C	0.02	Detail only
	6	6.4	8	300	2	Double	PbS-N	−175 °C	0.04	Detail only

proved to be impossible to calibrate since satisfactory Fabry-Perot fringes were not obtained.

Calibration of CHD_3

Three high resolution records of $\nu_1 + \nu_2$ of CHD_3 were calibrated and measured. Later, several other records were run for details not obtainable on a calibrated run. CHD_3 charts I and II were calibrated against Neon emission lines (98) recorded intermittently with the absorption spectrum while fringes were recorded continuously. The results of the calibration fits are given in Tables 7.5 and 7.6. Chart III was internally calibrated against average frequencies of infrared lines from Charts I and II with a standard deviation for 11 points fit of $\pm 0.0014 cm^{-1}$.

Calibration of CH_3D

Two records of $\nu_2 + \nu_3$ of CH_3D were run. CH_3D Chart I was run for a primary calibration against HCN standards (95). CH_3D Chart II is a second high resolution run for second measurement of lines and was internally calibrated against absorption lines contained on Charts I and II. Table 7.8 presents the calibration fit of Chart I vs. HCN standards. Table 7.9 presents the calibration fit of Chart II vs. absorption line frequencies from Chart I. Table 7.10 lists the experimental conditions for the two records.

Sample Preparation CH_3F

The CH_3F was prepared by transferring 97.6g (0.524 mole)

Table 7.5 Calibration of Fabry-Perot fringes of CHD_3 Chart I vs. Neon emission lines.

Neon Line Fringe Position Chart I	Standard Freq. cm^{-1}	Calculated Freq. cm^{-1}	Δ_1(o-c) cm^{-1}
9.157	4961.132	.131	+0.001
80.810	4989.930	.930	0.000
230.051	5049.912	.913	-0.001
357.120	5100.984	.985	-0.001
616.086	5205.071	.070	+0.001
655.142	5220.768	.768	0.000

$\nu = a + b(f\#)$
$a = 4957.450 cm^{-1}$
$b = 0.4019239 cm^{-1}$
$s = \pm 0.001 cm^{-1}$ Std. dev. of points

Table 7.6 Calibration of Fabry-Perot fringes of CHD_3 Chart II vs. Neon emission lines.

Neon Line Fringe Position	Standard Freq. cm^{-1}	Calculated Freq. cm^{-1}	Δ_1(o-c) cm^{-1}
9.212	4961.132	.134	+0.002
80.864	4989.930	.931	+0.001
230.098	5049.912	.909	-0.003
616.164	5205.071	.070	-0.001
655.228	5220.768	.770	+0.002

$\nu = a + b(f\#)$
$a = 4957.431 cm^{-1}$
$b = 0.4019036 cm^{-1}$
$s = \pm 0.002 cm^{-1}$ Std. dev. of points

Table 7.7 Experimental conditions for records of $\nu_1 + \nu_2$ of CHD_3.

Record Number	Pressure mm Hg	Path Length (meters)	Traversals	Grating	Order IR	Double or Single Pass	Detector	Detector Temperature	Spectral Slit Width (cm^{-1})
I	50	8	24	600	1	Single	PbS-P	−50°C	0.07
II	50	12.8	16	600	1	Single	PbS-P	−50°C	0.04
III	40	6.4	8	600	1	Single	PbS-N	−175°C	0.02

Table 7.8 Calibration of Fabry-Perot fringes of CH_3D Chart I vs. HCN absorption lines.

HCN Line Fringe Position		Standard Freq. cm^{-1}	Calculated Freq. cm^{-1}	Δ_i(o-c) cm^{-1}
R(9)	770.899	3339.8843	.8817	+0.0026
R(10)	779.385	3342.6077	.6108	-0.0031
R(18)	844.672	3363.6134	.6065	+0.0069
R(19)	852.562	3366.1405	.1438	-0.0033
R(20)	860.350	3368.6455	.6484	-0.0029
R(21)	868.042	3371.1283	.1221	+0.0062
R(23)	883.332	3376.0271	.0392	-0.0121
R(25)	898.252	3380.8366	.8373	-0.0007
R(26)	905.619	3383.2077	.2065	+0.0012
R(27)	912.910	3385.5563	.5512	+0.0051

$\nu = a + b(f\#)$
$a = 3091.9675 cm^{-1}$
$b = 0.3215911 cm^{-1}$
$s = \pm 0.0060 cm^{-1}$

Table 7.9 Calibration of CH_3D Chart II vs. frequencies of absorption lines from Chart I.

Fringe position Chart II	Standard Freq. Chart I cm^{-1}	Calculated Freq. Chart II cm^{-1}	Δ_1(o-c) cm^{-1}
937.191	3393.339	.327	+0.012
945.347	3395.942	.951	-0.009
946.173	3396.213	.217	-0.004
952.794	3398.345	.346	-0.001
98C.529	3407.284	.265	+0.019
1012.551	3417.559	.565	-0.006
1022.952	3420.909	.909	0.000
1025.281	3421.669	.658	+0.011
1053.428	3430.699	.711	-0.012
1059.052	3432.511	.519	-0.008
1112.240	3449.626	.625	+0.001
1146.345	3460.576	.593	-0.017
1168.026	3467.572	.566	+0.006
1214.386	3482.468	.456	-0.008
1248.465	3492.459	.437	+0.022
1249.276	3493.690	.698	-0.008
1264.519	3498.602	.600	+0.002
1265.531	3498.926	.925	+0.001
1379.838	3535.682	.687	-0.005
1396.580	3541.066	.071	-0.005
1398.879	3541.814	.811	+0.003
1417.119	3547.687	.677	+0.010
1434.659	3553.311	.318	-0.007
1437.801	3554.326	.328	-0.002
1441.840	3555.628	.627	+0.001
1454.526	3559.719	.707	+0.012
1495.721	3572.945	.956	-0.011
1497.845	3573.644	.639	+0.005

$\nu = a + b(f\#)$
$a = 3091.91889\ cm^{-1}$
$b = 0.321610337\ cm^{-1}$
$s = \pm 0.0096\ cm^{-1}$

Table 7.10 Experimental conditions for records of $\nu_2 + \nu_3$ of CH_3D.

Record Number	Pressure mm Hg	Path Length (meters)	Traversals	Grating	Order IR	Double or Single Pass	Detector	Detector Temperature	Spectral Slit Width (cm^{-1})
I	45	6.4	8	600	I	Single	PbS-P	−175 °C	0.02
II	70	6.4	8	600	I	Single	PbS-P	−175 °C	0.02

of methyl p-toluenesulfonate and 62.7g (1.08 mole) of dehydrated potassium fluoride into a flask. The pressure was reduced to 500mm Hg and the temperature raised to 250°C over a period of 1½ hours and maintained at 250°C for 3 hours. The reaction product was passed through a dry ice - acetone cooled trap to remove any water present and subsequently collected in a liquid air cooled trap. Fig. 7.1 illustrates the apparatus set-up used for the production of CH_3F. Yields were on the order of 85% with a small amount CO_2 contamination.

CHD_3 and CH_3D Samples

The samples of CHD_3 and CH_3D were obtained from Volk Radiochemical Co. and used without further purification.

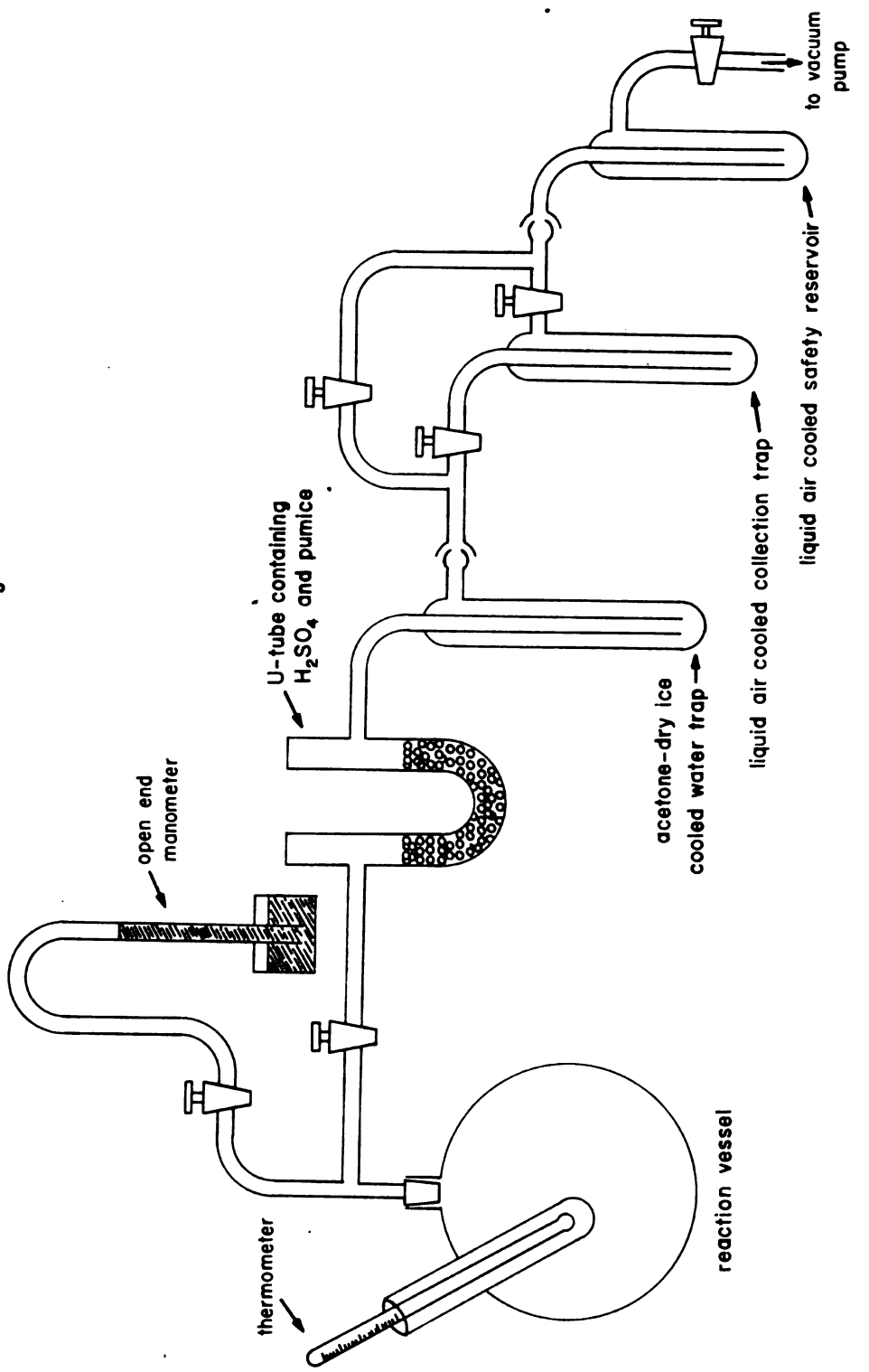


Fig. 7.1 Laboratory set-up for the production of CH_3F.

CHAPTER 8

A PERTURBED PERPENDICULAR BAND $\nu_3+\nu_4$ OF CH_3F

In the past, the infrared spectrum of CH_3F has been investigated in several laboratories. Bennet and Meyer first reported the spectrum of CH_3F (99). Subsequently Yates and Nielsen analyzed the fundamental bands with resolution $\approx 0.3cm^{-1}$ (100). The bands ν_1, ν_3, ν_4 and $2\nu_5$ were examined by Pickworth and Thompson with somewhat higher resolution $\approx 0.1cm^{-1}$ (101). Smith and Mills have recently re-analyzed the rotational structure of ν_3 and ν_6 with resolution $\approx 0.2cm^{-1}$ (102). A low resolution ($\approx 1.5cm^{-1}$) study of all perpendicular fundamentals was performed by Andersen, Bak, and Brodersen (103) who found the ζ_t^z constants from the zeta sum rule (12) and thus also obtained a value for A_0. The microwave spectra of CH_3F has been reported (52,53,58), and excellent values of B_0, D_0^J and D_0^{JK} are available.

General Features and Vibrational Assignment of the Observed Spectrum

In the region from 3900 - 4500 cm^{-1} the infrared absorption spectrum of CH_3F is very complex, with a number of overlapping bands. The subject of this chapter is a perpendicular band at $4058cm^{-1}$ which we have assigned to $\nu_3+\nu_4$. We have also found, overlapping the low wave number end of $\nu_3+\nu_4$, numerous transitions belonging to the parallel band $\nu_1+\nu_3$ at $4011cm^{-1}$. Another parallel band which may be $2\nu_2 + \nu_3$ is observed at $3905cm^{-1}$. We also observe several

Q branches of a perpendicular band near 4138cm^{-1} which may belong to $\nu_1+\nu_6$.

The band $\nu_3+\nu_4$ spans approximately 230cm^{-1} and we have measured approximately 1000 absorption lines in this region. About 700 have been assigned to $\nu_3+\nu_4$ and about 200 have been assigned to $\nu_1+\nu_3$. $\nu_3+\nu_4$ is particularly interesting since individual transitions of the types $^{R}R_K(J)$, $^{R}P_K(J)$, $^{R}Q_K(J)$, $^{P}R_K(J)$, $^{P}P_K(J)$, and $^{P}Q_K(J)$ have been resolved.[35] Fig. 8.1 is a slow speed "slave" recording of a high resolution record of the spectrum of $\nu_3+\nu_4$.

The resolution limit of the spectrometer in this region is $\approx$ 0.04cm^{-1} and CH_3F Chart III (cf. Chapter 7) was obtained with this high resolution. Charts I and II were obtained earlier with an apparent resolution of $\approx$ 0.06cm^{-1}. The working records were approximately 17 meters long and the Fabry-Perot fringes were separated by $\approx$ 0.32cm^{-1} which is $\approx$ 25mm of chart so that 1cm^{-1} $\approx$ 7.5cm of chart.

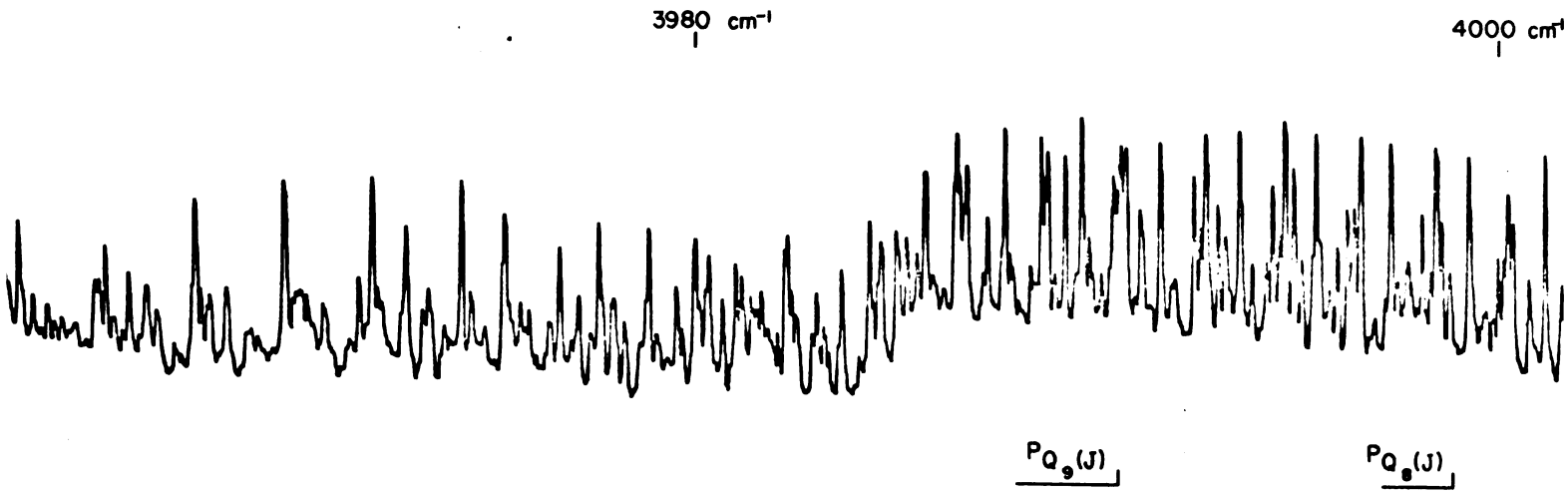
Assignment of Transitions

The assignment of rotational quantum numbers to individual lines was complicated by the large number of transitions observed, the relatively large rotational spacing ($2B \approx 1.7$cm^{-1}) and the rapid quadratic convergence and divergence of

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[35] In the perpendicular bands of the other members of the methyl halide family we have not seen Q branches, i.e., $^{R}Q_K$ and $^{P}Q_K$ lines, resolved into individual J transitions.

Fig. 8.1 Spectrum of $\nu_3+\nu_4$ and $\nu_1+\nu_3$ of CH_3F.



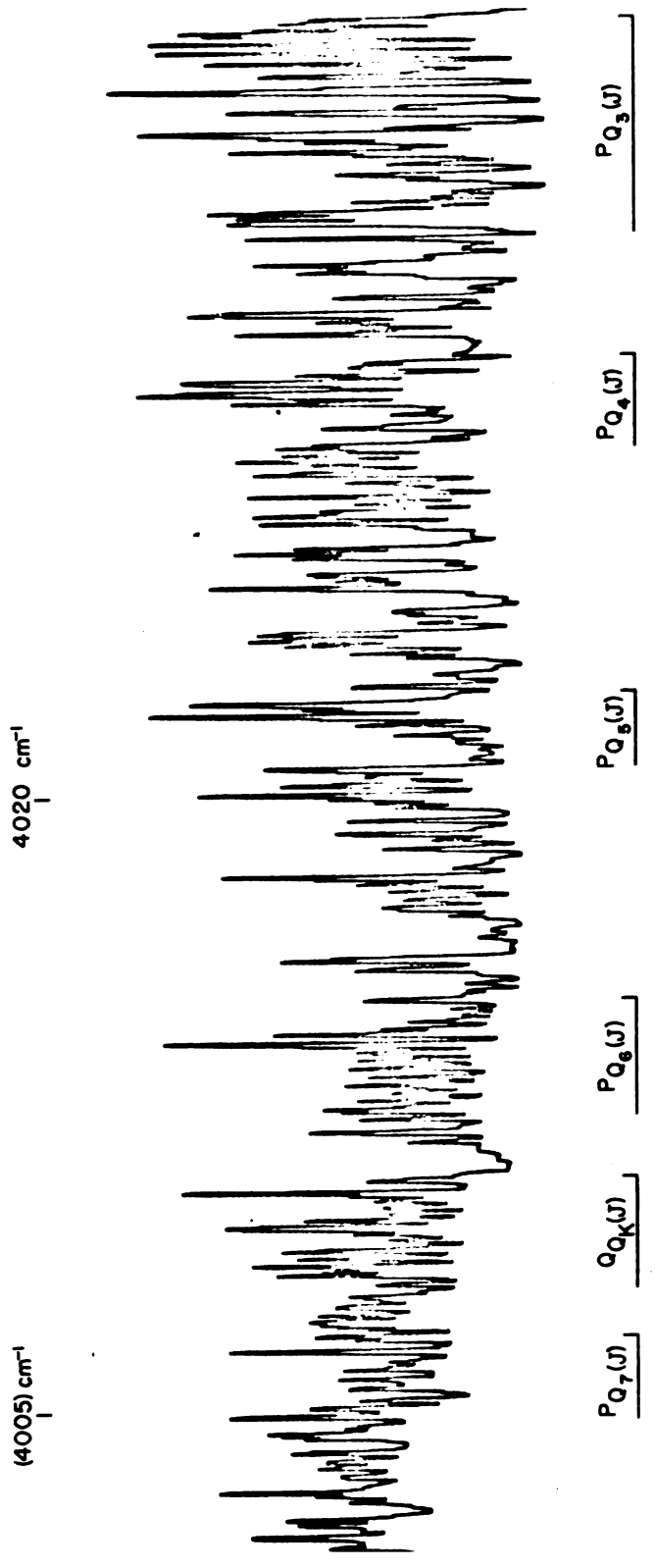


Fig. 8.1 Continued.

Fig. 8.1 Continued.

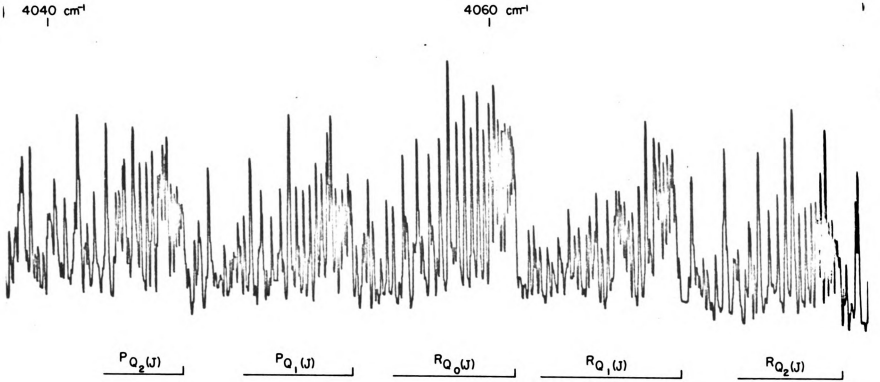
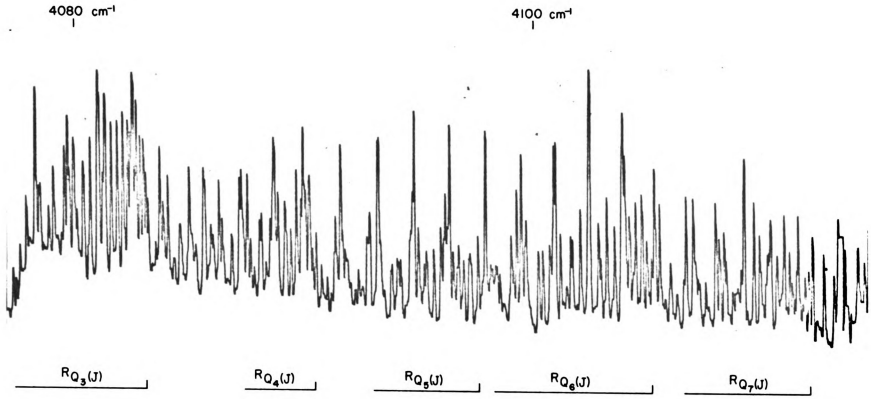


Fig. 8.1 Continued.



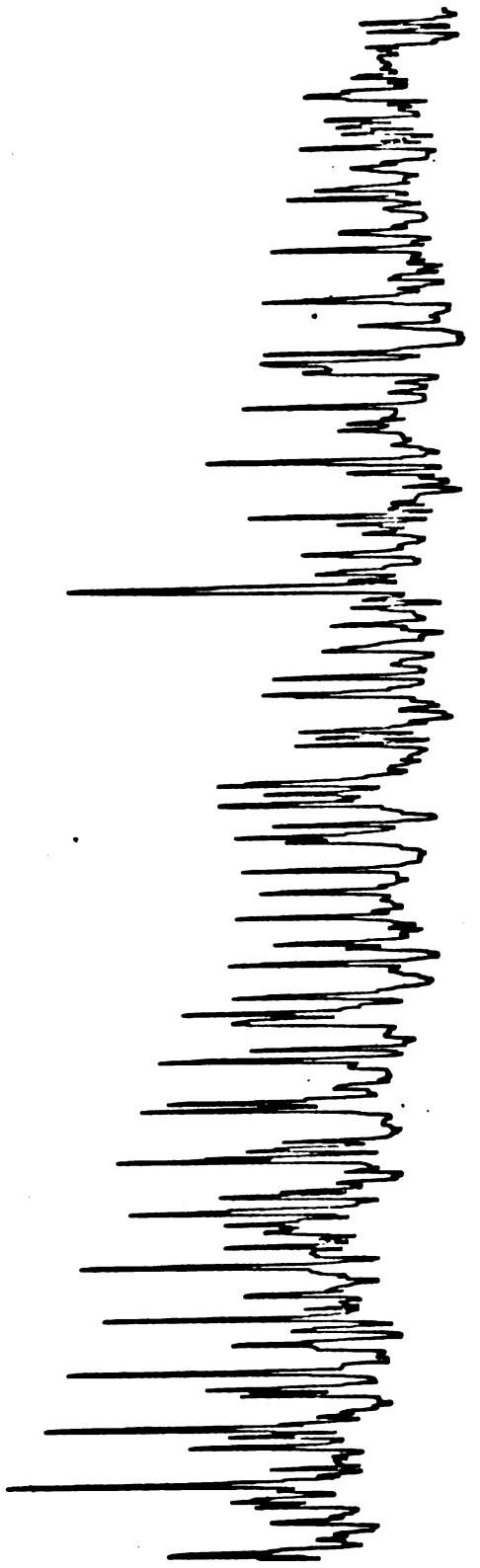


Fig. 8.1 Continued.

series of lines of fixed K. The latter effect is due to the large α^B ($\approx 0.01 cm^{-1}$) in this band.

Making use of calculated intensities of the six possible types of transitions and the criterion of missing lines for $J < K$ as discussed in Chapter 5, the Q branch transitions for several values of K were located. Then, following the procedure outlined in Chapter 4, calculated values of the ground state combination differences (using microwave values of B_o, D_o^J and D_o^{JK}) (52,53,58) were used to complete the assignment of the unperturbed levels.[36]

It is apparent from inspection of Eqs.(4.2a) and (4.2b) that, provided the proper K value has been assigned to a series of $^RQ_K(J)$ (or $^PQ_K(J)$) lines, the calculated ground state combination differences unequivocably fix the assignment of the corresponding ^RR and ^RP (or ^PP and ^PR) lines for the same K value.

At this point it is convenient to establish a convention of notation to be used in the following. We shall call the $^RR_K(J)$, $^RQ_K(J)$ and $^RP_K(J)$ lines, the $+|K|$ subband and the $^PR_K(J)$, $^PQ_K(J)$ and $^PP_K(J)$, the $-|K|$ subband, i.e., we shall designate the subbands by $K\Delta K$.

In the manner described above, the -6,-3,-2,-1,0,+2,+3, +4,+5,+6,+7,+8 and +9 subband lines were assigned without undue difficulty. The assignment of the -9,-8,-7,-5,-4, and the +1 subband lines, as well as the -3 subband lines above

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[36] The values of the ground state constants used are from the work of Thomas, Cox, and Gordy (58): $B_o = 0.851793$, $D_o^J = 1.98 \times 10^{-6}$, $D_o^{JK} = 1.48 \times 10^{-5} cm^{-1}$.

J = 10, presented a more complicated problem.

The +1 subband was obviously perturbed (as was the -3 subband) by a perturbation which varied in magnitude with J. The -9,-8,-7,-5, and -4 subbands were more difficult to locate due to less obvious perturbations and also because of the overlap of this region by the $^{Q}R_{K}(J)$ lines of $\nu_1+\nu_3$. The transitions in these subbands were successfully assigned when it was found that a large empirical K^3 term was needed to fit the subband origins from -3 to +9. The assignments were then made and verified in the -9,-8,-7,-5, and -4 subbands using the calculated ground state combination differences.

After all but the -3 and +1 subbands were assigned, it was possible to assign the transition in these two subbands from the remaining unassigned lines with reasonable certainty, again using the ground state combination differences to verify the assignments.

Fig. 8.2 is a medium resolution record of a large portion of the band $\nu_3+\nu_4$. Assignments of the principal series are indicated for $\nu_3+\nu_4$ and also $\nu_1+\nu_3$. The high resolution records are considerably expanded (a factor of 5:1) and show more detail.

All assigned transitions from $\nu_3+\nu_4$ are listed in Appendix V. The list contains the assignment, frequency, fringe number (for which the calibration given in Table 7.2 may be used to obtain the frequency), $\Delta\nu$ and weight (the weight = $.0001/(\Delta\nu)^2$), the observed line height, and line

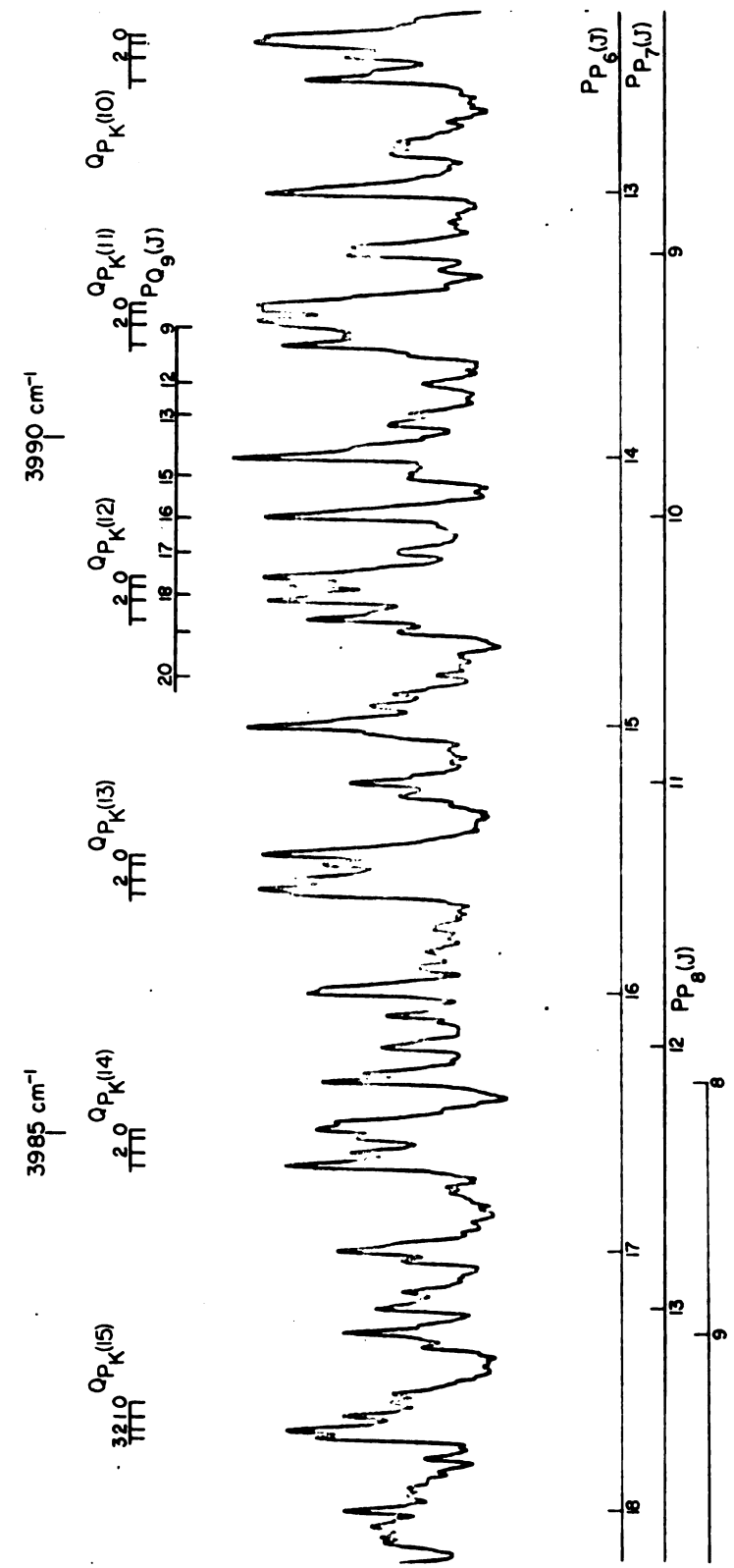


Fig. 8.2 $\nu_3+\nu_4$ and $\nu_1+\nu_3$ of CH_3F with assignments of the principal transitions.

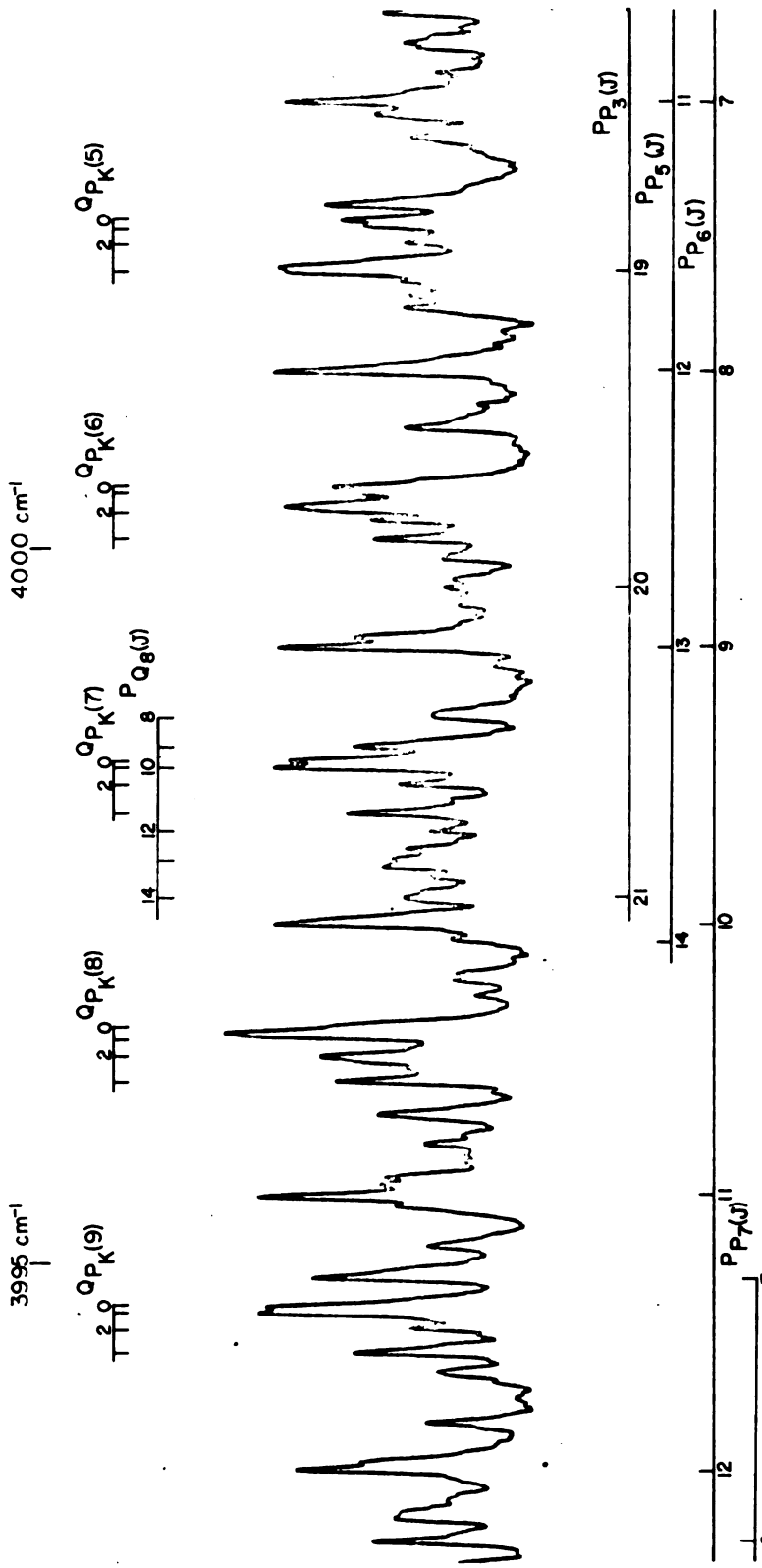


Fig. 8.2 Continued.

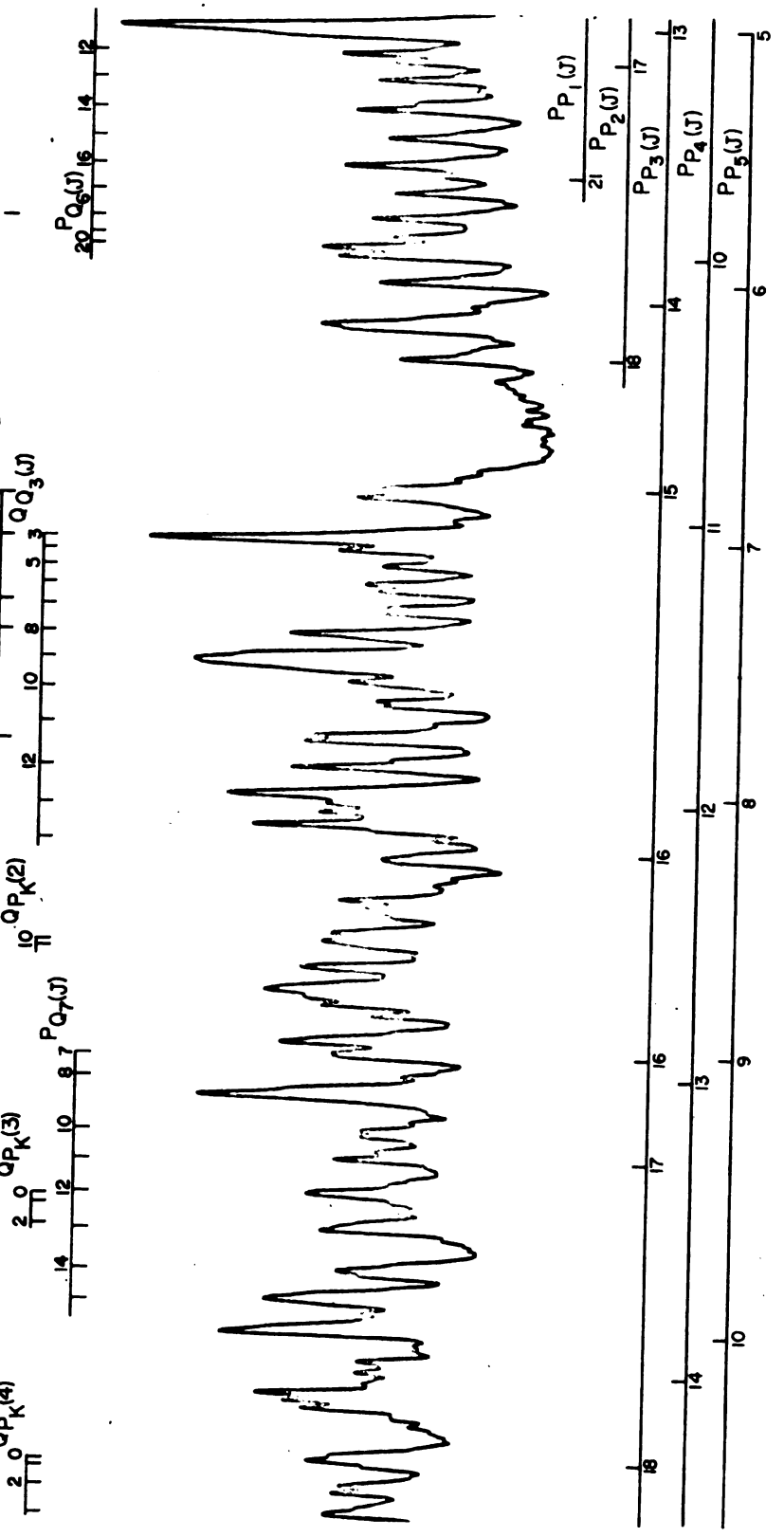


Fig. 8.2 Continued.

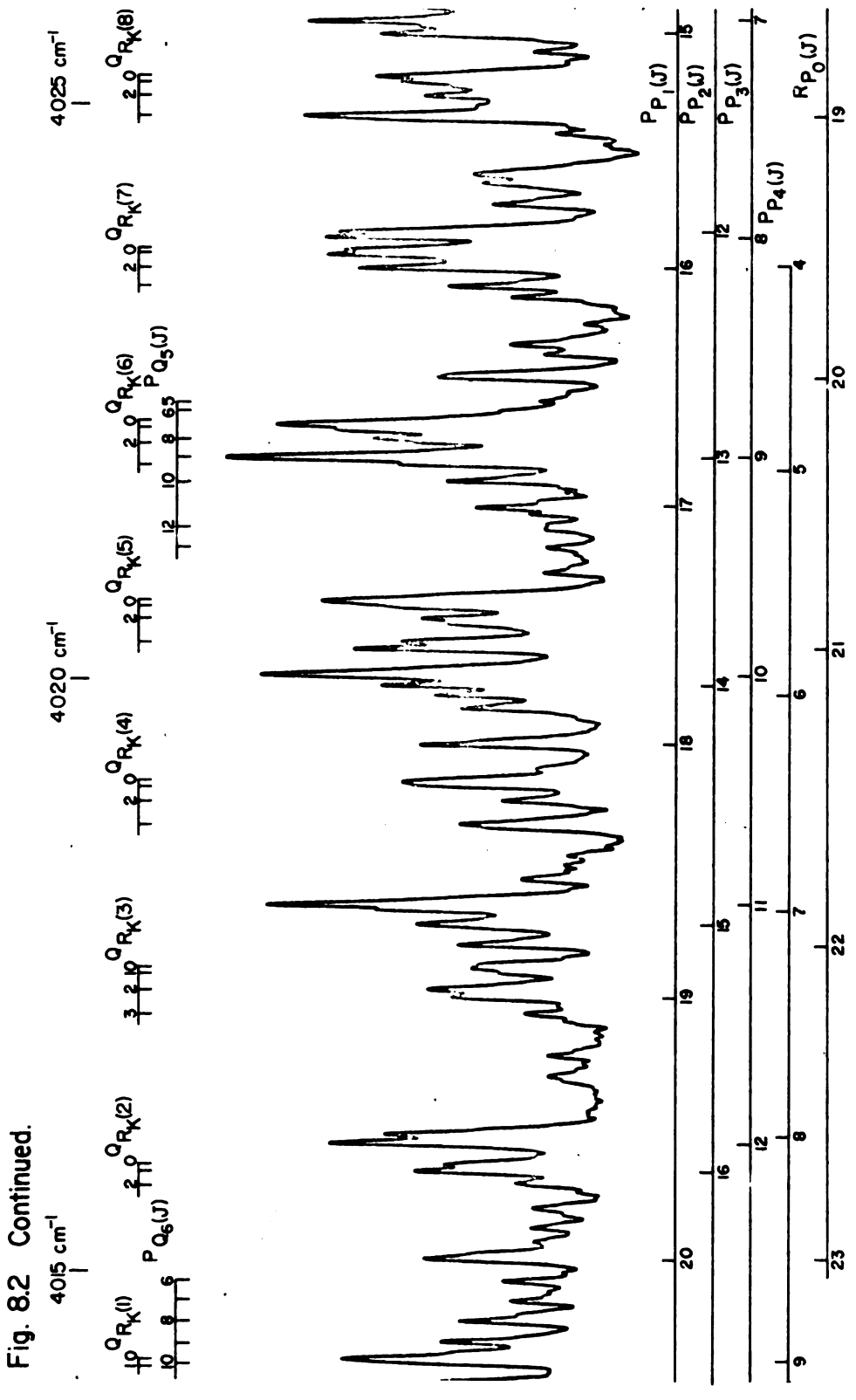


Fig. 8.2 Continued.

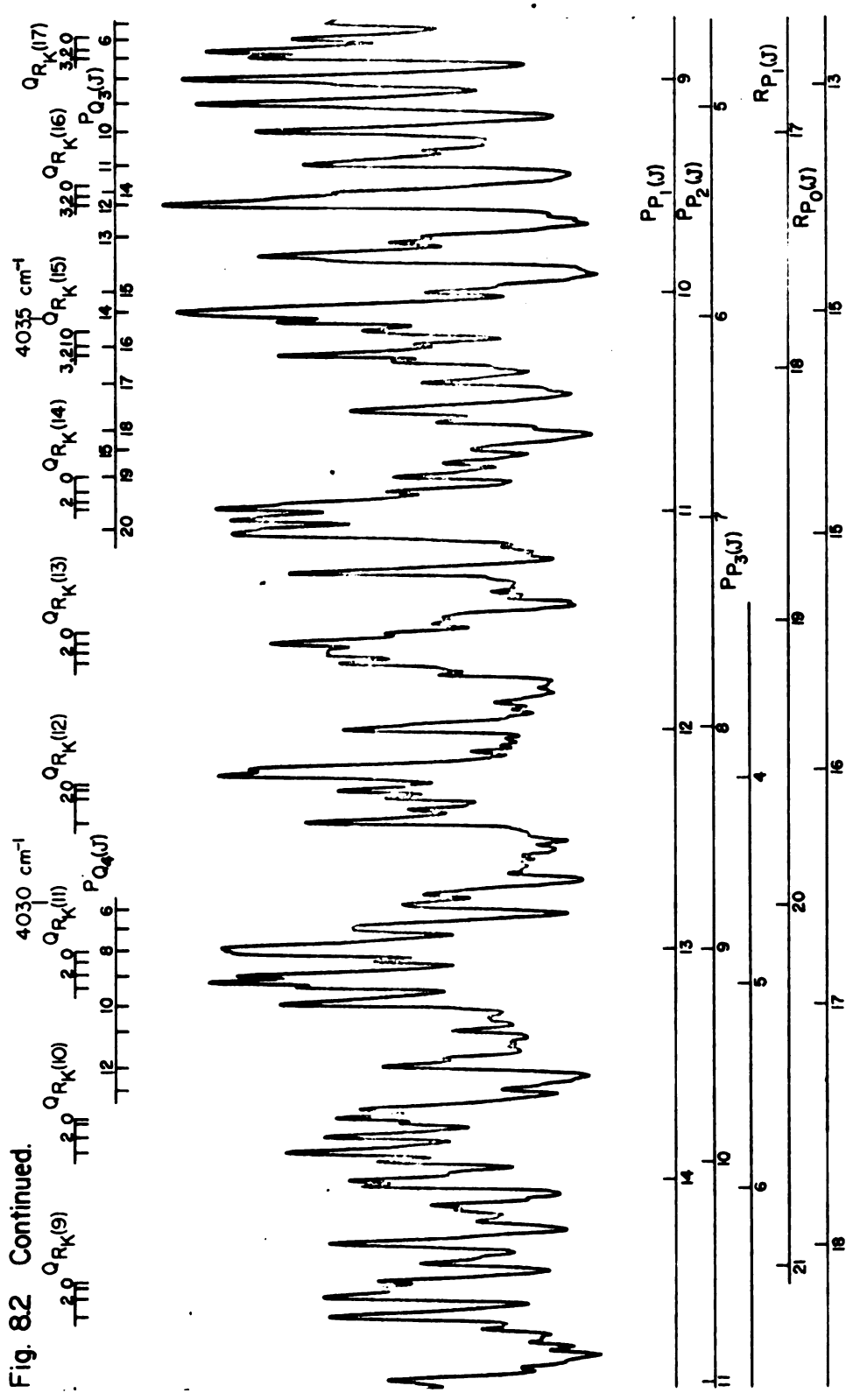
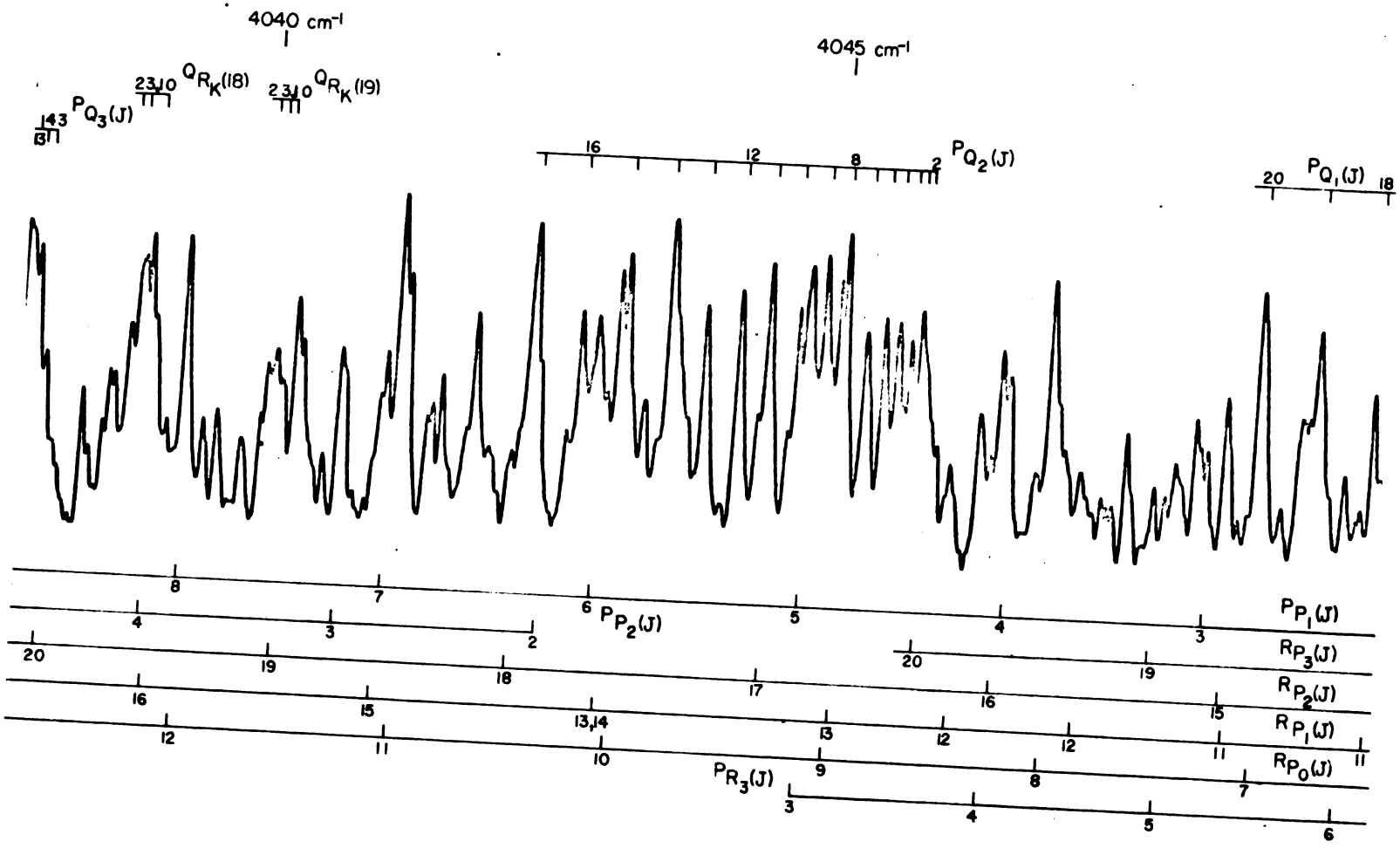


Fig. 8.2 Continued.

Fig. 8.2 Continued.



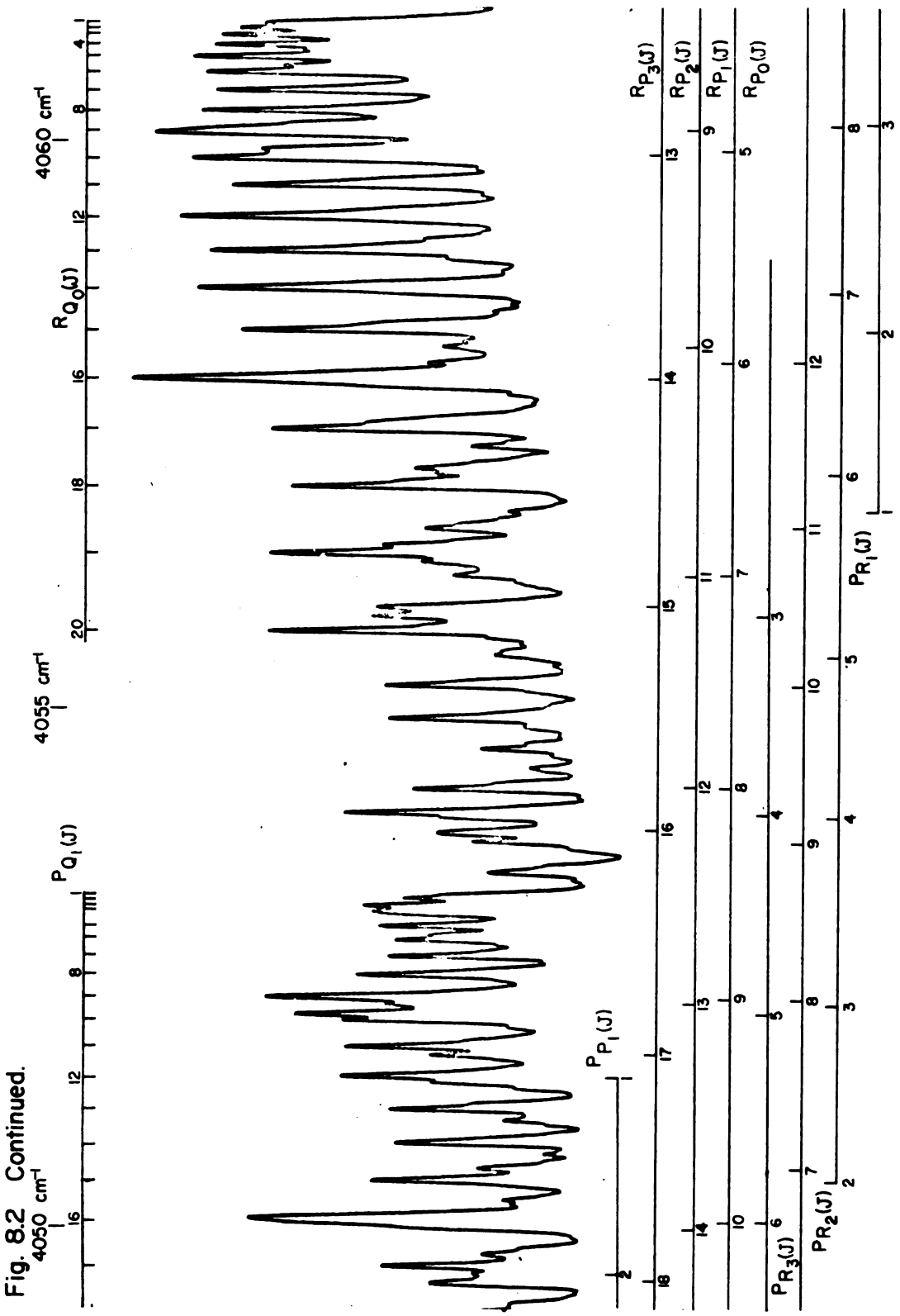


Fig. 8.2 Continued.

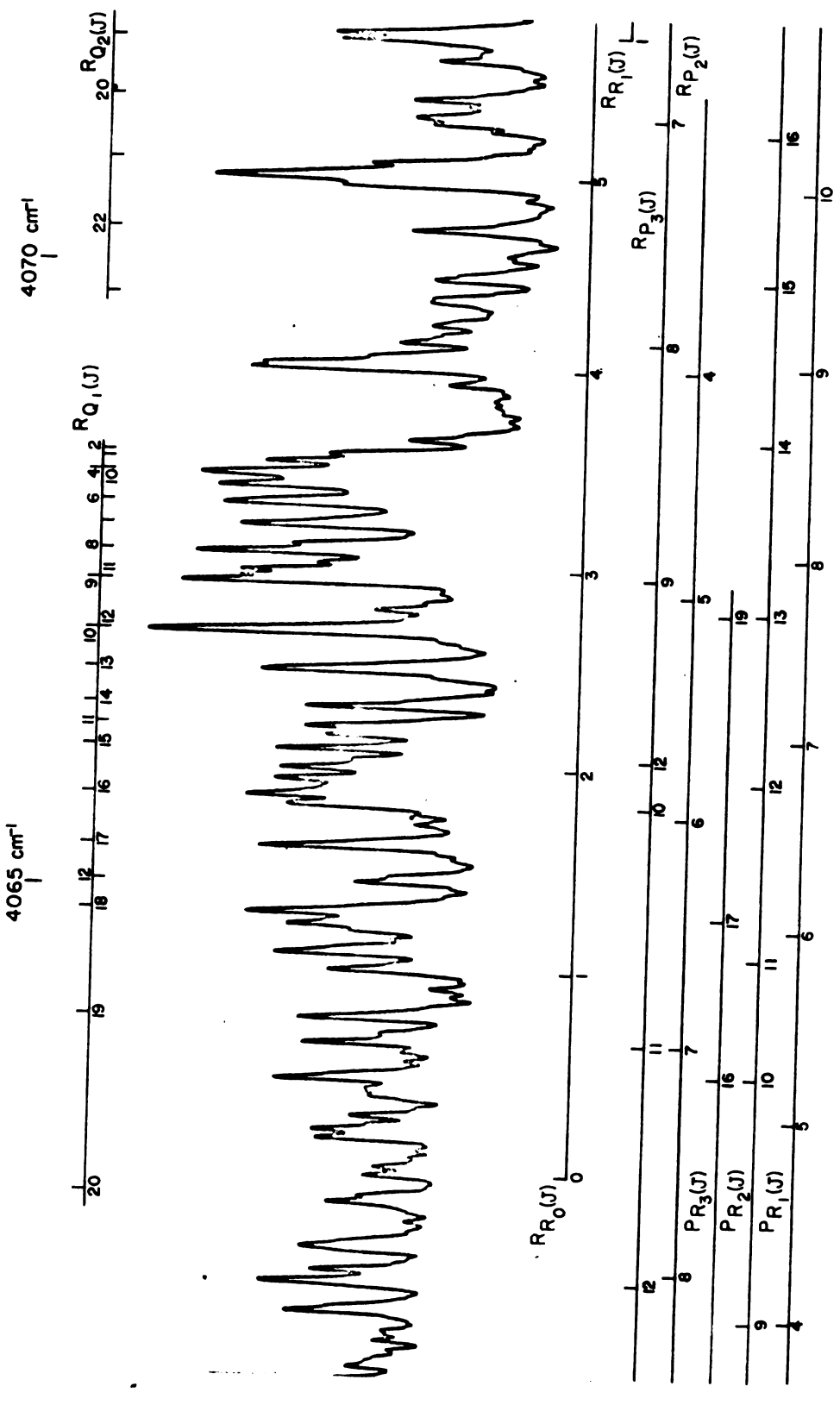


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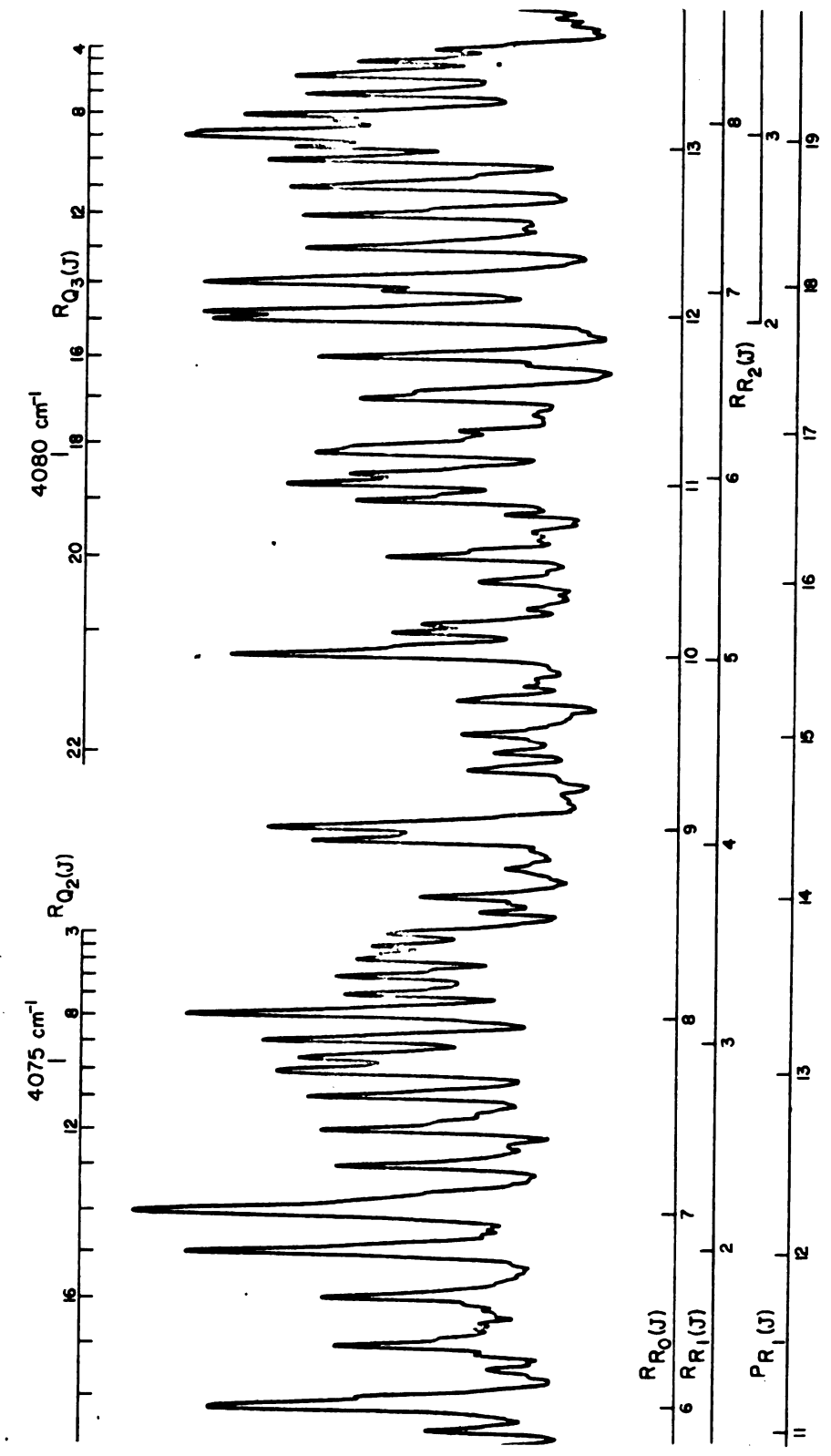


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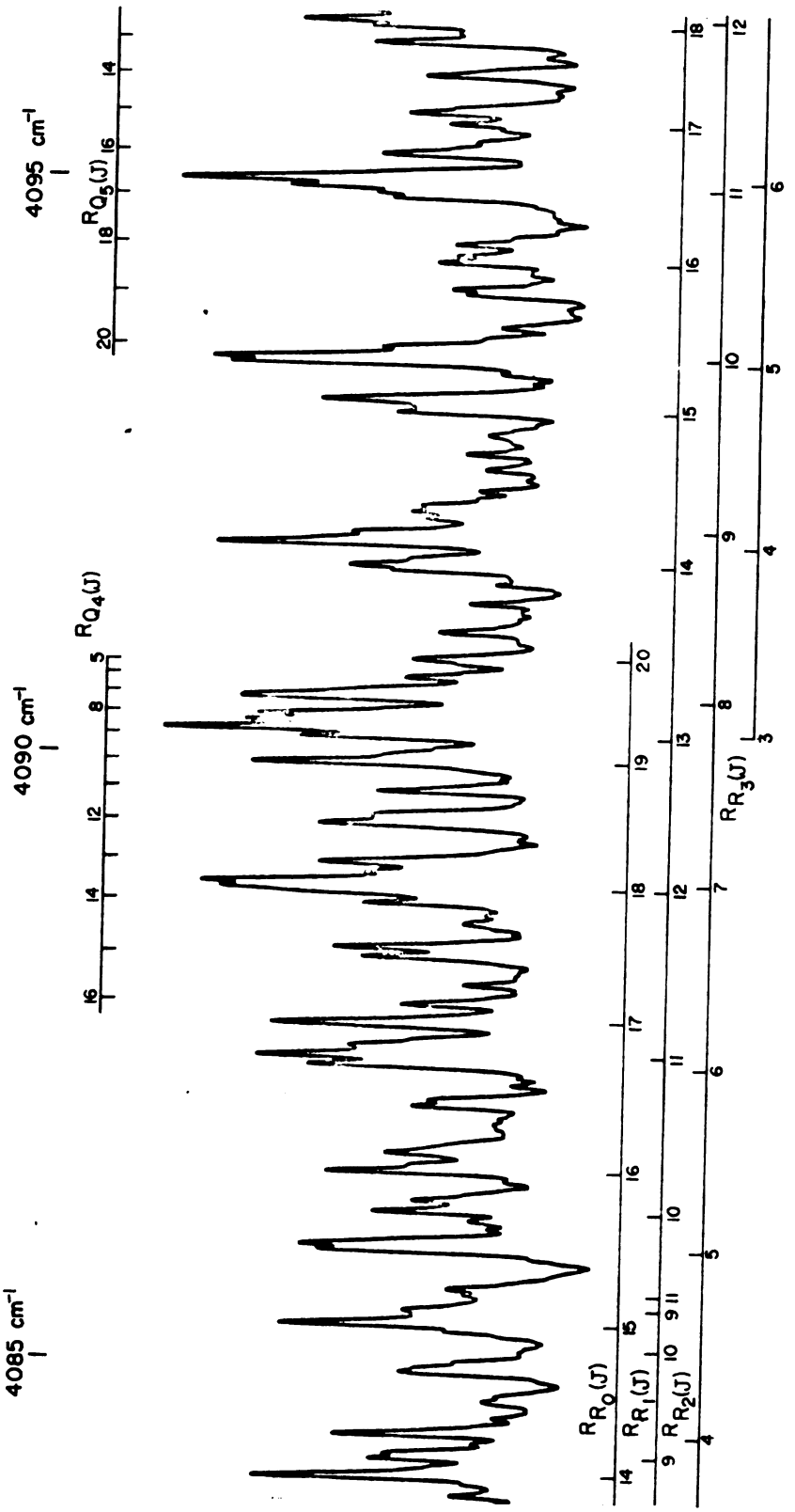


Fig. 8.2 Continued.

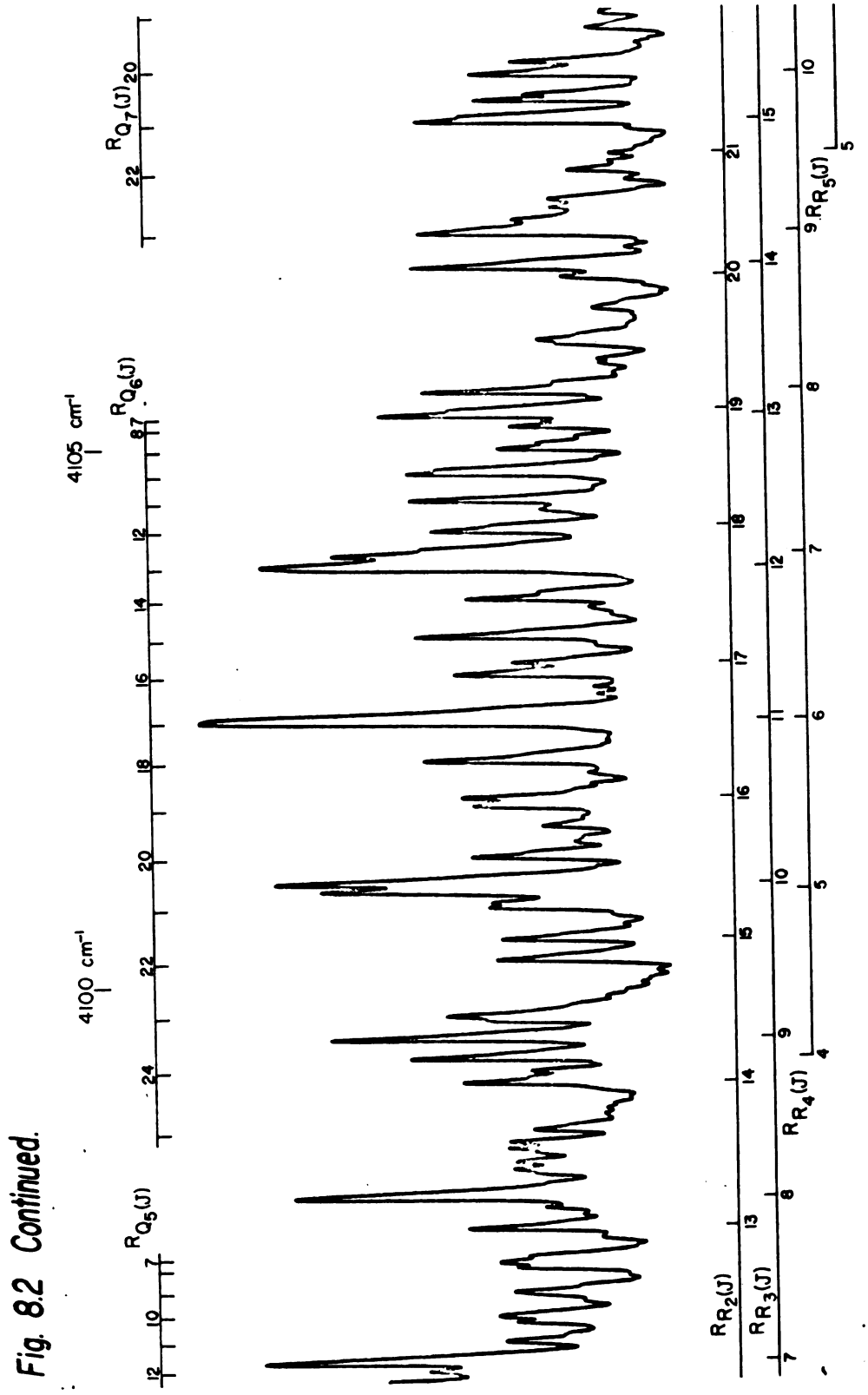


Fig. 8.2 Continued.

Fig. 8.2 Continued.

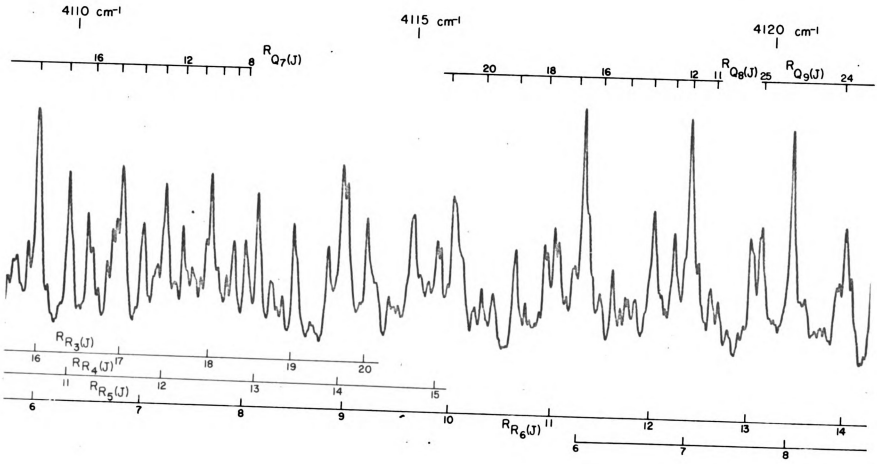
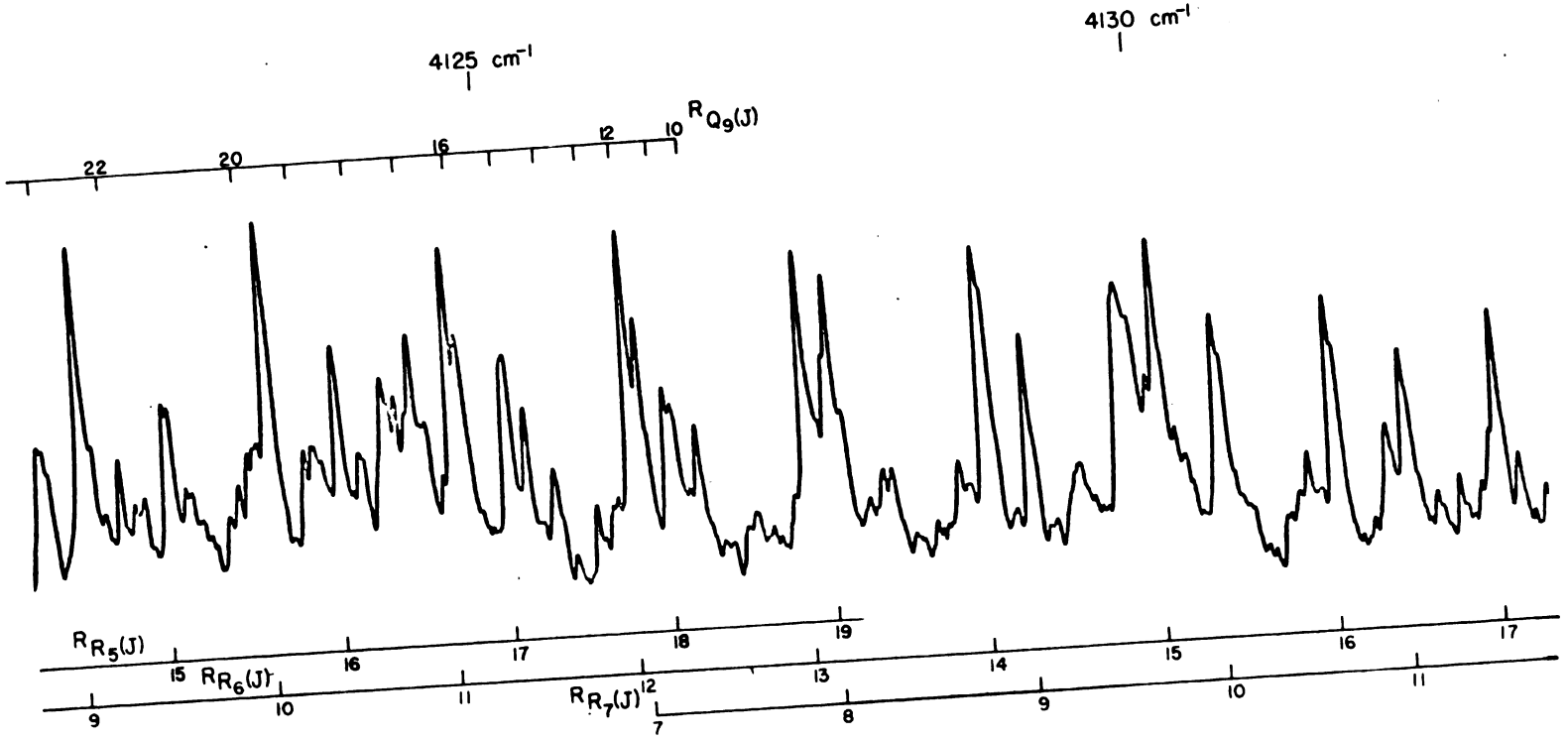


Fig. 8.2 Continued.



number. The observed ground state combination differences are listed in Appendix VI. This list presents the combination difference assignment in the notation of Eqs.(4.6), the observed combination difference, the combination difference calculated from microwave values of B_0, D_0^J and D_0^{JK} from Table 8.1, the $\Delta\nu$ and the Δ_1 (obs-calc).

All assigned transitions from $\nu_1+\nu_3$ are listed in Appendix VII, and the observed and calculated combination differences are listed in Appendix VIII.

Analysis of Ground State Combination Differences

All of the ground state combination differences which were observed for $\nu_3+\nu_4$ and $\nu_1+\nu_3$ and which received a non-zero weight [37] were simultaneously analyzed by the method of least squares using the method described in Chapter 4. A single exception is the ground state combination differences for the zero subband, i.e., the $^RQ_0(J) - {}^RP_0(J+1)$ and the $^RR_0(J-1) - {}^RQ_0(J)$ combination differences. These were not included in the simultaneous analysis since the $K' = \ell = \pm 1$ upper levels have had their degeneracy removed by a Coriolis resonance and the combination differences mentioned are not "true" ground state

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[37] The ground state combination differences were weighted by using the square root of the sum of the squares of the $\Delta\nu$'s assigned to the individual lines as the $\Delta\nu$ for the combination difference.

Table 8.1 Results of simultaneous analysis of all observed ground state combination differences from $\nu_3+\nu_4$ and $\nu_1+\nu_3$ of CH_3F[a,b].

Constant	Simultaneous analysis (cm^{-1})	Confidence intervals (cm^{-1})	Microwave results[c] (cm^{-1})	This work minus microwave (cm^{-1})
B_0	0.851940	± 0.000087	0.851793	$+0.000147$
D_0^{JK}	1.62×10^{-5}	$\pm 0.23 \times 10^{-5}$	1.48×10^{-5}	$+0.14 \times 10^{-5}$
D_0^{J}	2.15×10^{-6}	$\pm 0.15 \times 10^{-6}$	1.98×10^{-6}	$+0.17 \times 10^{-6}$

[a] 207 combination differences included in the least squares analysis

[b] Standard deviation of the observations = 0.0075 cm^{-1}

[c] Results of microwave observations of pure rotation spectra are taken from reference (58).

combination differences in that they do not go to upper levels of equal energy. This will be discussed in a later section.

The results of the simultaneous analysis are given in Table 8.1 together with a comparison with the microwave results (58). A detailed listing of the observed minus calculated value of each combination difference fit is not included in this work since the equivalent data is listed in Appendices VIII and X and we feel the microwave results are likely to be more accurate. [38]

Search for Possible Perturbations

When it became apparent that the band was perturbed, it was necessary to investigate the possible perturbation couplings with nearby rotation-vibration levels as discussed in Chapter 6, and to investigate the possible essential resonances.

Before one begins to look for possible perturbation couplings it is almost imperative that the results of any available investigations be gathered for reference since a search for possible couplings depends largely on a priori calculation of nearby rotation-vibration levels. Table 8.2 presents a summary of past work on CH_3F from a paper by Smith and Mills (102).

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[38] The difference between our calculated value of B_0 and the microwave value may lie in the calibration of the spectral record of $\nu_3+\nu_4$ and $\nu_1+\nu_3$. Some difficulty was encountered due to a lack of suitable calibration standards over a large portion of these bands. See note added in proof, p.220.

Table 8.2 Summary of rotation-vibration constants from references (58), (101), (102) and (103).

$A_o = 5.081 cm^{-1}$ (103)

$B_o = 0.851793 cm^{-1}$ (58)

$D_o^J = 1.98 \times 10^{-6} cm^{-1}$ (58)

$D_o^{JK} = 1.48 \times 10^{-5} cm^{-1}$ (58)

Assign.	Vibration Symmetry	Ref.	$\nu_o cm^{-1}$	$\alpha_s^B cm^{-1}$	$\alpha_s^A cm^{-1}$	ζ_t^z
ν_1	A_1	(101)	2964.54	-0.0017		
ν_2	A_1	(103)	1464	(not analyzed)		
ν_3	A_1	(102)	1048.60	+0.0113	+0.011	
ν_4	E_1	(101)	3005.8	-0.0019	+0.008	+0.091
ν_5	E_1	(103)	1466.5	(not analyzed)		-0.290
ν_6	E_1	(102)	1182.35	+0.0043	-0.013	+0.284
$2\nu_3-\nu_3$	A_1	(102)	1032.76			
$2\nu_3$	A_1	(101)	2081.42	+0.0223		
$\nu_3+\nu_6$	E_1	(102)	2222.6			
$2\nu_2$(?)	A_1	(100)	2818			
$2\nu_5$	A_1	(101)	2863.22	+0.0047		

Using the information in Table 8.2, the sums of fundamentals were formed for all possible overtone and combination bands in this region. These frequencies are not very accurate because they neglect anharmonicity, the effects of which may be quite large. However, the anharmonic constants are not available except for a few special cases, so that we had to use the sums of fundamentals. Table 8.3 lists all nearby rotation-vibration levels as sums of fundamentals. Then using Tables 6.5-6.8 a compilation of the principal perturbation couplings between all of these levels may be built up. Such a table is presented in Table 8.4. Listed in the table are: the formal order of magnitude of the coupling, the type of coupling described in Chapter 6.

Fig. 8.3 has the levels from Table 8.3 drawn to scale, and the perturbation couplings of expected order of magnitude 1 indicated in the left and right hand columns. The two center columns indicate the principal couplings of type I and type II between $\nu_3+\nu_4$ and the nearby bands. There is some overlap in the information shown in two outer columns and the two inner columns.

Examination of Fig. 8.3 leads to the conclusion that insufficient vibrational information is available to make possible a rigorous treatment at the present time. However, the possible couplings are indicated and some correlation with observation is possible. We shall return to the perturbation considerations a number of times in the following discussion.

Table 8.3 Overtone and combination levels as sums of fundamentals in the vicinity of $\nu_3+\nu_4$.

Level		Sum of Fundamentals (cm^{-1})
$4\nu_3$	=	4194.40
$\nu_4 + \nu_6$	=	4188.15
$\nu_1 + \nu_6$	=	4146.84
$2\nu_5 + \nu_6$	=	4115.35
$\nu_2 + \nu_5 + \nu_6$	=	4112.85
$2\nu_2 + \nu_6$	=	4110.35
$\nu_3 + \nu_4$	=	4054.40
$\nu_1 + \nu_3$	=	4013.14
$\nu_3 + 2\nu_5$	=	3981.6
$\nu_2 + \nu_3 + \nu_5$	=	3979.1
$\nu_3 + 2\nu_2$	=	3976.6

Fig. 8.3 Perturbation couplings near 4100 cm^{-1}.

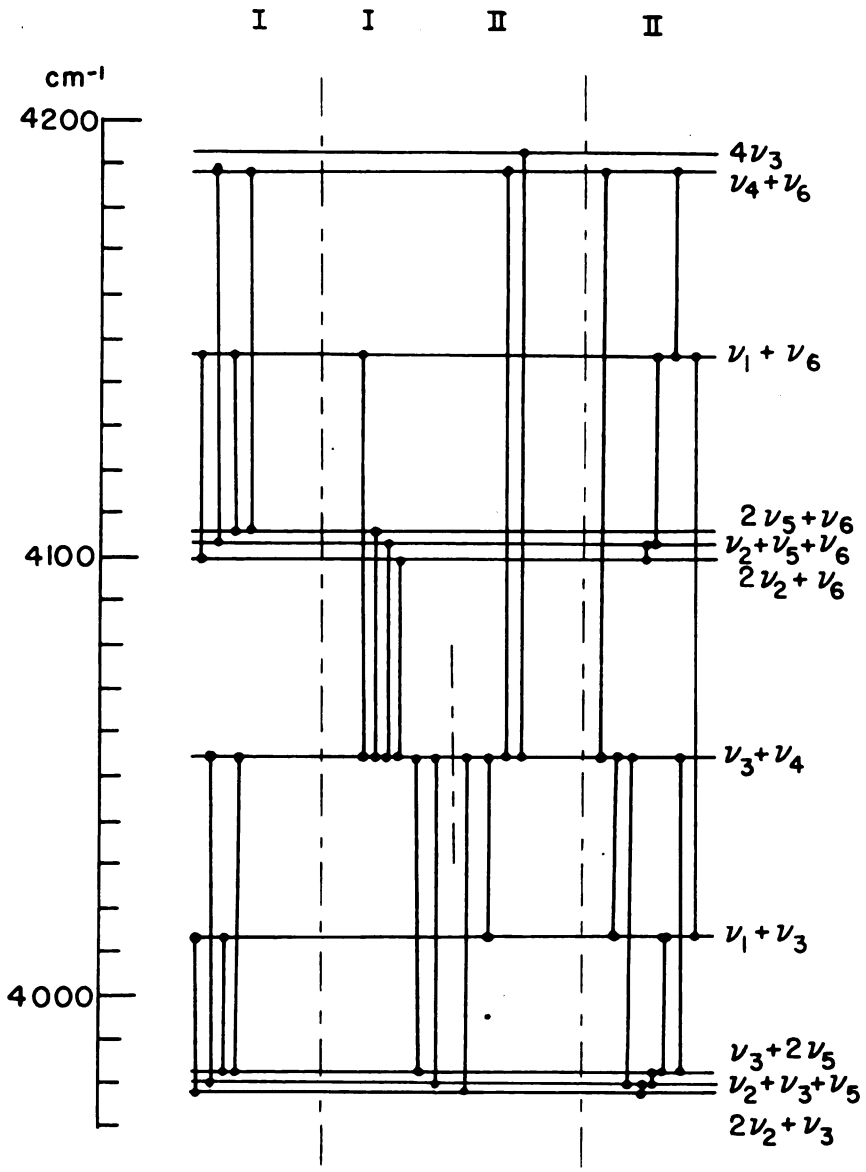


Table 8.4 Principal perturbation couplings between levels near $\nu_3 + \nu_4$.

3	I	3	I	X	X	2	I	2	I	X	X	X	X	X	X	X	X	$4\nu_3$	
3	I	3	I	3	I	2	I	1	II	2	I	1	I	1	I	1	II	$\nu_4+\nu_6$	
3	I	3	I	3	I	1	II	2	I	1	I	2	II	1	I	$\nu_1+\nu_6$			
X	X	2	II	2	II	3	I	3	I	2	I	1	II	$2\nu_5+\nu_6$					
2	I	1	I	2	I	3	I	3	I	1	II	$\nu_2+\nu_5+\nu_6$							
1	II	2	I	X	X	3	I	3	I	$2\nu_2+\nu_6$									
2	II	1	I	1	I	1	II	$\nu_3+\nu_4$											
1	I	2	II	1	I	$\nu_1+\nu_3$													
2	I	1	II	$\nu_3+2\nu_5$															
1	II	$\nu_2+\nu_3+\nu_5$																	
$\nu_3+2\nu_2$																			

Analysis of the Unperturbed Transitions of $\nu_3+\nu_4$

Once the majority of the perturbed transitions were found and excluded from the data, the remaining lines, which are assumed to be either unperturbed or only slightly perturbed, were simultaneously analyzed, following the procedure outlined in Chapter 5. The equation

$$\left\{(\Delta K)_{(\Delta J)_K(J)}\right\}_{obs} - B_o\left[(J+\Delta J)\,(J+1+\Delta J) - J(J+1)\right] +$$

$$D_o^J\left[(J+\Delta J)^2(J+1+\Delta J)^2 - J^2(J+1)^2\right] +$$

$$D_o^{JK}\left[(K+\Delta K)^2(J+\Delta J)(J+1+\Delta J) - K^2J(J+1)\right] =$$

$$(\nu_o - A_e\,\zeta_4^z - \tfrac{1}{4}\eta_4^K) + (A_o - A_e\,\zeta_4^z - \tfrac{1}{2}\eta_4^K)\left[2K\Delta K + (\Delta K)^2\right] +$$

$$(\alpha_3^A + \alpha_4^A - \alpha_3^B - \alpha_4^B - (3/2)\eta_4^K)\left[-(K+\Delta K)^2\right] +$$

$$(\alpha_3^B + \alpha_4^B)\left[-(J+\Delta J)\,(J+1+\Delta J)\right] +$$

$$(D_o^K - \tfrac{1}{4}\eta_4^K)\left[-(K+\Delta K)^4 + K^4\right] +$$

$$(\eta_4^J)\left[(J+\Delta J)\,(J+1+\Delta J)\,(K+\Delta K)\,\Delta K\right] \qquad (8.1)$$

was found to represent the data adequately, and no other terms were found to be significant. The results of the simultaneous least squares analysis of 156 transitions are presented in Table 8.5 with their simultaneous confidence

Table 8.5 Results of a simultaneous least squares analysis of $\nu_3 + \nu_4$ of CH_3F including transitions from the $^{J}-3$, -2, -1, 0, $+1$, $+2$, $+3$, $+4$, $+6$, $+7$, $+8$ and $+9$ subbands (in cm^{-1}).

$\nu_o - A_e\zeta_4^z - \frac{1}{4}\eta_4^K$	=	4057.2074 ± 0.0074
$A_o - A_e\zeta_4^z - \frac{1}{2}\eta_4^K$	=	4.6684 ± 0.0018
$\alpha_3^A + \alpha_4^A - \alpha_3^B - \alpha_4^B - (3/2)\eta_4^K$	=	$1.390\times10^{-2} \pm 0.097\times10^{-2}$
$\alpha_3^B + \alpha_4^B$	=	$1.0816\times10^{-2} \pm 0.0080\times10^{-2}$
$D_o^K - \frac{1}{4}\eta_4^K$	=	$1.46\times10^{-4} \pm 0.21\times10^{-4}$
η_4^J	=	$4.7\times10^{-5} \pm 1.2\times10^{-5}$
Std. dev. of observations included in the analysis	=	$\pm 0.011 cm^{-1}$

intervals (discussed in Chapter 5). The computer output is contained in Appendix IX which consists of three sections; the first is a summary of the observed and the calculated frequencies, the $\Delta\nu$ (Weight = $(\text{Norm})^2/(\Delta\nu)^2$), and the Δ_1(obs-calc) discussed in Chapter 5. The second section is a similar listing for lines which were not included in the analysis because of perturbations, while the third section is the same type of listing for all zero weighted lines (usually badly overlapped with other lines).

Figs. 8.4 - 8.22 are graphs of the observed minus the calculated frequencies[39] based on the results in Appendix IX. In principle each would be a horizontal straight line if no perturbations were present. From Figs. 8.4 - 8.22 it is possible to obtain a qualitative idea of the nature of several perturbations which are present in this band. In the following sections we discuss these perturbations and our analysis of some of the perturbations.

Coriolis Resonance

An interesting perturbation affects the zero subband of $\nu_3+\nu_4$. The effect of the perturbation may be seen in Fig. 8.13. The perturbation is ascribed to a first order Coriolis resonance between $\nu_3+\nu_4$ and $\nu_1+\nu_3$, although an appropriate coupling with another vibration band of

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[39] No distinction in Figs. 8.4 - 8.22 is made between ΔJ = +1, 0, -1 transitions since this information is contained in detail in Appendix IX.

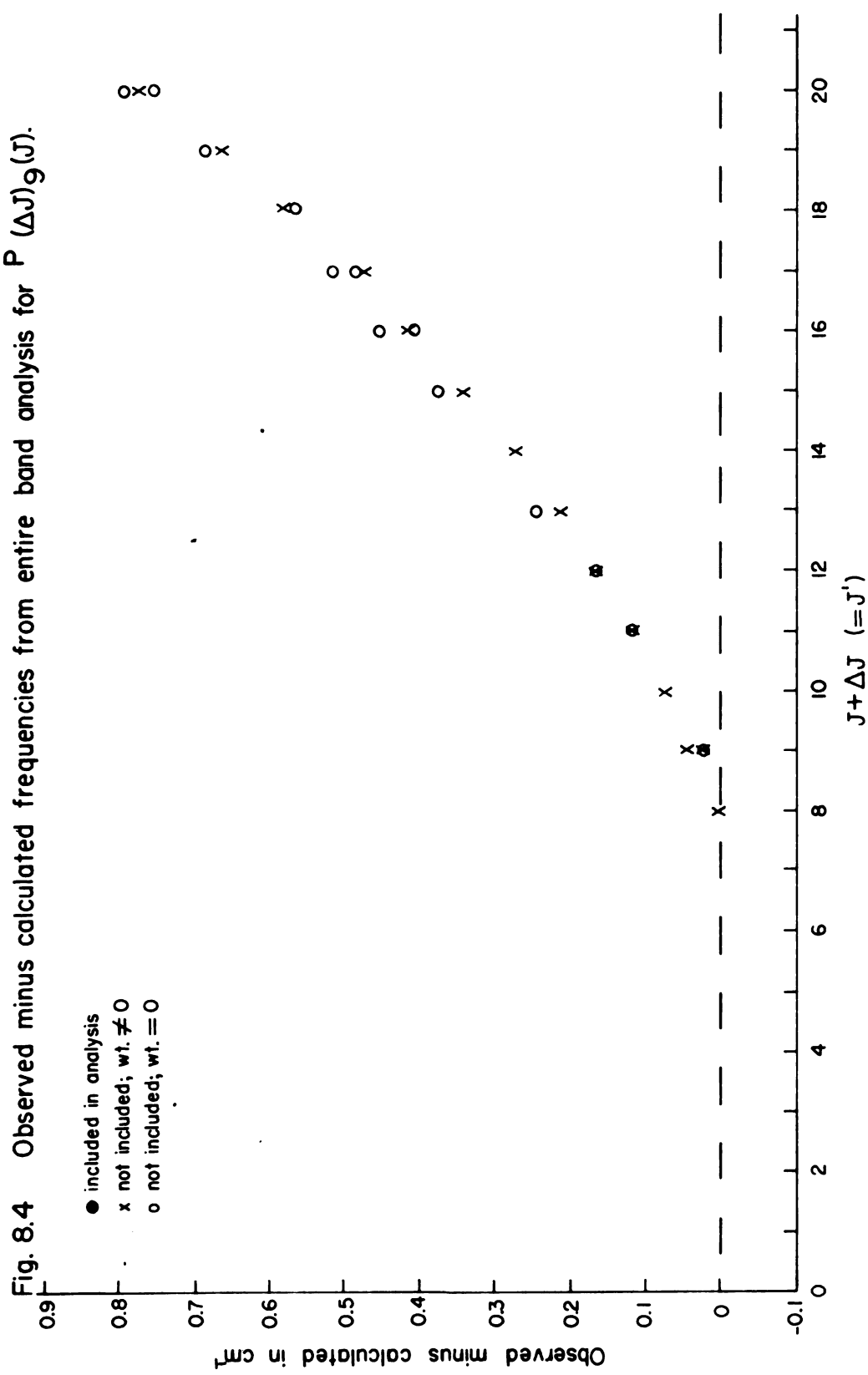


Fig. 8.4 Observed minus calculated frequencies from entire band analysis for $^{P}(\Delta J)_{g}(J)$.

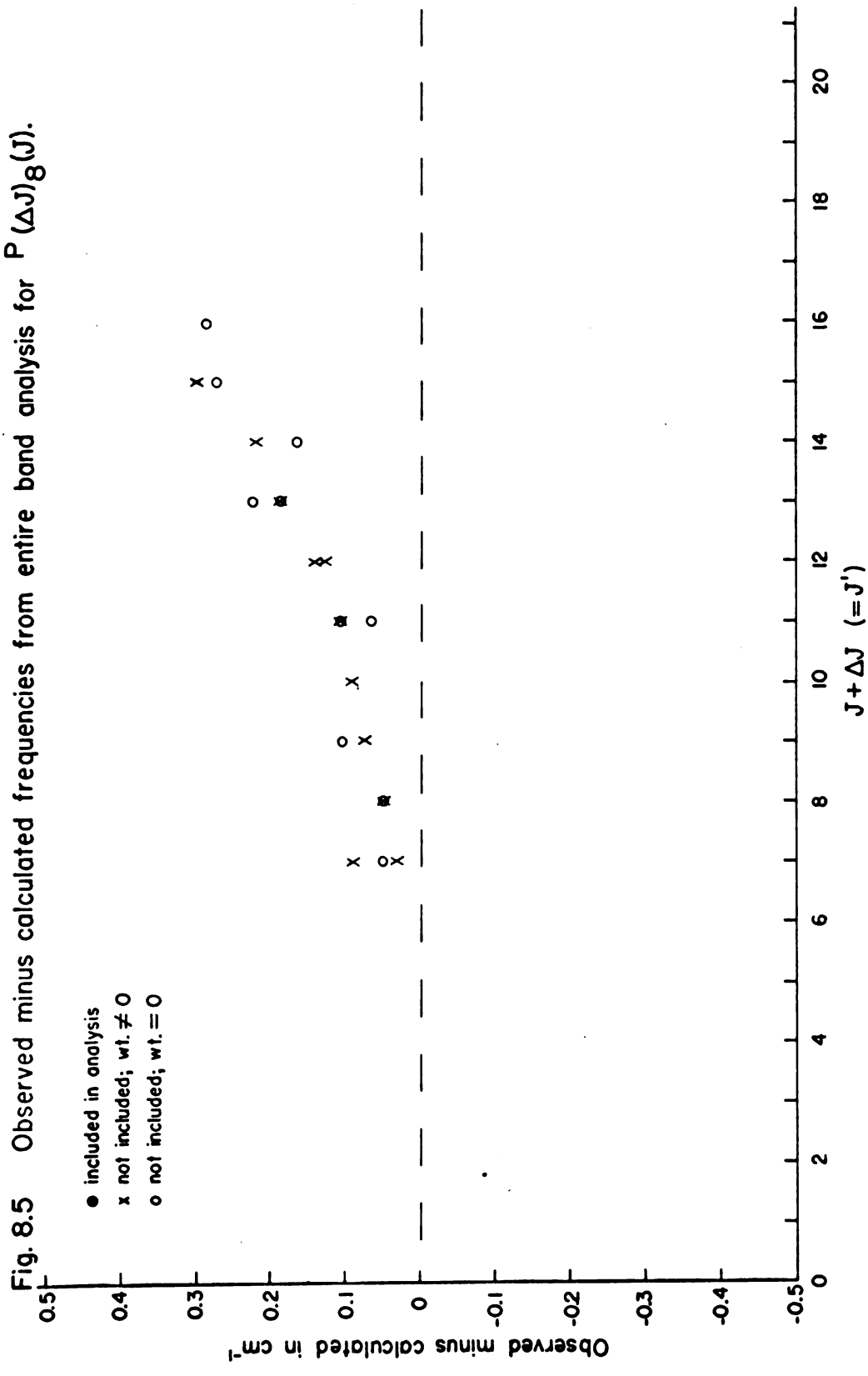


Fig. 8.5 Observed minus calculated frequencies from entire band analysis for $P(\Delta J)_8(J)$.

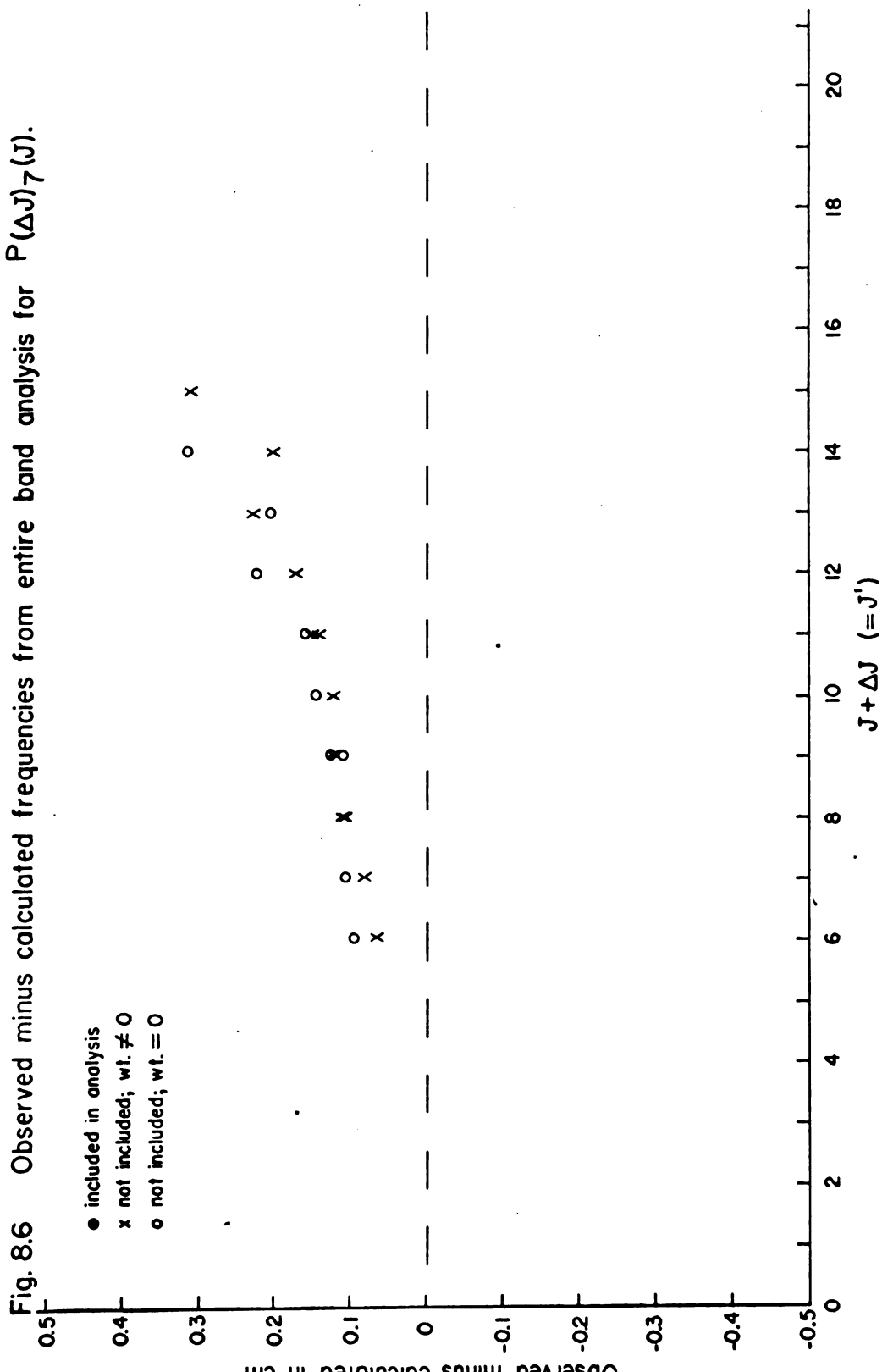


Fig. 8.6 Observed minus calculated frequencies from entire band analysis for $P(\Delta J)_7(J)$.

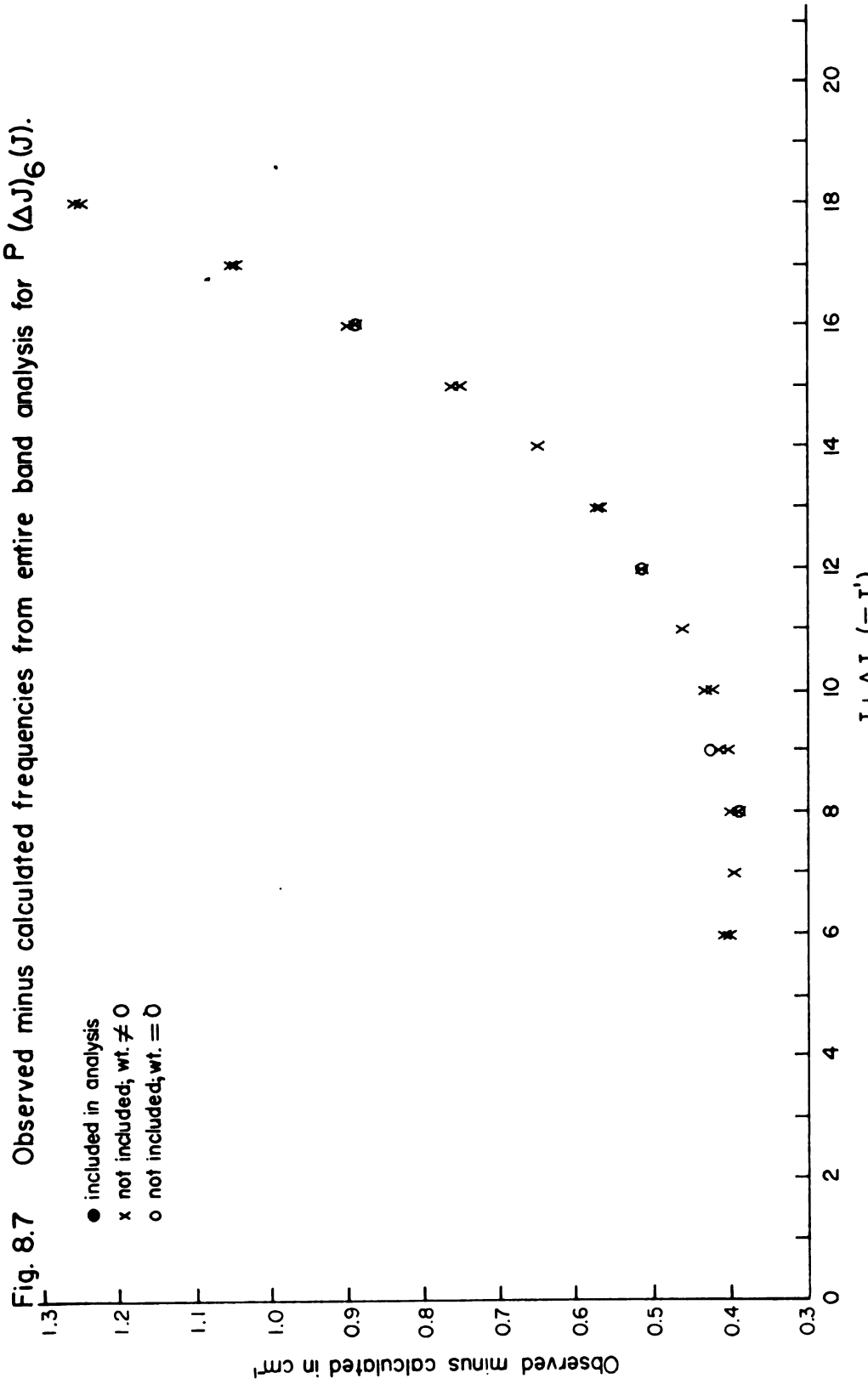


Fig. 8.7 Observed minus calculated frequencies from entire band analysis for $P(\Delta J)_6(J)$.

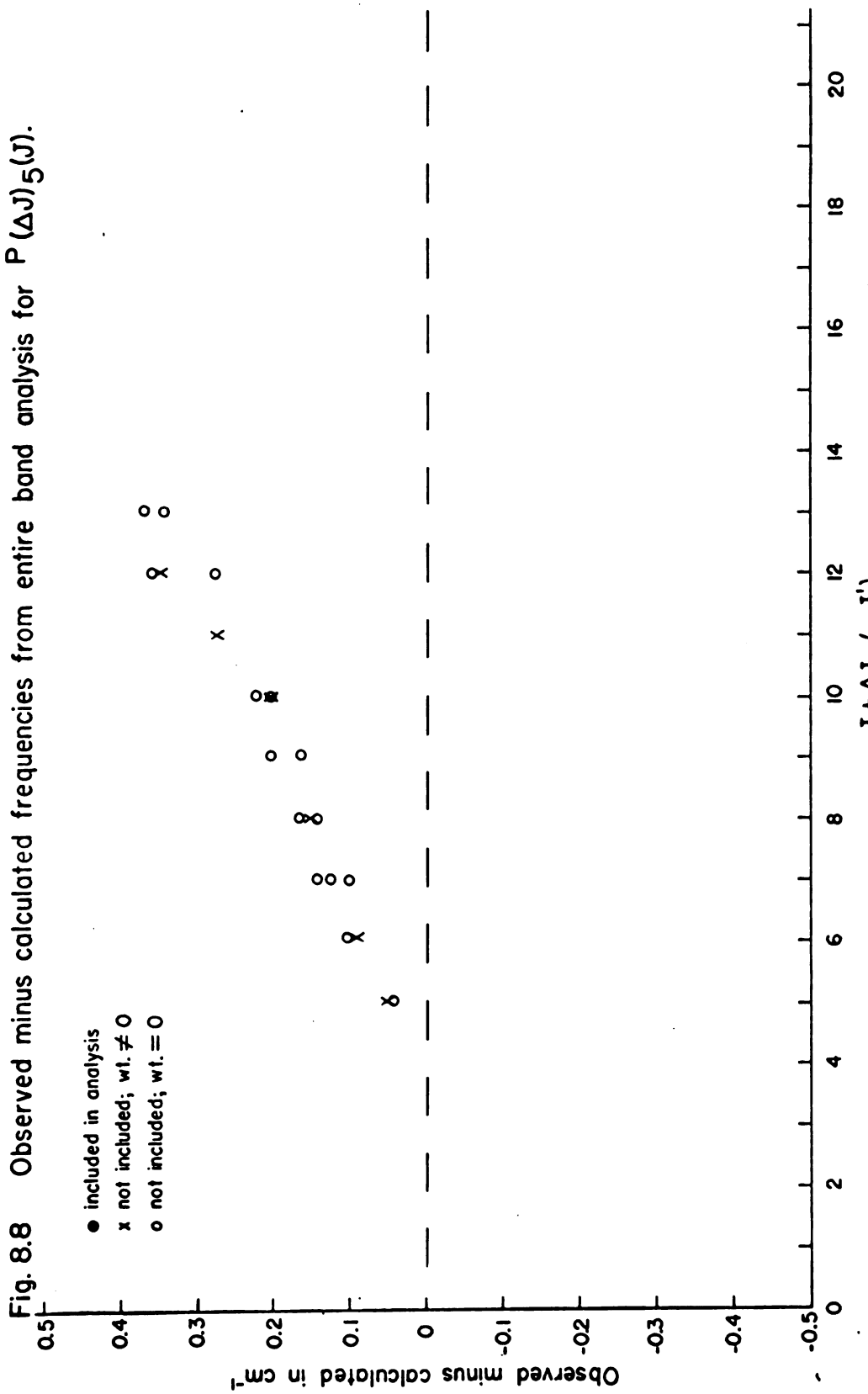


Fig. 8.8 Observed minus calculated frequencies from entire band analysis for $P(\Delta J)_5(J)$.

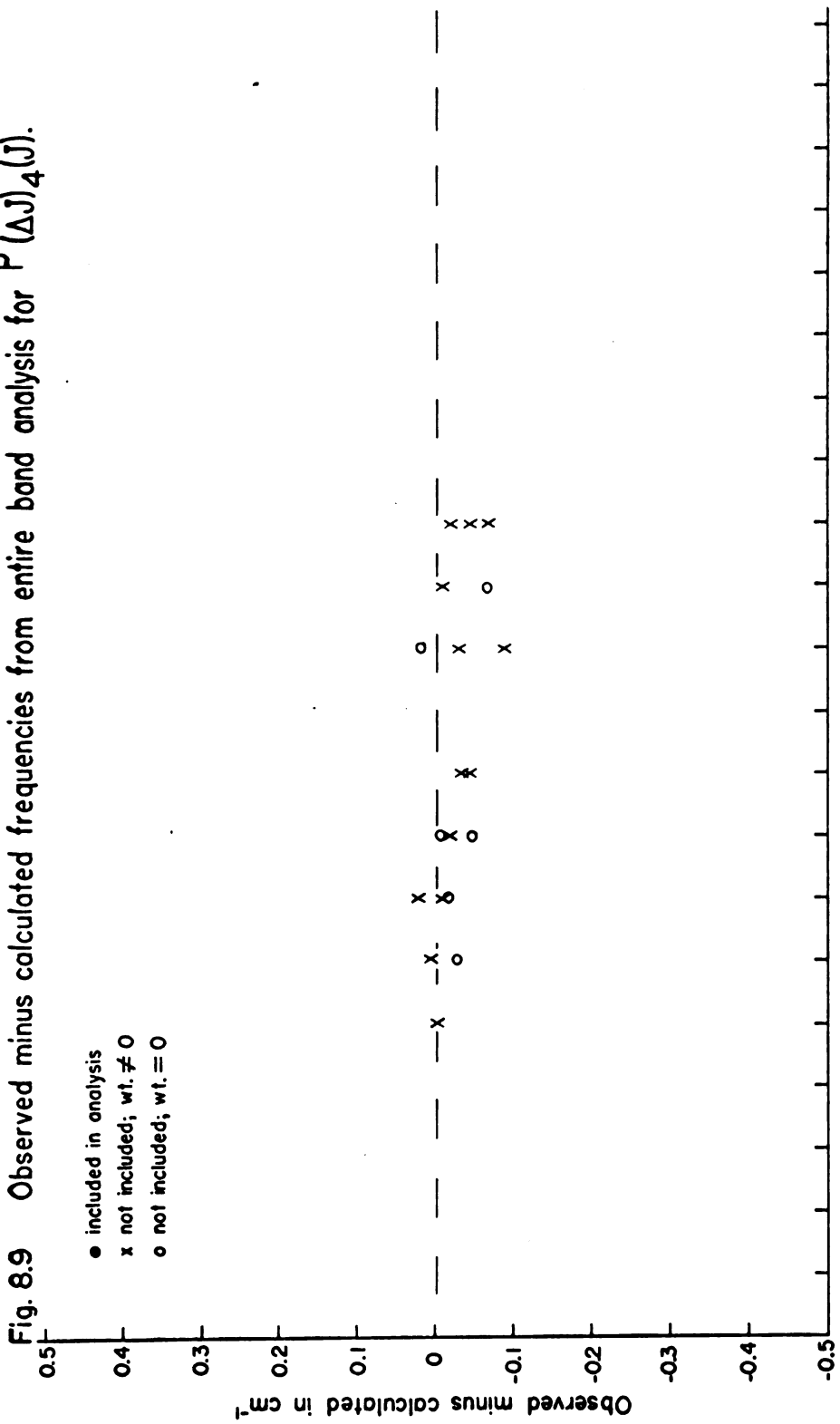


Fig. 8.9 Observed minus calculated frequencies from entire band analysis for $P(\Delta J)_4(J)$.

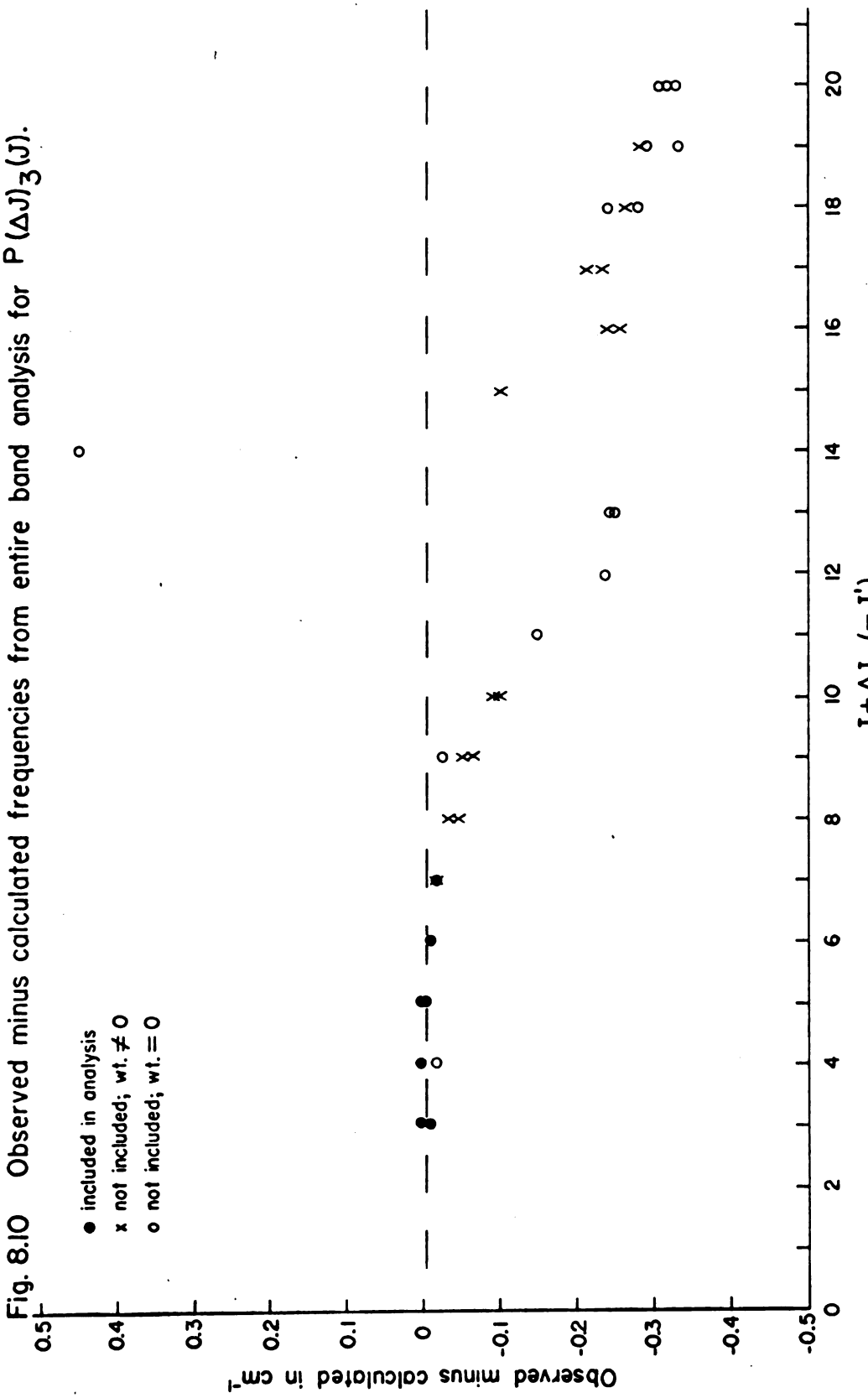


Fig. 8.10 Observed minus calculated frequencies from entire band analysis for $P(\Delta J)_3(J)$.

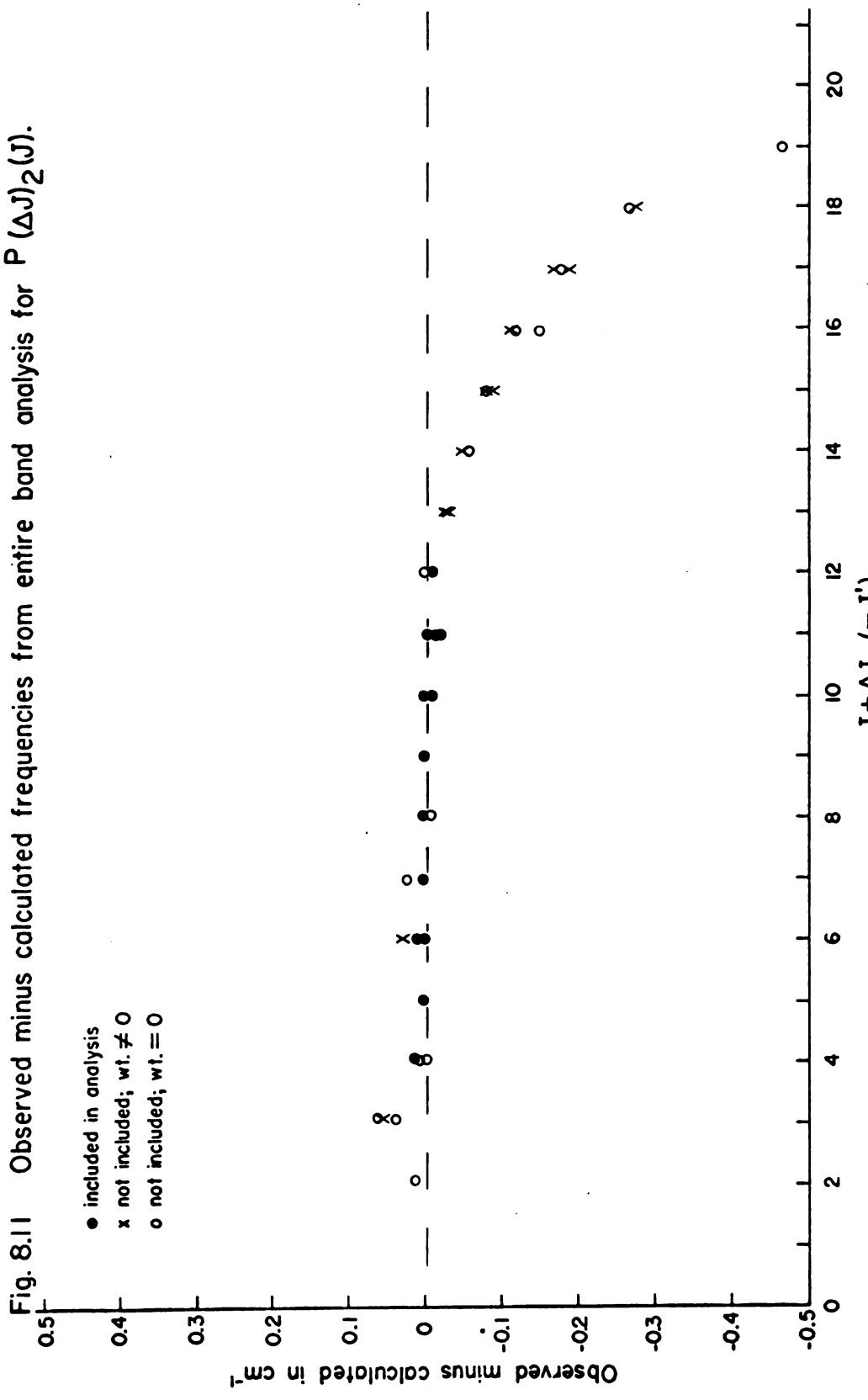


Fig. 8.11 Observed minus calculated frequencies from entire band analysis for $P(\Delta J)_2(J)$.

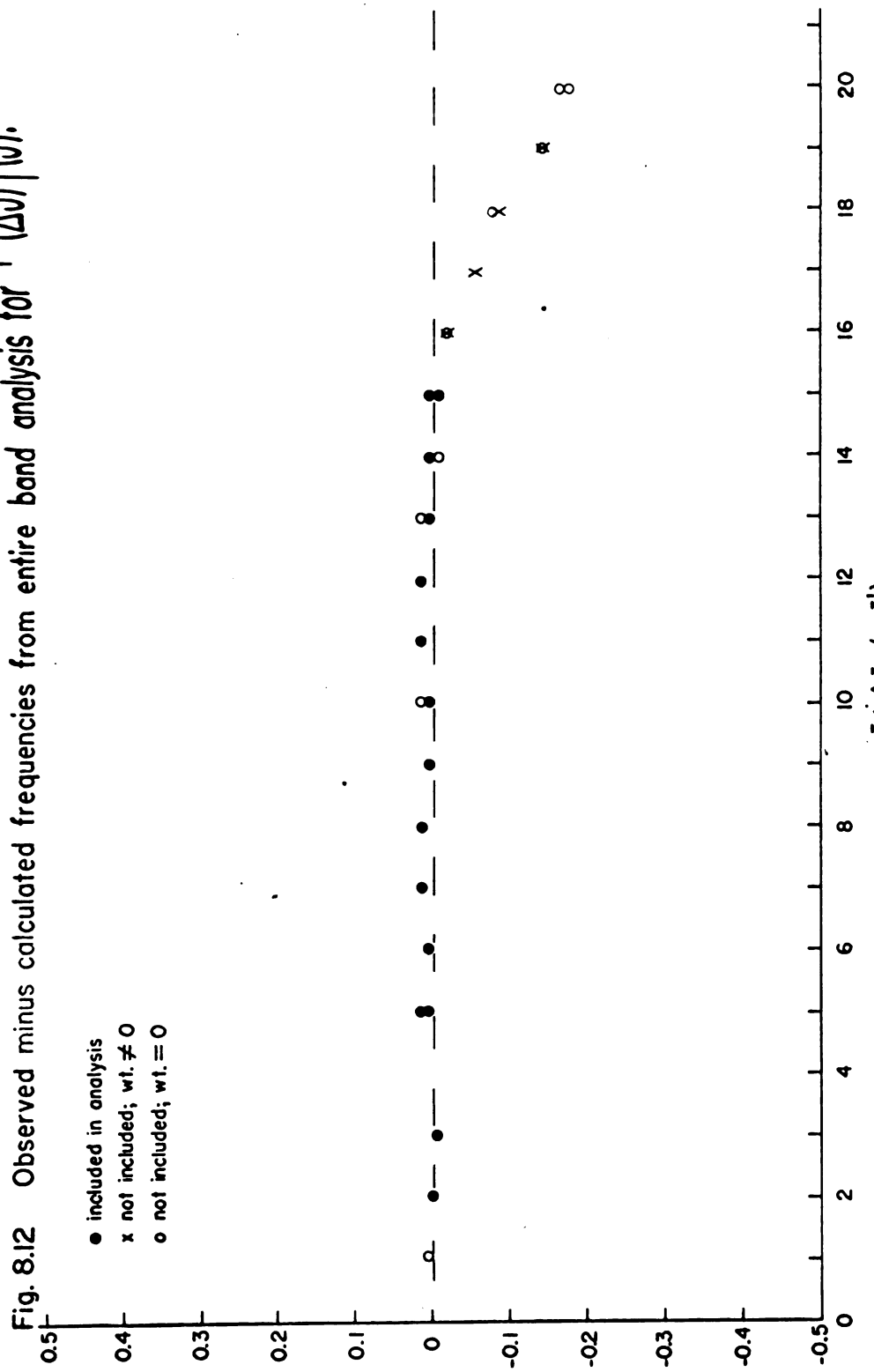


Fig. 8.12 Observed minus calculated frequencies from entire band analysis for $P(\Delta J)(J)$.

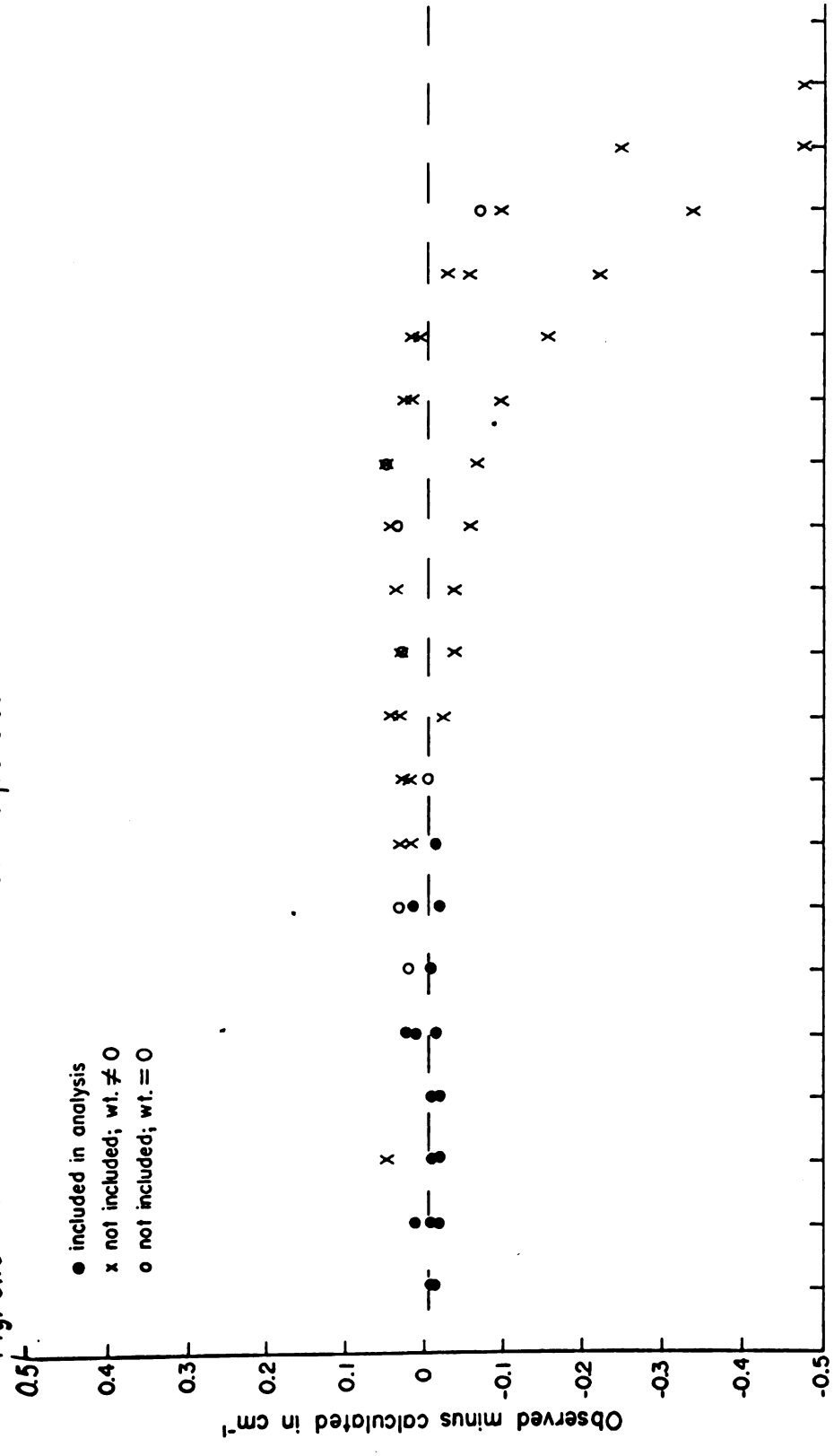


Fig. 8.13 Observed minus calculated frequencies from entire band analysis for $^{R}(\Delta J)_{O}(J)$.

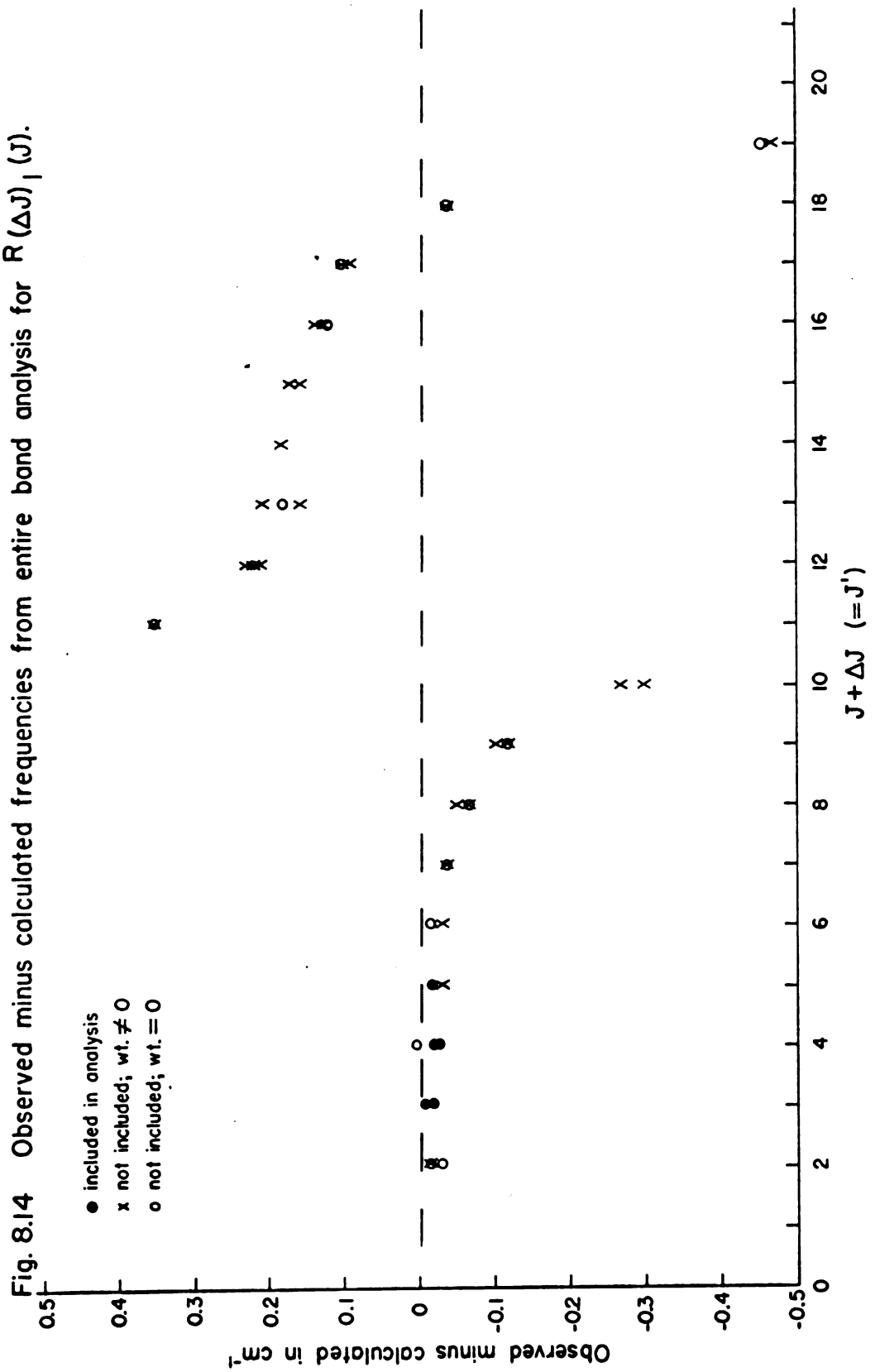


Fig. 8.14 Observed minus calculated frequencies from entire band analysis for $R(\Delta J)_1(J)$.

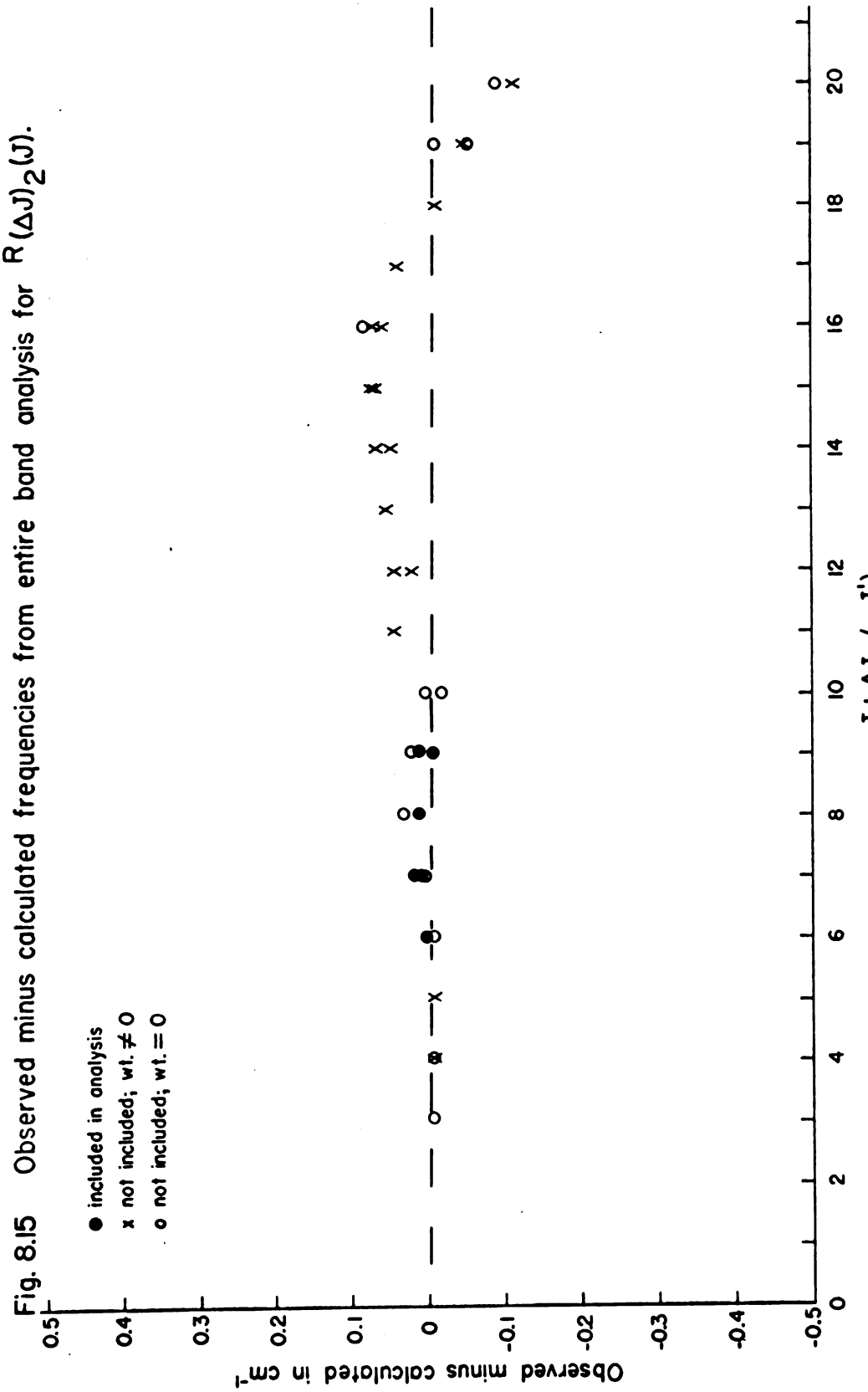


Fig. 8.15 Observed minus calculated frequencies from entire band analysis for $R(\Delta J)_2(J)$.

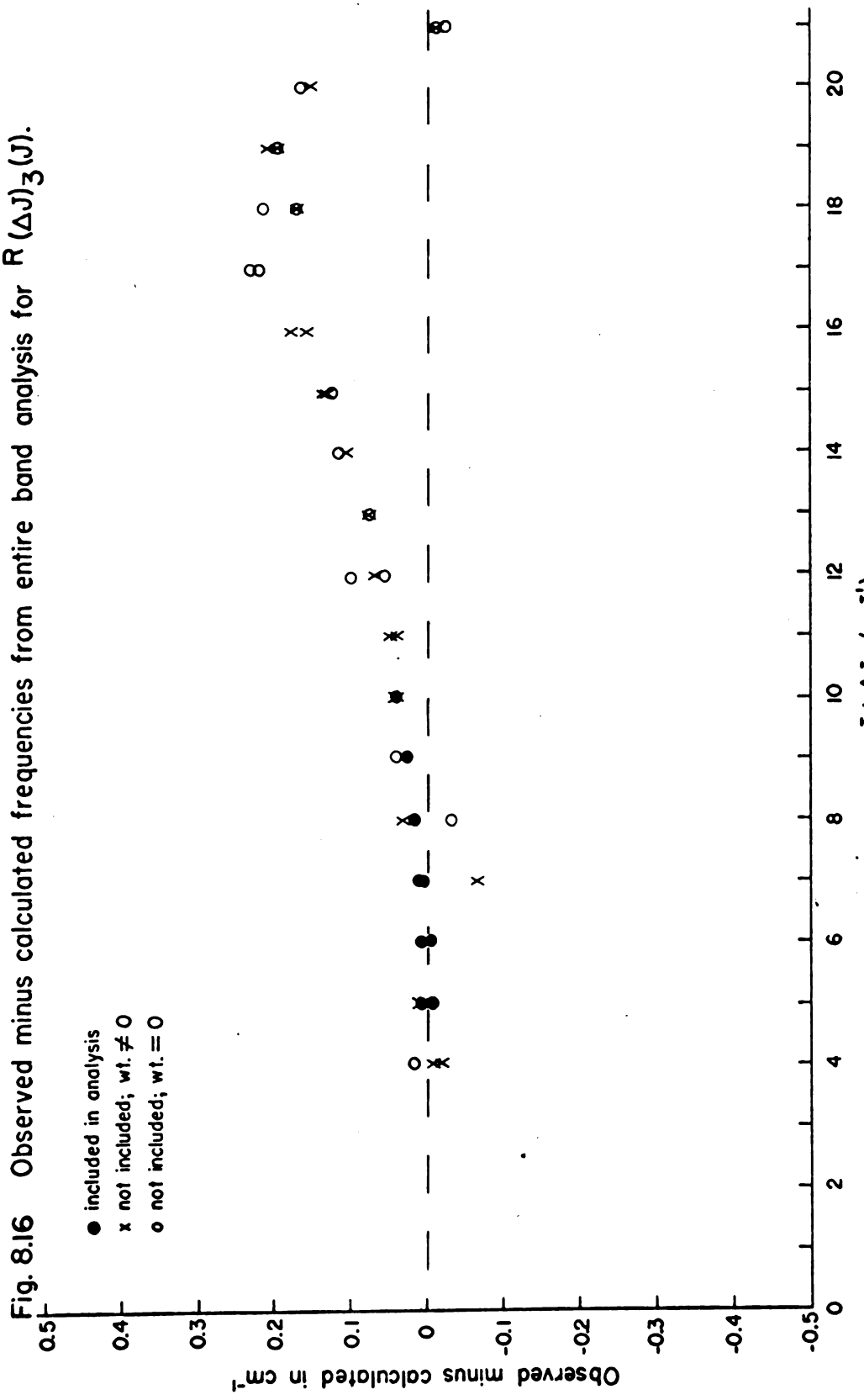


Fig. 8.16 Observed minus calculated frequencies from entire band analysis for $R(\Delta J)_3(J)$.

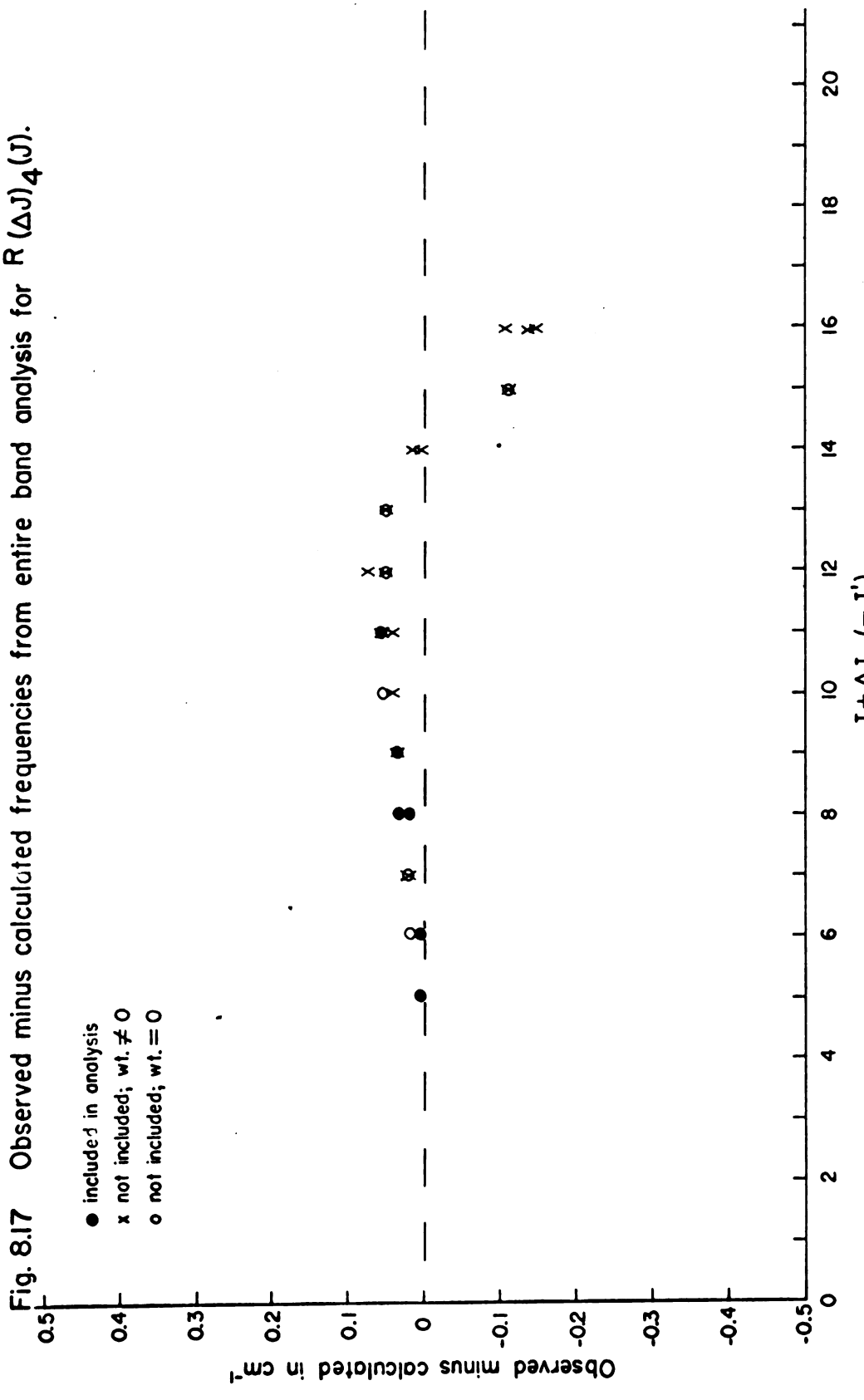


Fig. 8.17 Observed minus calculated frequencies from entire band analysis for $R(\Delta J)_4(J)$.

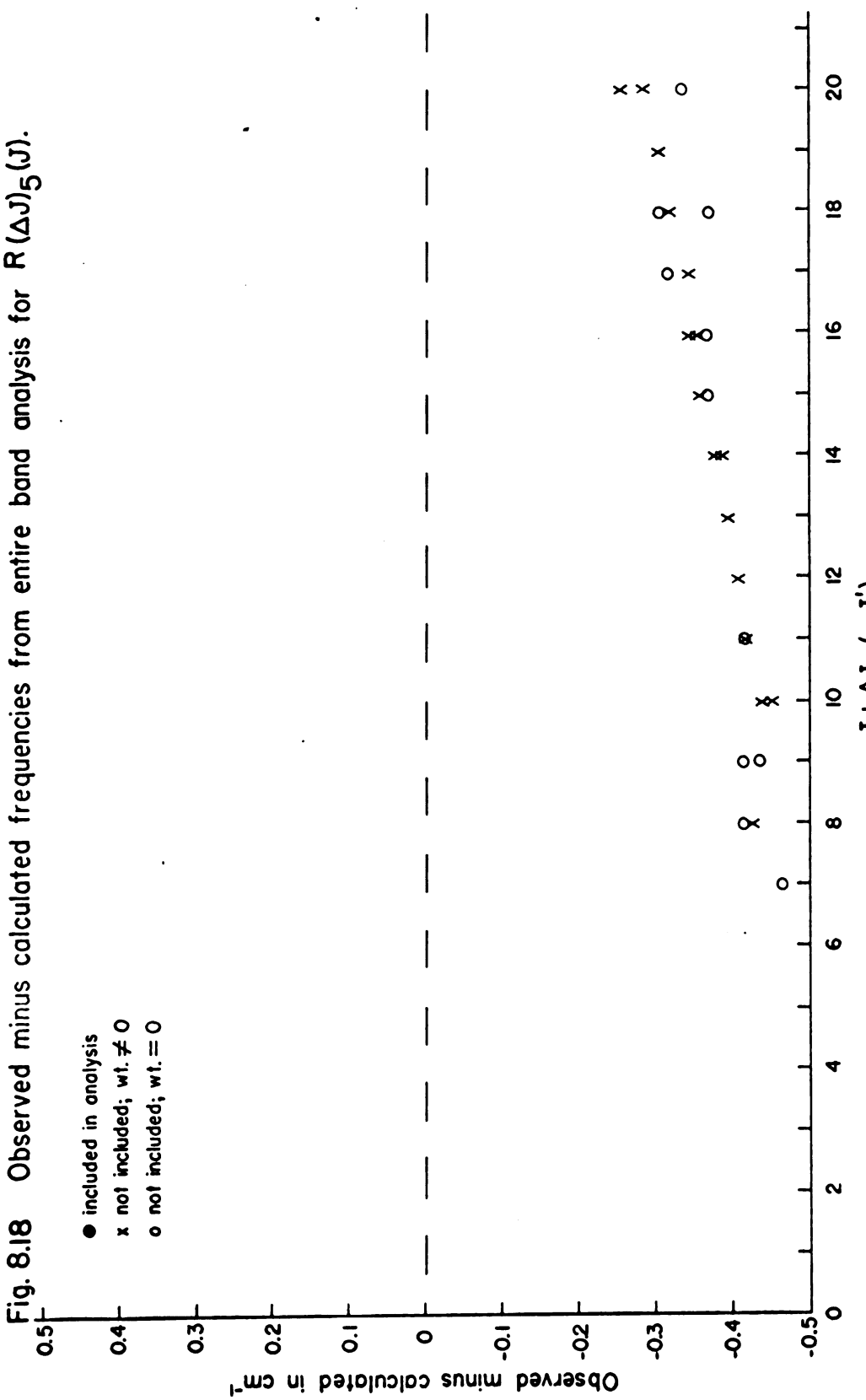


Fig. 8.18 Observed minus calculated frequencies from entire band analysis for $R(\Delta J)_5(J)$.

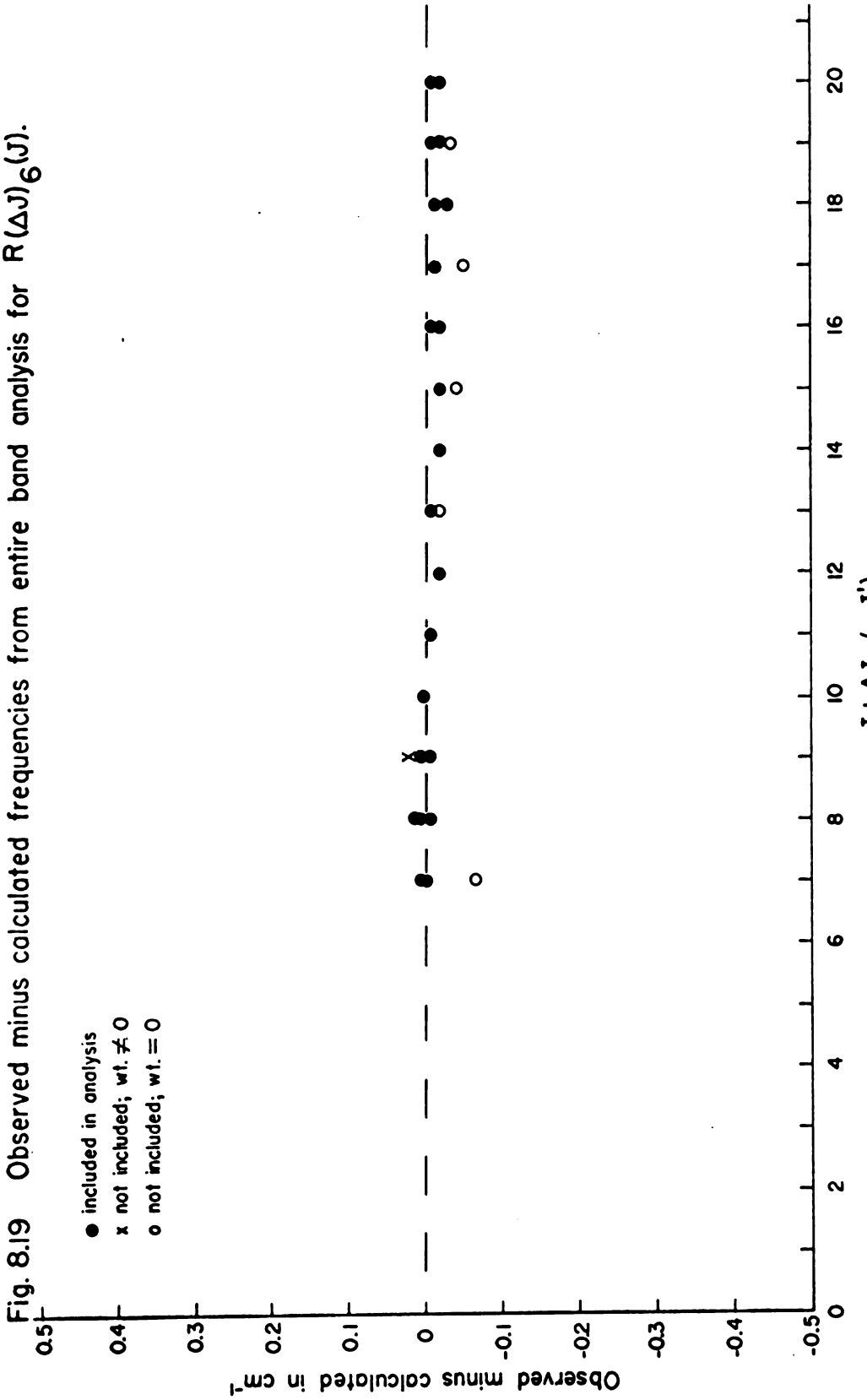
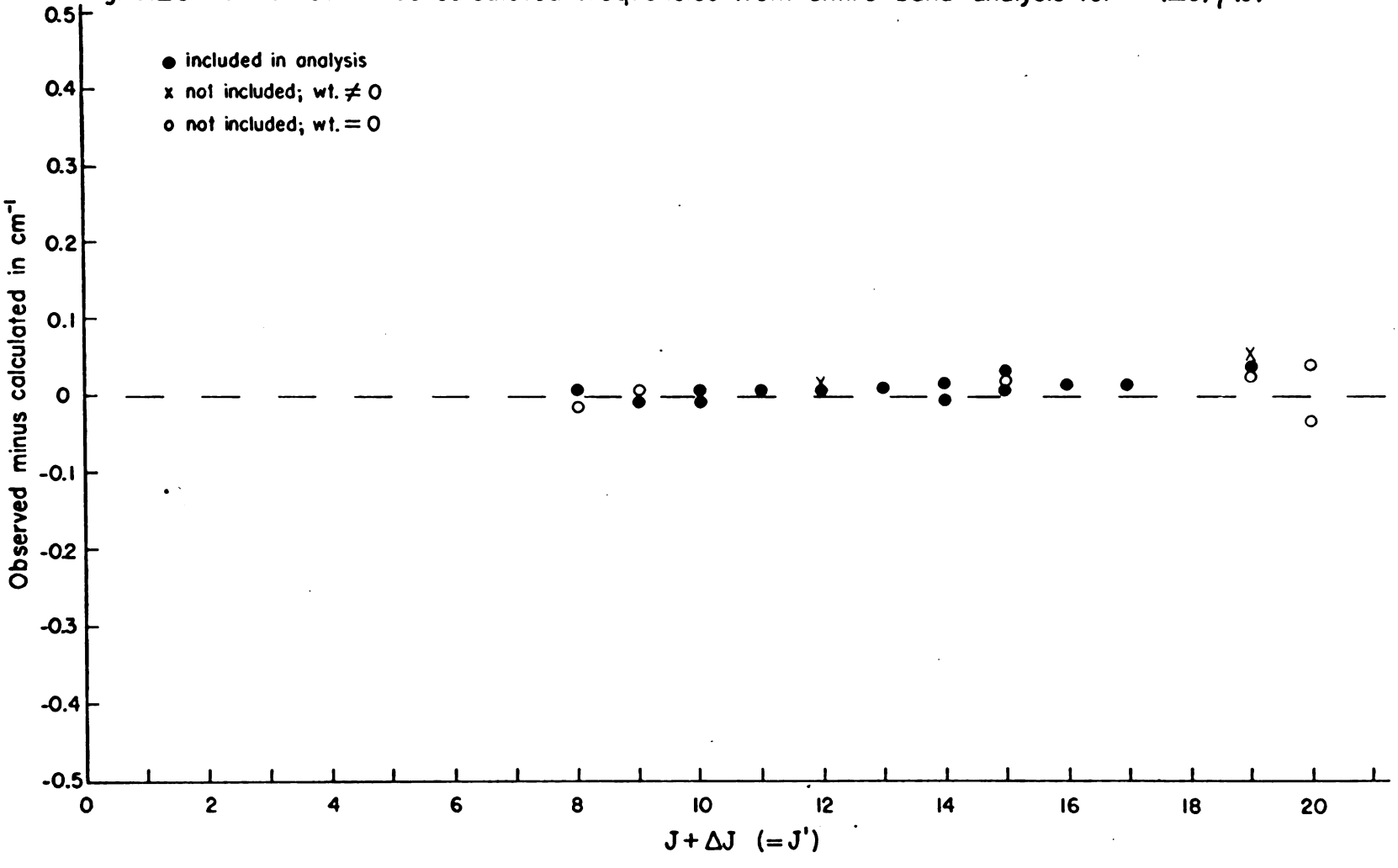


Fig. 8.19 Observed minus calculated frequencies from entire band analysis for $R(\Delta J)_6(J)$.

Fig. 8.20 Observed minus calculated frequencies from entire band analysis for $^{R}(\Delta J)_{7}(J)$.



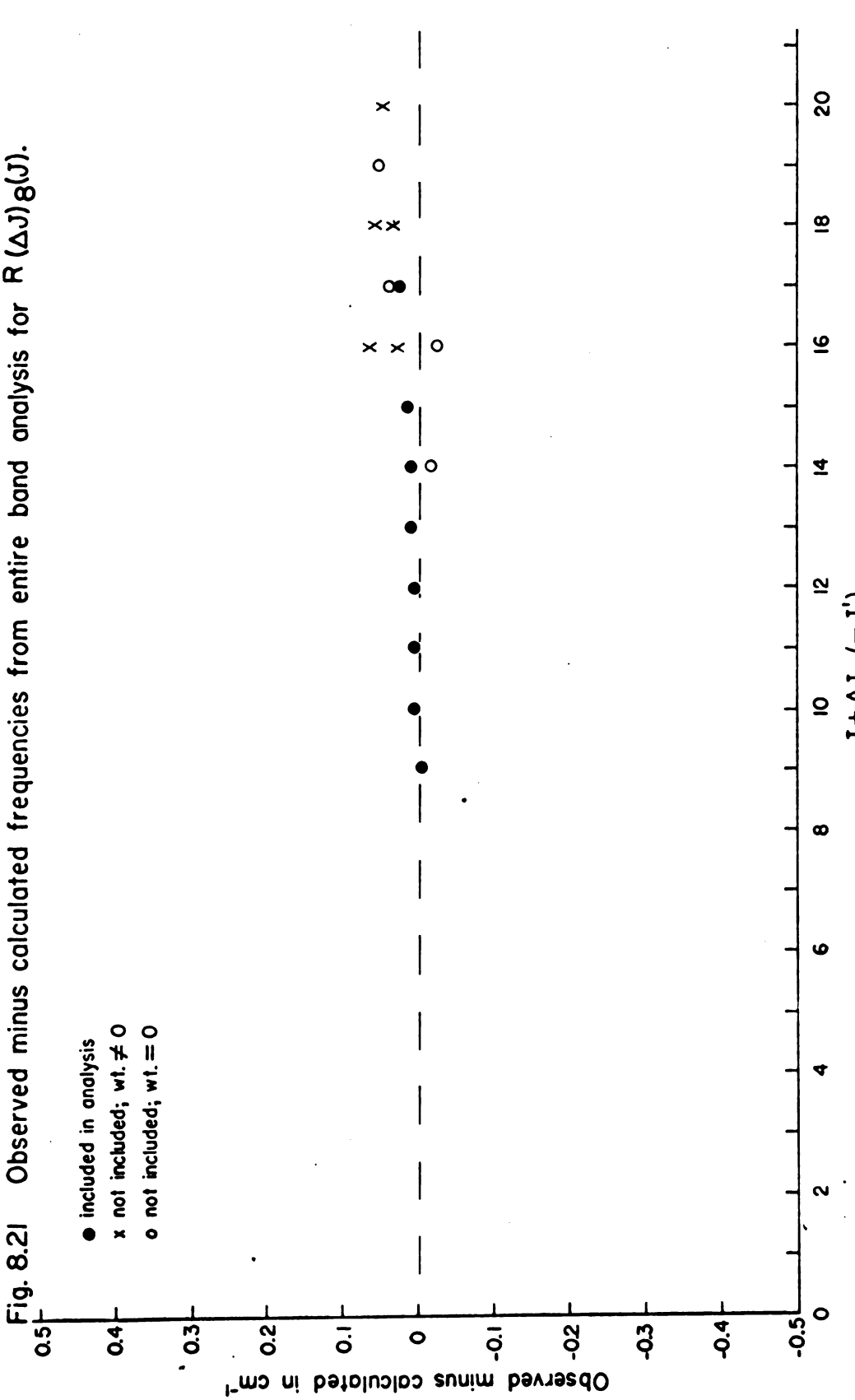


Fig. 8.21 Observed minus calculated frequencies from entire band analysis for $R(\Delta J)_8(J)$.

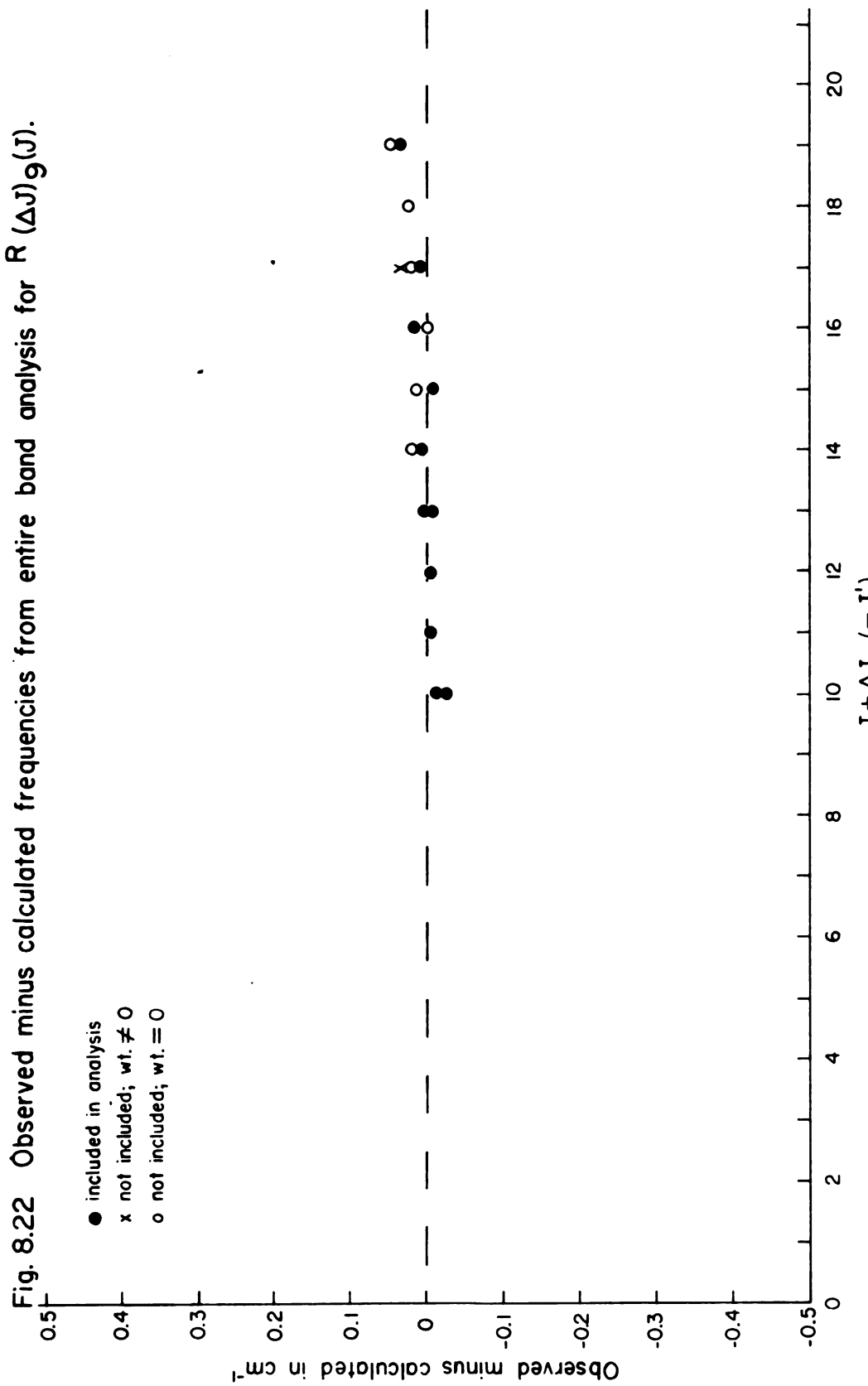


Fig. 8.22 Observed minus calculated frequencies from entire band analysis for $^{R}(\Delta J)g(J)$.

symmetry species A_1 would cause a similar effect.

The Coriolis resonance splits the $K' = \ell = \pm 1$ levels in $\nu_3+\nu_4$, i.e., the resonance lifts the degeneracy of the $K' = \ell = \pm 1$ levels. The effect on the observed spectrum will be discussed below.

Nielsen has studied extensively the first order Coriolis resonance especially as applied to XY_3 molecules of the ammonia type (8-11,67-69). We shall use the results of these investigations in the following as well as the results from Chapters 2 and 6.

From the work of Nielsen (as well as from the considerations of Chapter 6) the secular equation for the Coriolis resonance is given in Fig. 8.23 where $\gamma = \alpha^{\frac{1}{2}}\sqrt{J(J+1)}$. From the work of Nielsen, assuming that the perturbing band is $\nu_1+\nu_3$,

$$\alpha = 2(\zeta_{14}^{x})^2 B_e^2. \qquad (8.2)$$

By using a symmetrized set of wave functions the secular equation in Fig. 8.24 results. Thus the levels corresponding to the wave function

$$\frac{1}{\sqrt{2}}\left[\psi^{+1}_{+1} - \psi^{-1}_{-1}\right] .\equiv. \psi^{-}$$

are unaffected by the Coriolis resonance while the energy levels described by the wave function

$$\frac{1}{\sqrt{2}}\left[\psi^{+1}_{+1} + \psi^{-1}_{-1}\right] .\equiv. \psi^{+}$$

are affected by the perturbation as are the ψ^{o}_{o} levels of

Fig. 8.23 Secular equation for the $K=\ell=\pm 1$ levels.

	$v_1=0$ $v_3=1$ $v_4=1$ Ψ^{+1}_{+1}	$v_1=1$ $v_3=1$ $v_4=0$ Ψ^{0}_{0}	$v_1=0$ $v_3=1$ $v_4=1$ Ψ^{-1}_{-1}
Ψ^{+1}_{+1}	$E^1_1-\epsilon$	γ	
Ψ^{0}_{0}	γ	$E^0_0-\epsilon$	γ
Ψ^{-1}_{-1}		γ	$E^1_1-\epsilon$

Fig. 8.24 Factored secular equation.

	$v_1=0$ $v_3=1$ $v_4=1$ $\frac{1}{\sqrt{2}}\left[\Psi^{+1}_{+1}+\Psi^{-1}_{-1}\right]$	$v_1=1$ $v_3=1$ $v_4=0$ Ψ^{0}_{0}	$v_1=0$ $v_3=1$ $v_4=1$ $\frac{1}{\sqrt{2}}\left[\Psi^{+1}_{+1}+\Psi^{-1}_{-1}\right]$
$\frac{1}{\sqrt{2}}\left[\Psi^{+1}_{+1}+\Psi^{-1}_{-1}\right]$	$E^{1}_{1}-\epsilon$	$\sqrt{2}\,\gamma$	
Ψ^{0}_{0}	$\sqrt{2}\,\gamma$	$E^{0}_{0}-\epsilon$	
$\frac{1}{\sqrt{2}}\left[\Psi^{+1}_{+1}+\Psi^{-1}_{-1}\right]$			$E^{1}_{1}-\epsilon$

$\nu_1+\nu_3$. The resulting solutions of the secular equation thus are

$$\epsilon = E_1^1 \tag{8.3}$$

$$\epsilon = \frac{E_1^1 + E_0^0}{2} \pm \sqrt{\frac{(E_1^1 - E_0^0)^2}{4} + 2\alpha(J(J+1))} \tag{8.4}$$

where, in the event of a weak resonance, an approximate solution corresponding to Eq.(8.4) may be used. In the event that the parallel band is at a lower frequency than the perpendicular band (as is the case for $\nu_3+\nu_4$ and $\nu_1+\nu_3$), the approximate solutions corresponding to Eq.(8.4) are

$$\epsilon_0^0 = E_0^0 - \frac{2\alpha J(J+1)}{E_1^1 - E_0^0} \tag{8.5}$$

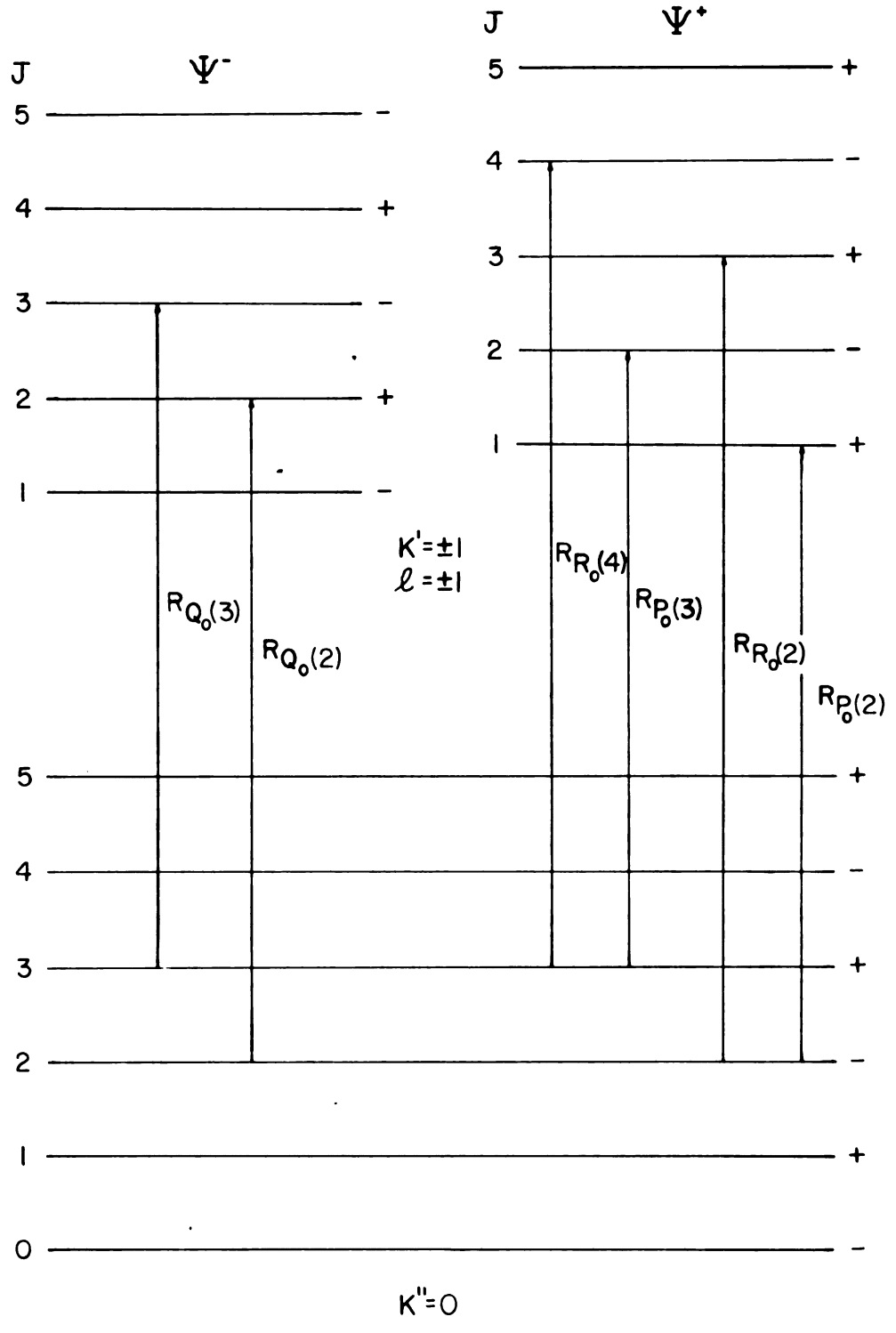
and

$$\epsilon_1^1 = E_1^1 + \frac{2\alpha J(J+1)}{E_1^1 - E_0^0} \tag{8.6}$$

where ϵ_1^1 is a function of J, as are E_1^1 and E_0^0.

Although, as mentioned in Chapter 2, the complete symmetry classification of the rotation-vibration levels for C_{3v} molecules has not been worked out (48), it has been found that the $^RQ_0(J)$ transitions terminate on the Ψ^- levels while the $^RR_0(J)$ and $^RP_0(J)$ transitions terminate on the Ψ^+ levels. This leads immediately to the level structure shown in Fig. 8.25 (8,9,11). Only levels of overall symmetry A_2 are shown since these are the only levels which may be populated due to the fact that the

Fig. 8.25 Level structure for $R_{(\Delta J)_0}(J)$ transitions.



three identical H atoms obey Fermi-Dirac statistics (38, 39,40).

The + and - indicate the overall inversion symmetry. Due to the + $\leftrightarrow$ - selection rule and the existence of levels of either (but not both) + or - inversion symmetry for each $K''= 0$ level of different J, no doubling of transitions is observed.[40]

Thus in a Coriolis resonance, the $^{R}Q_{0}(J)$ lines are unaffected while the energy of the $^{R}R_{0}(J)$ and $^{R}P_{0}(J)$ upper states is given by Eq.(8.6). This is in contrast to ℓ-type doubling in which both upper levels are shifted by the perturbation.

Immediately one may deduce that the observed ground state combination differences are now given by[41]

$$\left[{}^{R}R_{0}(J-1) - {}^{R}P_{0}(J+1)\right]_{c} = \left[{}^{R}R_{0}(J-1) - {}^{R}P_{0}(J+1)\right] \qquad (8.7)$$

$$\left[{}^{R}R_{0}(J-1) - {}^{R}Q_{0}(J)\right]_{c} = \left[{}^{R}R_{0}(J-1) - {}^{R}Q_{0}(J)\right] + 2qJ(J+1) \qquad (8.8)$$

$$\left[{}^{R}Q_{0}(J) - {}^{R}P_{0}(J+1)\right]_{c} = \left[{}^{R}Q_{0}(J) - {}^{R}P_{0}(J+1)\right] - 2qJ(J+1). \qquad (8.9)$$

---

[40] $K''= 0$ levels are a special case in this respect since for all other K values each J level has both + and - inversion components. It is interesting to note that even though inversion doubling is negligible, i.e., the levels are still degenerate, for CH_3F (37), the inversion symmetry still plays an important role.

[41] Equations of the same form also apply for the ℓ-type doubling case.

Referring to Appendix VI it is evident that Eq.(8.7) is satisfied. Fig. 8.26 is a plot of the observed Coriolis combination difference minus the calculated value taken from Appendix II. The resulting function should be $2qJ'(J'+1)$. It is apparent that through $J' = 15$ the expected result is found. The added curvature above $J' = 15$ may be due to a J^6 perturbation discussed in a later section.

Fig. 8.27 shows an expanded effective Q branch plot vs. $J'(J'+1)$ for the zero subband. The splitting of the $K' = \ell = \pm 1$ levels is apparent as a difference between the Q branch curve and the R and P branch curve. The rapid divergence of both curves to low wave numbers as J exceeds 10 is due to the J^6 perturbation discussed below.

A simultaneous least squares analysis was made on the $^{R}R_0(J)$, $^{R}Q_0(J)$ and $^{R}P_0(J)$ to the equation given as follows:

$$^{R}(\Delta J)_0(J) - B_0(2J+1+\Delta J)\,\Delta J + D_0^{JK}(J+\Delta J)\,(J+1+\Delta J) +$$

$$D_0^{J}\left[\{(J+\Delta J)(J+1+\Delta J)\}^2 - \{J(J+1)\}^2\right] = \nu_{sub} + \qquad (8.20)$$

$$(a_3^{B}+a_4^{B})(J+\Delta J)(J+1+\Delta J) + 2q\,(\Delta J)^2(J+\Delta J)(J+1+\Delta J) +$$

$$\rho\left[(J+\Delta J)\,(J+1+\Delta J)\right]^3$$

where q is the Coriolis resonance constant and ρ is the constant coefficient of a J^6 perturbation discussed below. Table 8.6 presents the results of this simultaneous analysis

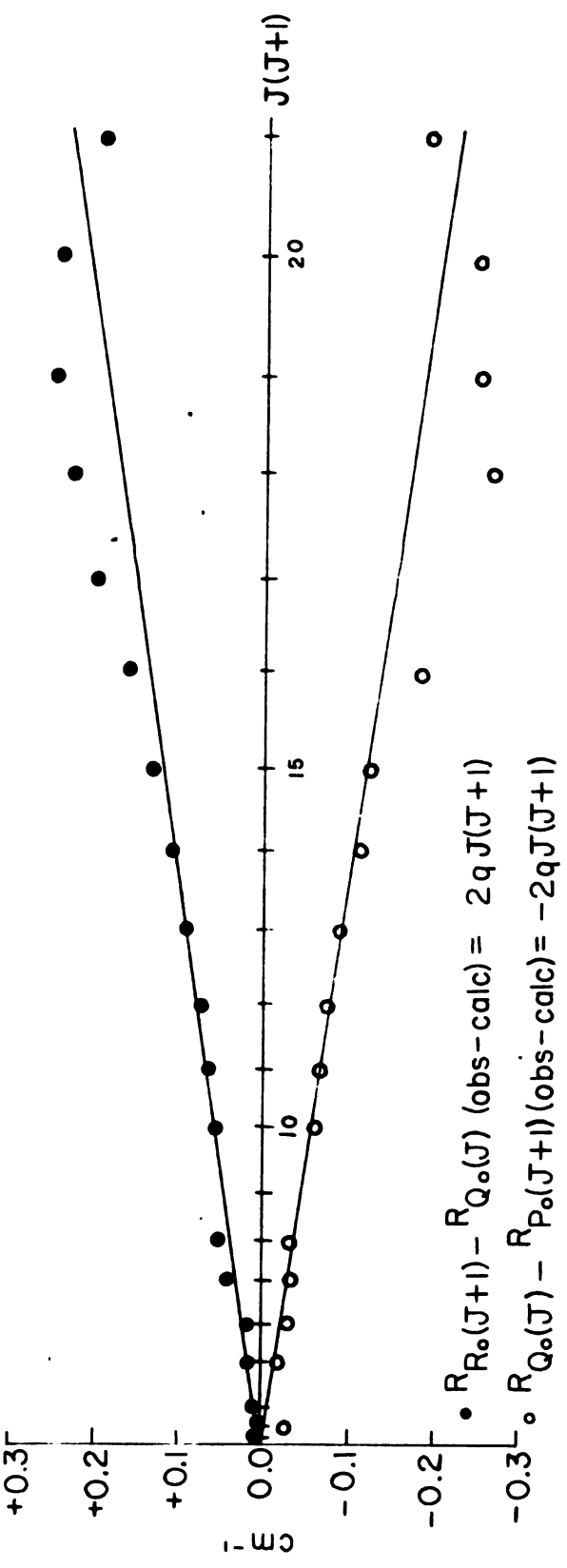


Fig. 8.26 K=0 ΔK=+1 observed minus calculated ground state combination differences.

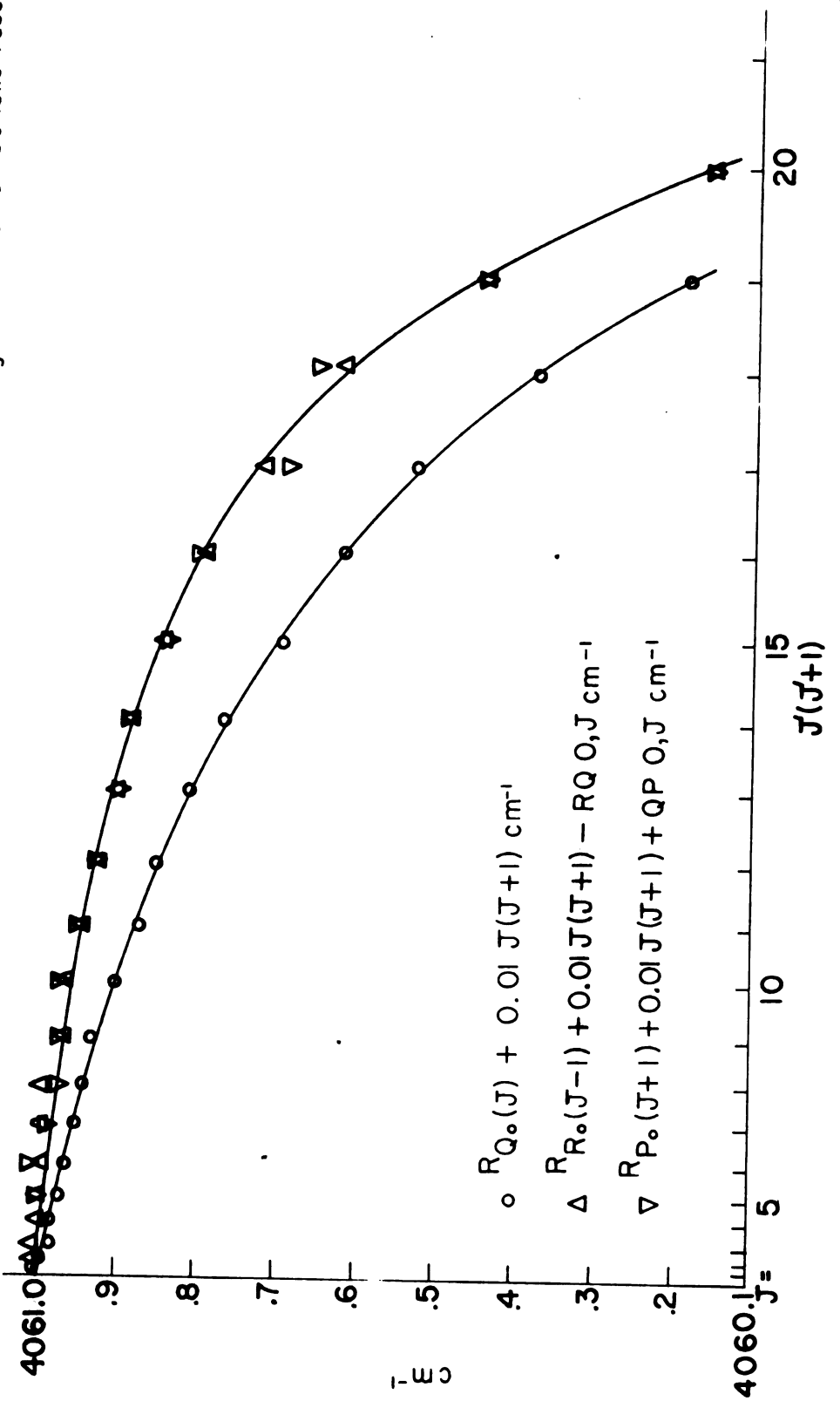


Fig. 8.27 Expanded graph of $R_{Q_o}(J)$, $R_{R_o}(J)$, $R_{P_o}(J)$ indicating the effect of Coriolis resonance.

Table 8.6 Results of a simultaneous least squares analysis of $^{R}R_{0}(J)$, $^{R}P_{0}(J)$ and $^{R}Q_{0}(J)$ transitions of $\nu_3+\nu_4$.

$$\nu_{sub} = 4060.987 \pm 0.014 \text{ cm}^{-1}$$

$$\alpha_3^B + \alpha_4^B = 0.01057 \pm 0.0016 \text{ cm}^{-1}$$

$$q = 2.73 \times 10^{-4} \pm 0.57 \times 10^{-4} \text{ cm}^{-1}$$

$$\rho = 1.06 \times 10^{-8} \pm 0.10 \times 10^{-8} \text{ cm}^{-1}$$

$$s = 0.015 \text{ cm}^{-1} \text{ std. dev.}$$

where q is the Coriolis resonance constant,

ρ is constant coefficient of $[J'(J'+1)]^3$

with their simultaneous confidence intervals (cf. chapter 5) and Appendix X contains the computer output from the analysis.

Additional Observed Perturbations

Accidentally Strong Resonance Affecting the $K'=\pm2$, $\ell=\pm1$ and $K'=\pm2$, $\ell=\mp1$ Levels

The perturbation which affects the $K'=\pm2$, $\ell=\pm1$ and the $K'=\pm2$, $\ell=\mp1$ levels[42] is interesting since it is an example of a localized perturbation involving a single, fixed K' value and showing up as a J dependent shift of the levels for this particular K. Fig. 8.28 shows a relatively high resolution record of the $^{R}Q_1(J)$ lines. Included in the figure are a calculated (unperturbed) spectrum, and an observed spectrum. The shift of the various lines from their unperturbed positions is indicated. (The tails of the arrows mark the unperturbed positions of the lines, while the heads of the arrows indicate the observed position of the line.) Fig. 8.29 presents the same results for $^{P}Q_3(J)$. The double transitions, i.e., transitions for which J has the same value in either one figure or the other result from the "mixing" of wave functions of the observed band and the perturbing band as discussed in Chapter 6. Fig. 8.30 is a graph of the $^{R}Q_1(J)$ transitions vs. $J'(J'+1)$ after modifying the $^{R}Q_1(J)$ frequencies by

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[42] These are the terminal levels of the $^{R}(\Delta J)_1(J)$ and $^{P}(\Delta J)_3(J)$ transitions.

Fig. 8.28 Observed transitions of $^{R}Q_{1}(J)$ indicating the effect of the perturbation.

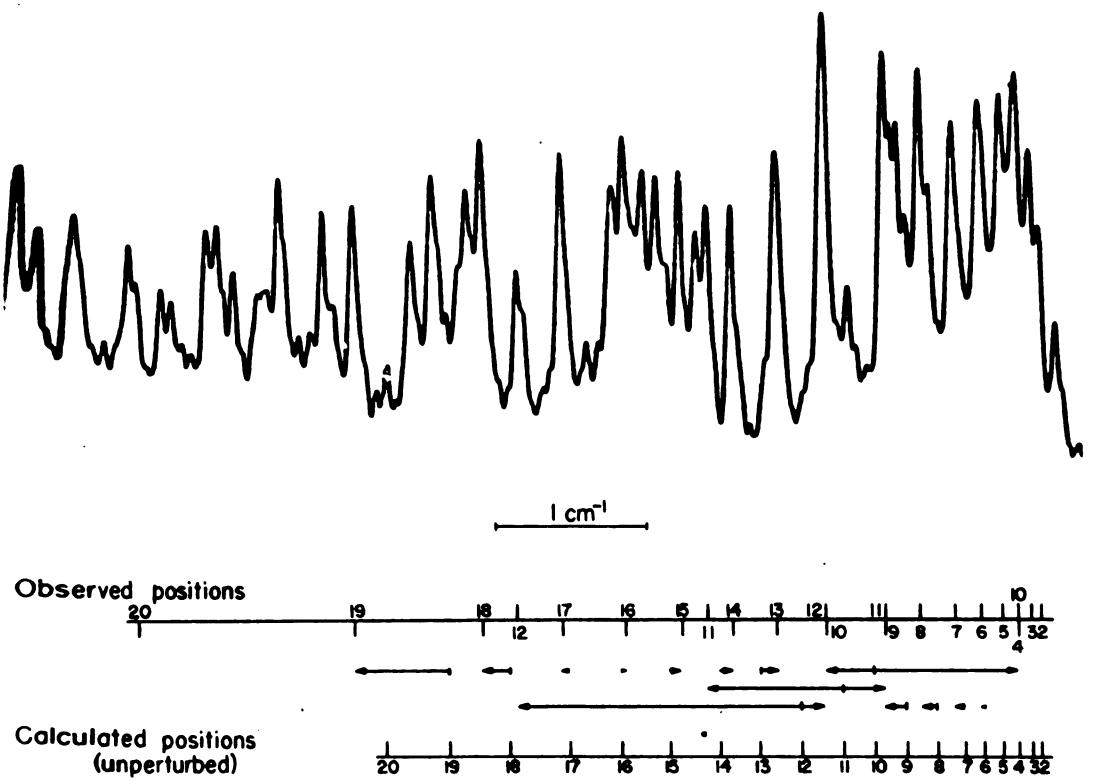


Fig. 8.29 Observed transitions of $PQ_3(J)$ indicating the effect of the perturbation.

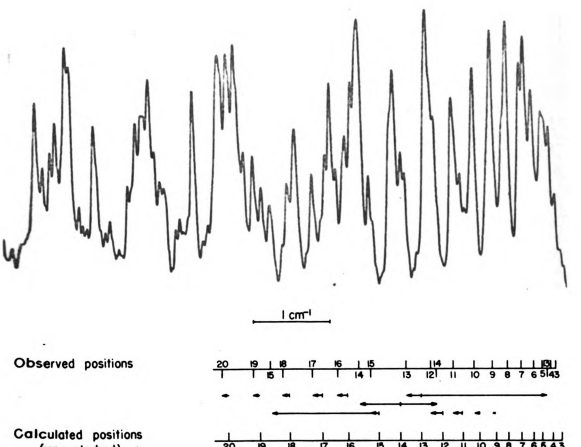
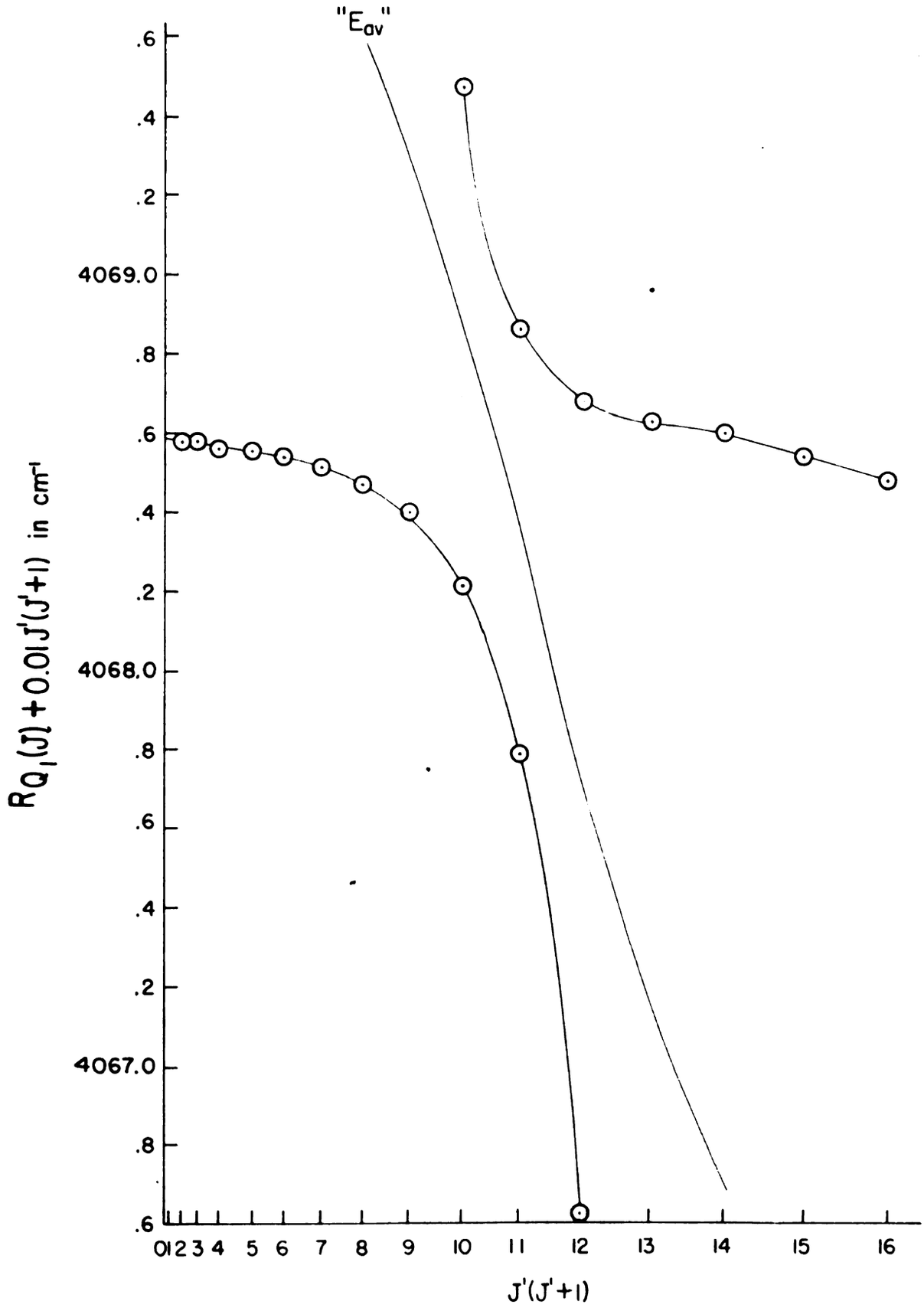


Fig. 8.30 $^{R}Q_{1}(J)$ transitions vs. $J'(J'+1)$ indicating the effect of an accidental resonance.

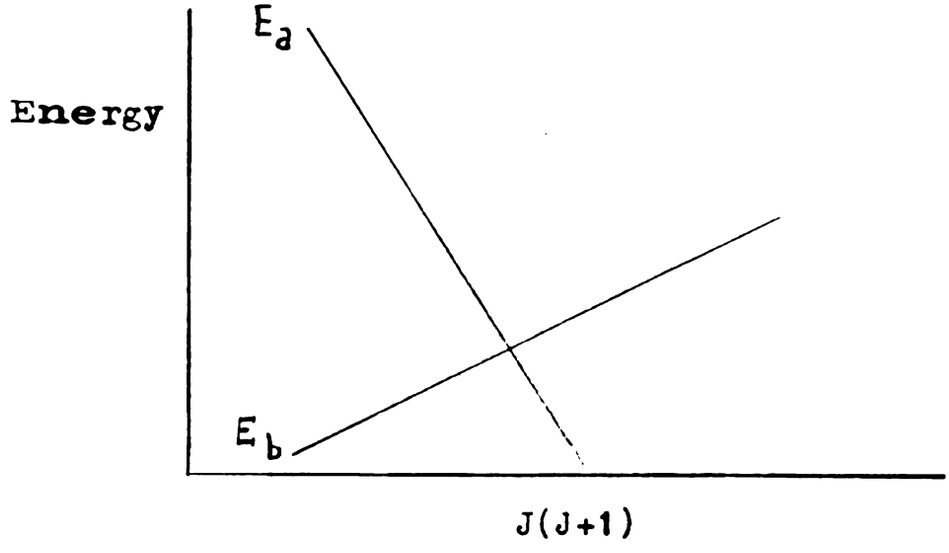


adding 0.01 $J'(J'+1)cm^{-1}$ to each transition[43] in order to expand the scale of the graph. Fig. 8.31 is a similar graph for the $^{P}Q_{3}(J)$ lines.

The assignments which we have made are fairly certain since for most transitions among those included, $^{\Delta K}P_{K}(J)$ and $^{\Delta K}R_{K}(J)$ lines were found which give good agreement with the calculated ground state combination differences in Appendix II.

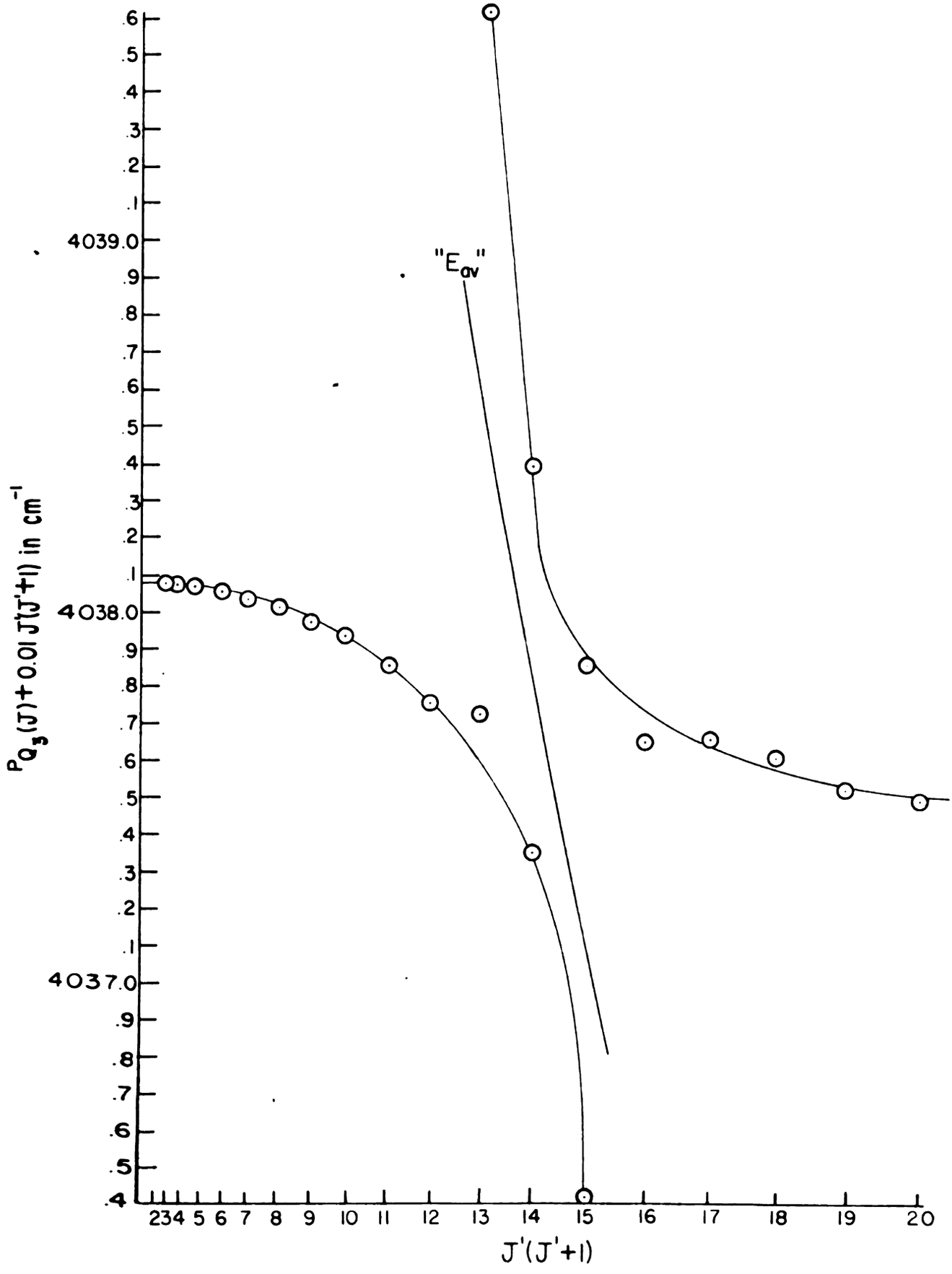
If we now assume that the perturbation involves two levels, as in Chapter 6, then Eq.(6.3) is the secular equation and Eq.(6.10), the solution of the secular equation.

Plotting the unperturbed energy levels of two bands assumed to be in resonance, we have



[43] The $^{\Delta K}Q_{K}(J)$ frequencies are equivalent to an expanded set of upper state energy levels as may be seen by comparing the Q branch line position expression with the upper state energy level expression. Since that is the case we shall speak of energy levels and Q branch frequencies interchangeably.

Fig. 8.31 $^{P}Q_{3}(J)+0.01\,J'(J'+1)$ cm^{-1} vs. $J'(J'+1)$ indicating the effect of an accidental resonance.



where the slope of the lines is the unperturbed value of $B_o - \Sigma_s \alpha_s^B v_s$ if the energy levels themselves are plotted or $-\Sigma_s \alpha_s^B v_s$ if the Q(J) line frequencies are plotted.

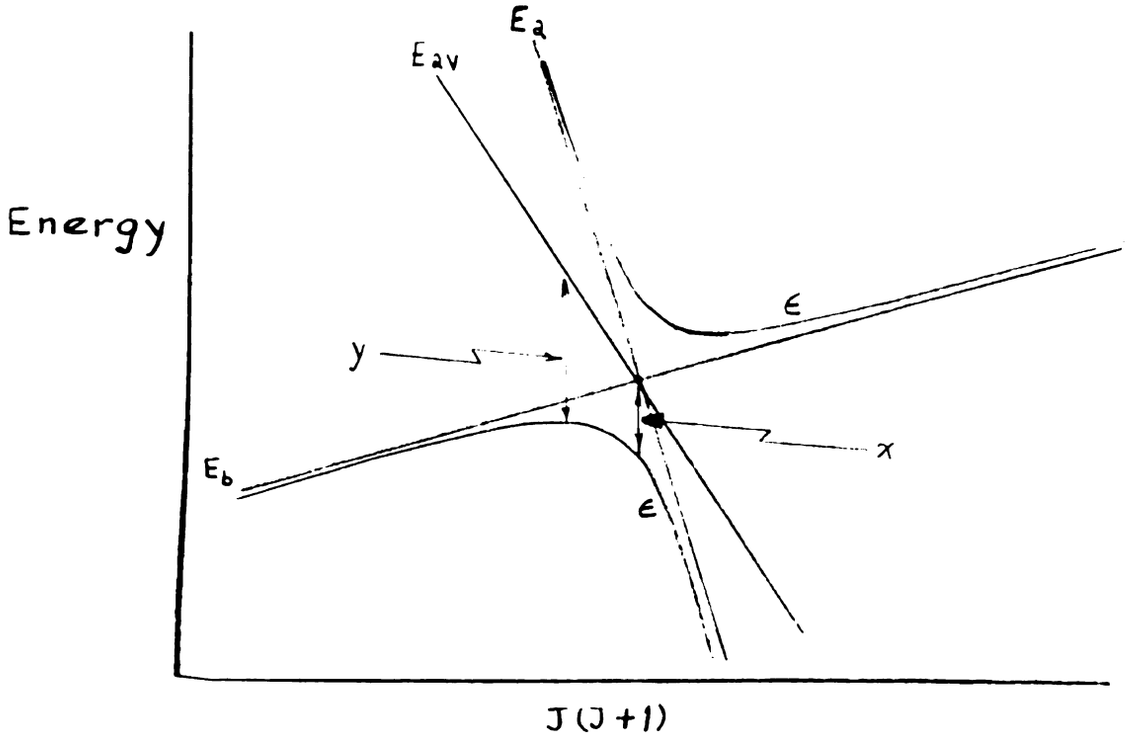
Since the two cases are equivalent we shall assume that it is the Q(J) frequencies which are plotted as is the case in Figs. 8.30 and 8.31. Below, the levels are redrawn with the corresponding solution of the secular equation from Eq.(6.10), i.e.,

$$\epsilon = \frac{E_a + E_b}{2} \pm \sqrt{\frac{(E_a - E_b)^2}{4} + W^2}$$

or

$$\epsilon = E_{av} \pm \sqrt{\delta^2/4 + W^2}$$

where E_{av} is the average energy of the two unperturbed sets of levels whose individual separations from E_{av} are given by $\delta/2 = (a/2) + (b/2)J(J+1)$.



In the diagram above, y is the energy separation of E_{av} and either leg of the hyperbola and is given by

$$y = |\epsilon - E_{av}| = \sqrt{\delta^2/4 + W^2} \tag{8.21}$$

while x is equivalent to y but is equal to it only at the point of exact resonance[44] where

$$x = W \tag{8.22}$$

since at this point $\delta = 0$.

That ϵ describes an hyperbola may be shown as follows. Consider the case of a type II coupling (cf. Chapter 6) where the perturbing matrix element has the form $W\sqrt{J(J+1)-K(K\pm1)}$. Then, in order to simplify the following, we assume without loss of generality, that we have transformed coordinates such that $E_{av} = 0$ and is parallel to the J(J+1) axis (identical to the J(J+1) axis since $E_{av} = 0$).[45]

Then

$$\epsilon^2 = \tfrac{1}{4}(a+bJ(J+1))^2+W^2J(J+1)-W^2K(K+1) \tag{8.23}$$

where

$$\delta = a + bJ(J+1)$$

---

[44] As we shall see below, this figure must not be taken too literally, since E_a and E_b are not always the asymptotes of the hyperbolae and thus, $\delta = 0$ does not occur exactly at the intersection of E_a, E_b and E_{av}.

[45] In the event that E_{av} is not a straight line vs. J(J+1) we take the J(J+1) axis to be the tangent to E_{av} at exact resonance.

which may be written as

$$\frac{\epsilon^2}{D} - \frac{[J(J+1) + (a/b) + 2W^2/b^2\ ]^2}{(4/b^2)D} = 1 \quad (8.24)$$

where

$$D = W^2[(-W^2/b^2) - K(K+1) - a/b]$$

Eq.(8.24) is the equation of an hyperbola with its origin at $-(a/b + 2W^2/b^2)$, 0 and asymptotes whose slope is b/2. For a type I coupling (i.e., W = constant) the center is at $-(a/b)$, 0 so that for a type II coupling the asymptotes are not exactly equal to the unperturbed energy whereas for a type I coupling they are equal to the unperturbed energy. For a type IV coupling, i.e.,

$$W\sqrt{J(J+1) - K(K\pm1)}\ \sqrt{J(J+1) - (K\pm1)(K\pm2)}$$

the asymptotes have a different slope as well as a different origin from that of the unperturbed energy levels.

From the expanded version of the graphs in Figs. 8.30 and 8.31 we have obtained values of $(\epsilon - E_{av})$ for several values of J(J+1). Using these values, the hyperbolae in Figs. 8.32 and 8.33 were constructed.[46]

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[46]The existence of two points for each J value in Figs. 8.32 and 8.33 does not imply that two lines were actually observed in all cases. However, from Eq.(8.24) it is apparent that the branches of an hyperbola are symmetric about the major axis and those in Figs. 8.32 and 8.33 were so constructed.

Fig. 8.32 Perturbation hyperbola for the $K'=\pm 2$, $\ell=\pm 1$ levels.

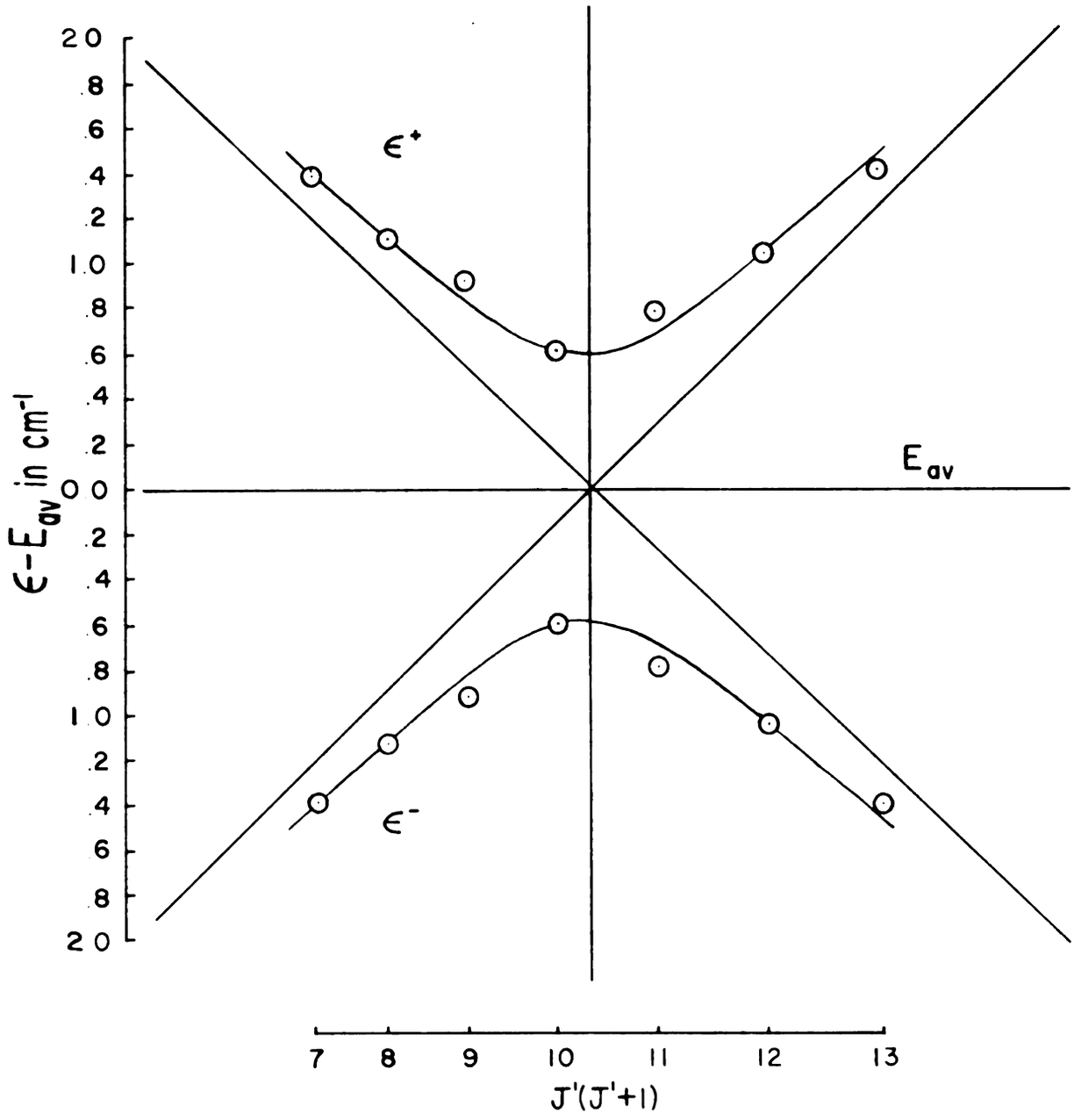
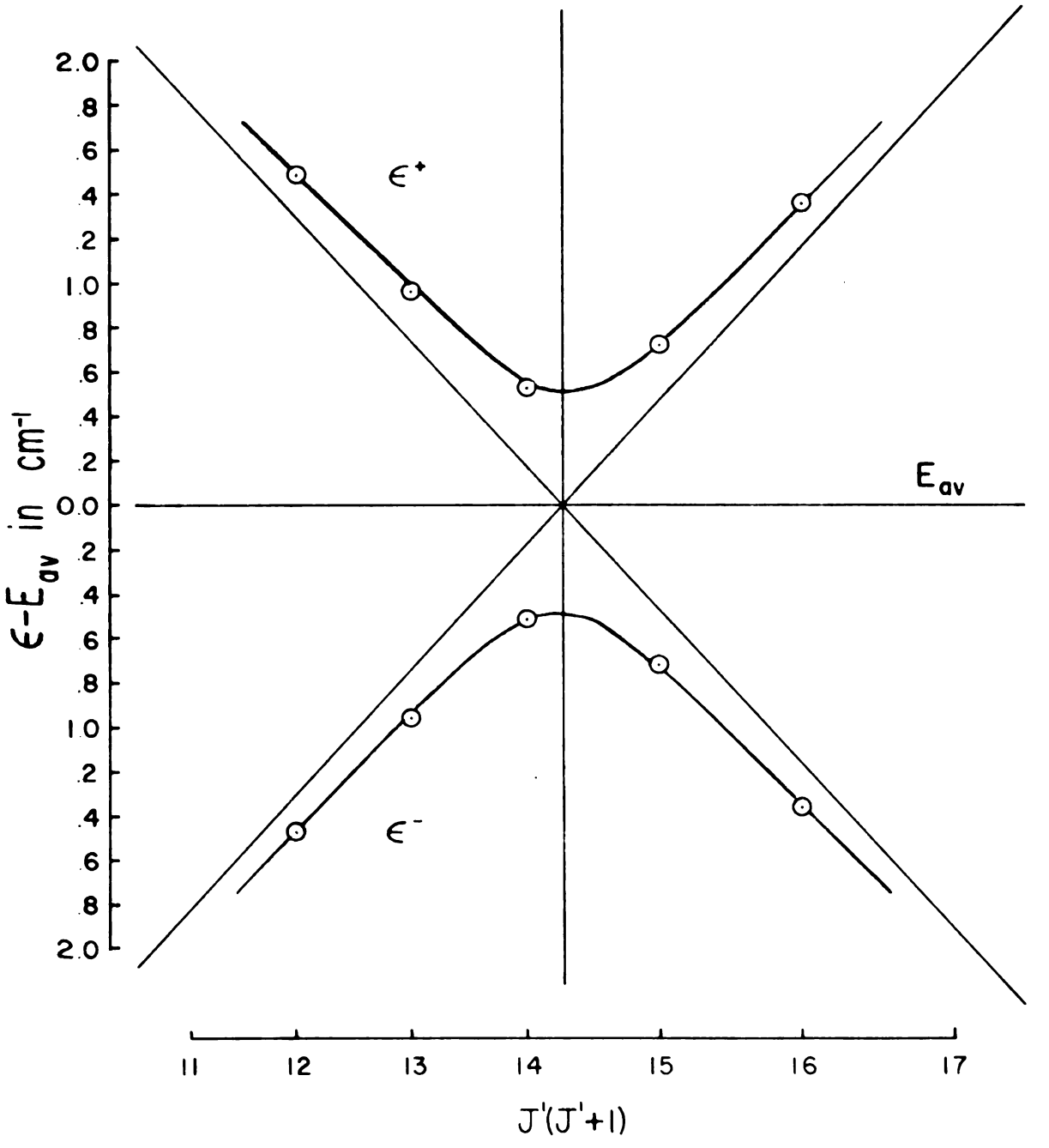


Fig. 8.33 Perturbation hyperbola for the $K'=\pm 2$, $\ell=\mp 1$ levels.



The data used to plot Figs. 8.32 and 8.33 is presented in Table 8.7.

Figure 8.34 shows an hyperbola in its principal axis system; the equation of such an hyperbola is given by

$$\frac{\epsilon^2}{c^2} - \frac{[x(x+1)]^2}{d^2} = 1 \qquad (8.25)$$

where c and d are the lengths of the semi-axes of the hyperbola which has its origin at $(x(x+1), \epsilon) = (0,0)$. In Fig. 8.34, $x(x+1)$ is equivalent to $J(J+1)$ but is measured from the $J(J+1)$ value at exact resonance, i.e., $x(x+1) = 0$ at exact resonance. As shown in Fig. 8.34, the equation of the asymptotes is given by

$$\dot{\epsilon} = \pm (c/d)\, x\, (x+1). \qquad (8.26)$$

From Figs. 8.32 and 8.33, the value of c may be obtained immediately since it is a well defined quantity. Then using Eq.(8.25) written as

$$\frac{\epsilon^2}{c^2} - 1 = (1/d^2)\, [x(x+1)]^2 \qquad (8.27)$$

the value of d may be found from a least squares analysis of several points on the hyperbola. Thus, the asymptotes of the hyperbola are well defined when the perturbation data is reduced in this fashion. On the other hand, the asymptotes are not well defined in any simple way in Figs. 8.30 and 8.31. From Figs. 8.32 and 8.33, using the results of the above discussion, we find the results given in Table 8.8, where

Table 8.7 ($\epsilon - E_{av}$) for $K'=\pm2$, $\ell=\pm1$ and $K'=\pm2$, $\ell=\mp1$ levels.

$K'=\pm2$, $\ell=\pm1$ levels

J'	$\epsilon - E_{av}(cm^{-1})$
7	1.38
8	1.14
9	0.88
10	0.72
11	0.79
12	1.04
13	1.44

$K'=\pm2$, $\ell=\mp1$ levels

J'	$\epsilon - E_{av}(cm^{-1})$
16	1.40
17	0.96
18	0.61
19	0.54
20	1.50
22	2.09

Fig. 8.34 An hyperbola with its center at the coordinate origin.

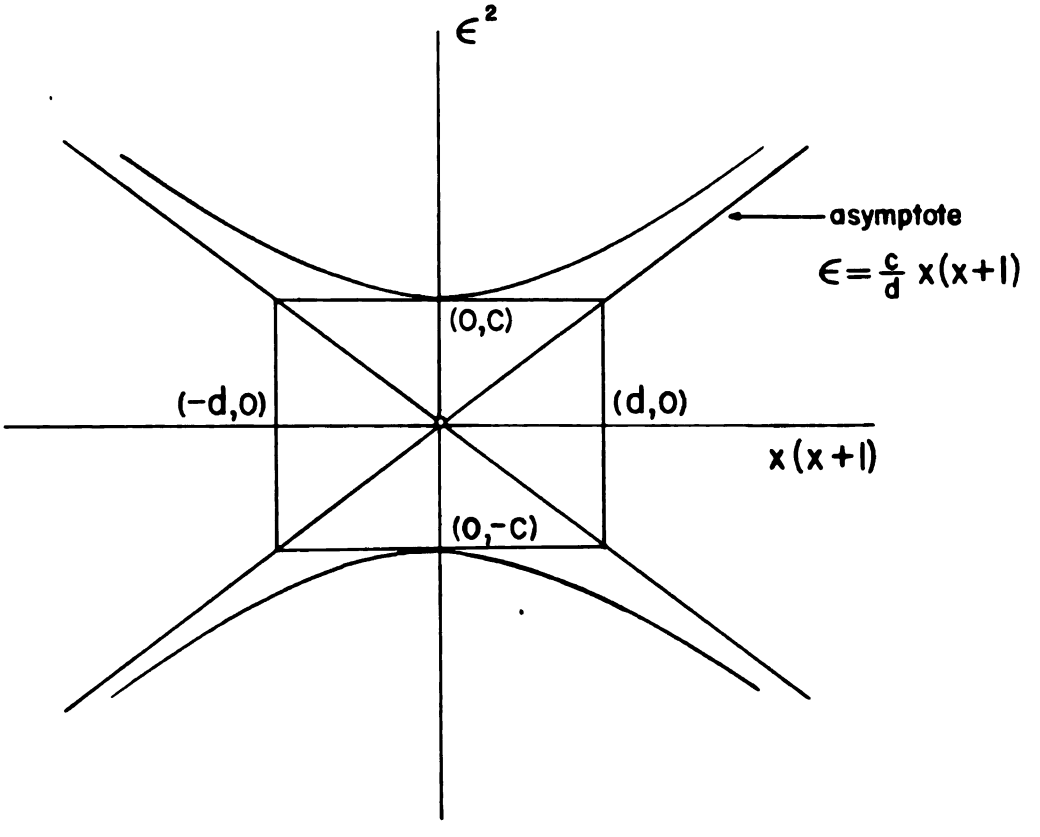


Table 8.8 Summary of results of the analysis of the perturbation affecting the $K' = \pm 2$, $\ell = \pm 1$, and the $K' = \pm 2$, $\ell = \mp 1$ levels of $\nu_3 + \nu_4$.

Equation of the perturbation hyperbola

$$\frac{\epsilon^2}{c^2} - \frac{x(x+1)}{d^2} = 1$$

$x(x+1) = 0$ at resonance

For $K' = \pm 2$, $\ell = \pm 1$ levels

$J'(J'+1) = 117$ at resonance

$c = 0.62\ cm^{-1}$

$d = 30$

$\epsilon_{asym} = \pm 0.0206\ x\ (x+1)\ cm^{-1}$ (asymptotes)

$\delta = 4.82 - 0.0412\ J'(J'+1)\ cm^{-1}$

For $K' = \pm 2$, $\ell = \mp 1$ levels

$J'(J'+1) = 207$ at resonance

$c = 0.50\ cm^{-1}$

$d = 24$

$\epsilon_{asym} = \pm 0.0206\ x\ (x+1)\ cm^{-1}$ (asymptotes)

$\delta = 8.52 - 0.0412\ J'(J'+1)\ cm^{-1}$

c and d are the semi-axes of the hyperbolae, $\epsilon = \pm (c/d) \times (x+1)$ is the equation of the asymptotes, and δ is the resulting equation for the separation of the two perturbing levels in each case. Using the information in Tables 8.5 and 8.8 we obtain the relative energy level positions of the 2^+ and 2^- lines of $\nu_3+\nu_4$ and the perturbing levels.[47] These results are given schematically in Fig. 8.35 and include the symmetry species of the levels under the rotational subgroup C_3 (cf. Chapter 2).

The question of the assignment of the perturbing band is a perplexing one since there are so many possible resonances between nearby bands, as depicted in part by Fig. 8.3 and Table 8.4, so that in this instance we are not certain of the location of the levels of the unobserved bands. In fact, as mentioned earlier, for most molecules at present the anharmonic constants are unknown and thus accurate placement of even the unperturbed rotation-vibration levels is nearly impossible in a majority of the cases.

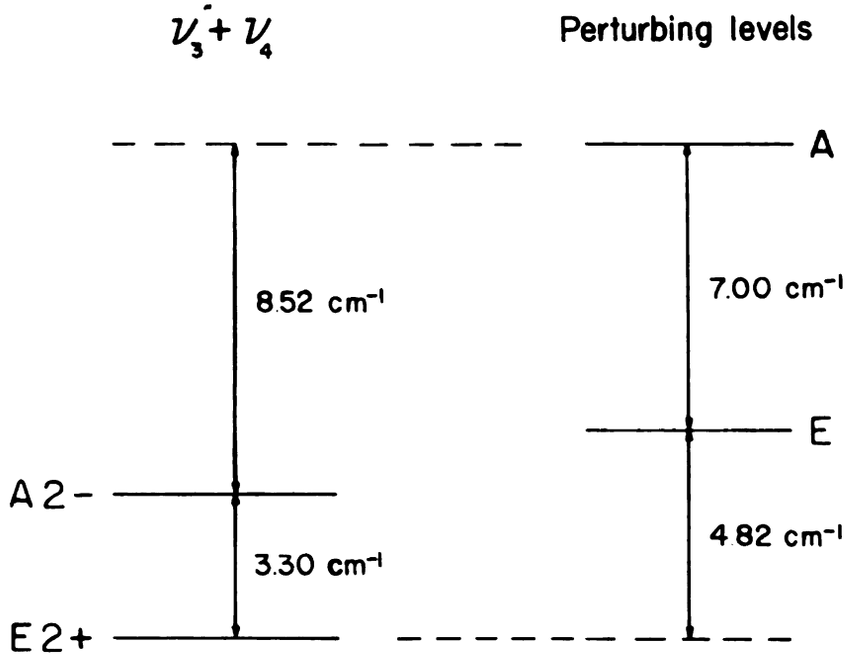
We have investigated the possibility of the perturbing levels belonging to the overtone and combination levels believed to be in the vicinity of $\nu_3+\nu_4$ (cf. Table 8.3).

It is indeed unfortunate as well as frustrating that we have not been able to find a complete explanation for the observed data. Several levels have provided interesting

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[47] For brevity, the $K' = \pm 2$, $\ell = \pm 1$ levels are designated as 2^+ levels and the $K' = \pm 2$, $\ell = \mp 1$ levels as 2^- levels.

Fig. 8.35 Level structure of J=0 levels for the perturbation of the $K'=\pm 2, \ell=\pm 1$ and $K'=\pm 2, \ell=\mp 1$ levels of $\nu_3+\nu_4$.



possibilities but have not separately been able to account for the perturbations in the $K' = \pm 2$, $\ell = \pm 1$ and the $K' = \pm 2$, $\ell = \pm 1$ levels without giving rise to apparent contradictions. From the results of our study of the possible perturbing levels, it is quite likely that the perturbations observed in $\nu_3+\nu_4$ are the result of an interaction between $\nu_3+\nu_4$ and two or more overtone or combination levels. This is quite plausible since although we do not know the anharmonic constants and thus cannot place the vibrational origins of the other nearby levels accurately, we can calculate the $J=0$ levels for the various K values in a given set of combination or overtone levels quite accurately (to within $\approx \pm 2\text{cm}^{-1}$) if they are unperturbed. Even so, by making the most favorable assumptions about the vibrational origin (i.e., the J=0, K=0 level), we still cannot arrive at a consistent explanation based on a single perturbing overtone or combination level. However, a mutual interaction between $\nu_3+\nu_4$ and two or more other overtone or combination levels could easily invalidate the considerations which we have made while considering one perturbing overtone or combination level at a time. However, with the current data available on the anharmonic constants for CH_3F, the problem of a resonance involving two or more unobserved overtone or combination levels with $\nu_3+\nu_4$ is nearly impossible to solve satisfactorily.

At this point we shall describe several other perturbations we have observed and whose effects may be seen in the

observed minus calculated graphs in Figs. 8.4-8.22.

Perturbation of Levels with High J and Low K

In Figs. 8.11-8.17 for the -2 through the +4 subbands the effect of a perturbation on the high J levels is apparent. We have examined two possible interpretations of this perturbation. The first is that an accidental resonance involving a coupling of type V, i.e., a

$$W \sqrt{J(J+1) - K(K\pm1)}\ \sqrt{J(J+1) - (K\pm1)(K\pm2)}\ \sqrt{J(J+1) - (K\pm2)(K\pm3)}$$

coupling, with nearby overtone or combination levels causes the rapid divergence to low wave numbers with high J values. If this is the proper interpretation, it appears that in this case there is no crossing of levels in contrast to the situation for the K'=2 levels described in the previous section. Under these assumptions, one would expect the leading term of the second order non-degenerate perturbation expansion to be a $(J+\Delta J)^3(J+1+\Delta J)^3$ term. A least squares analysis of the subband lines for the -2,-1,0,+2,+4 subbands including such a term resulted in a good fit of the lines for each subband analyzed. The coefficients of the $(J+\Delta J)^3(J+1+\Delta J)^3$ term ranged from 4×10^{-9} to 11×10^{-9} cm^{-1}. An example of the "goodness of fit" is given in Appendix X for the K"=0 subband which was mentioned previously in the section dealing with Coriolis resonance.

A second possible interpretation is that the rapid divergence to low wave numbers is caused by a crossing of

unperturbed energy levels in the same manner as for the $K' = \pm 2, \ell = \pm 1$ and $\ell = \mp 1$ levels discussed in the preceding section. In these cases the crossing must be for a value of J above 15. Indeed, we have been able to find partial sets of lines for the +1 and the -2 subbands which might represent such an effect. However, since these occur at such high J values where the lines are very weak, we cannot be certain that the lines observed actually belong to the subbands in question. However we present the data here for the sake of completeness and with an eye to further work on this band.

It should be noted that the +1 subband involves the $K' = \pm 2$, $\ell = \pm 1$ levels where we observed another, more certain, crossing of unperturbed energy levels. This portion of the discussion was not mentioned at that point because of its speculative nature. Tables 8.9 and 8.10 list the Q(J) (and corresponding R(J-1) and P(J+1) where found) transition frequencies in the region of resonance. Those marked with an asterisk are of uncertain assignment and are not included in Appendix V. Figures 8.36 and 8.37 present the Q(J) frequencies vs. $(J+\Delta J)(J+1+\Delta J)$ for the +1 and -2 subbands respectively. In Figs. 8.38 and 8.39 the perturbation hyperbolae for the +1 and -2 subbands are reproduced and Table 8.11 presents the results of an analysis of these hyperbolae.

Although we have not been able to find the corresponding transitions for the -1,0,+2,+3 and +4 subbands, we feel that

Table 8.9 $^{R}(\Delta J)_1(J)$ **frequencies in the region of resonance.**

Lower Frequency Branch[a]

Assignment	Frequency	Line
$^{R}Q_1(J)$		
16	4065.76	536
17	4065.34	563
18	4064.82	531
19	4064.44	527
20	4063.97	520A

Higher Frequency Branch

Assignment	Frequency	Line
$^{R}Q_1(18)$	4066.05*	538B
$^{R}R_1(17)$	4096.69*	674
$^{R}P_1(19)$	4033.76*	376
$^{R}Q_1(19)$	4065.08*	532A
$^{R}R_1(18)$	4097.41*	677A
$^{R}P_1(20)$	4030.99*	362
$^{R}Q_1(20)$	4064.52*	529A
$^{R}R_1(19)$	4098.54*	681A
$^{R}P_1(21)$	4028.77*	350B
$^{R}Q_1(21)$	4064.01*	527A
$^{R}Q_1(22)$	4063.51*	525A
$^{R}Q_1(23)$	4063.16*	521A

[a] Corresponding $^{R}R_1(J)$ and $^{R}P_1(J)$ lines are found in Appendix V

Table 8.10 $^{P}Q_{2}(J)$ frequencies in the region of resonance.

	Higher Freq. Branch		Lower Freq. Branch[a]	
$^{P}Q_{2}(J)$	Frequency	Line	Frequency	Line
12	4044.79*	430	4044.06	426
13	4044.49*	428	4043.77	425
14	4044.07*	426	4043.44	423A
15	4043.57*	424A	4043.09	422A
16	4043.12*	422B	4042.71	420
17	4042.62*	419	4042.28	417B
18	4041.14*	417	4041.84	415
19	4041.67*	414A	4041.38	413
20	4041.20*	412A	4040.76	410B
21	4040.76*	410B	4040.08	407C
22	4040.24*	408A	4039.39	404A
23	4039.72*	406*		

a Corresponding $^{P}R_{2}(J)$ and $^{P}P_{2}(J)$ lines are found in Appendix V.

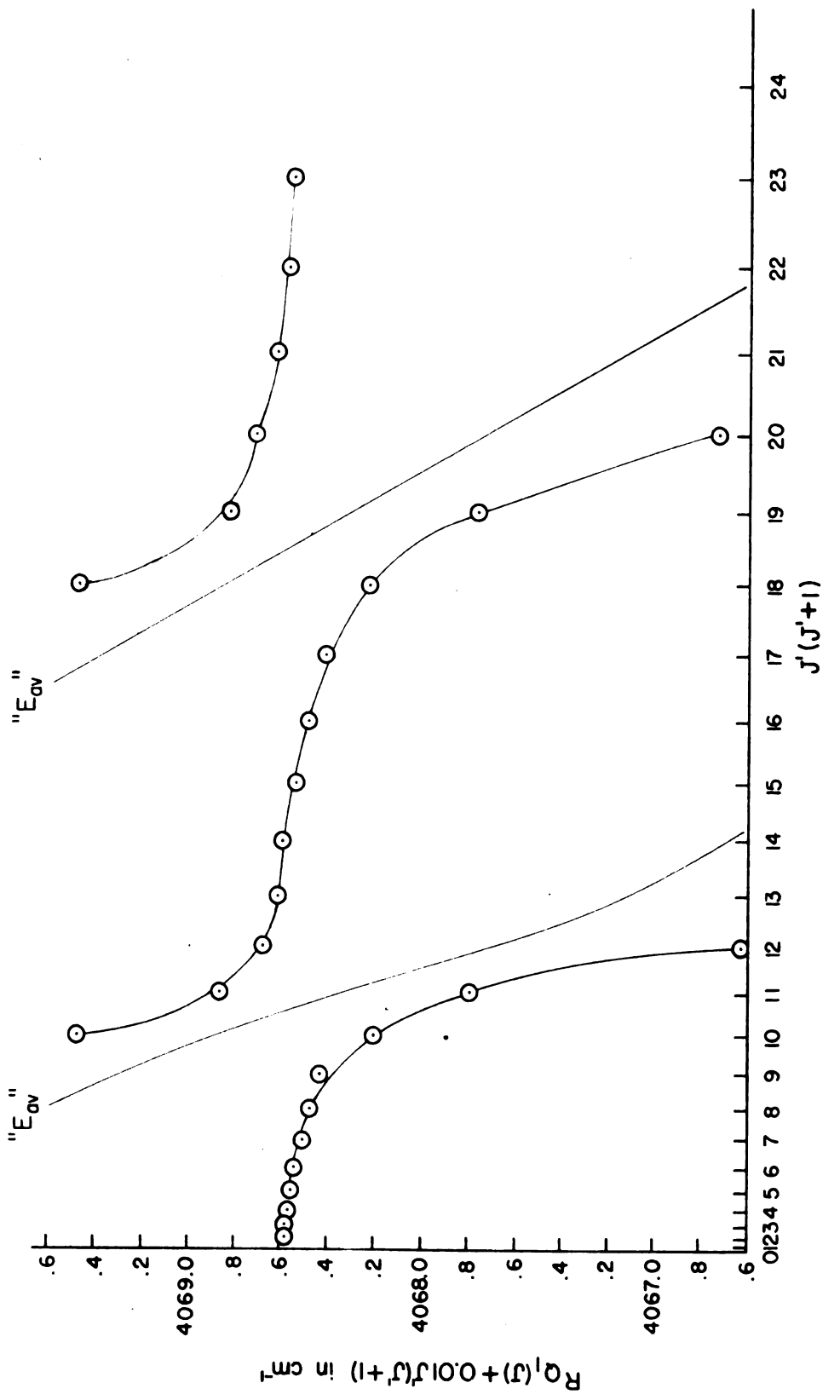


Fig. 8.36 $R_{Q_1}(J)$ transitions vs. $J'(J'+1)$ indicating the effects of two accidental resonances.

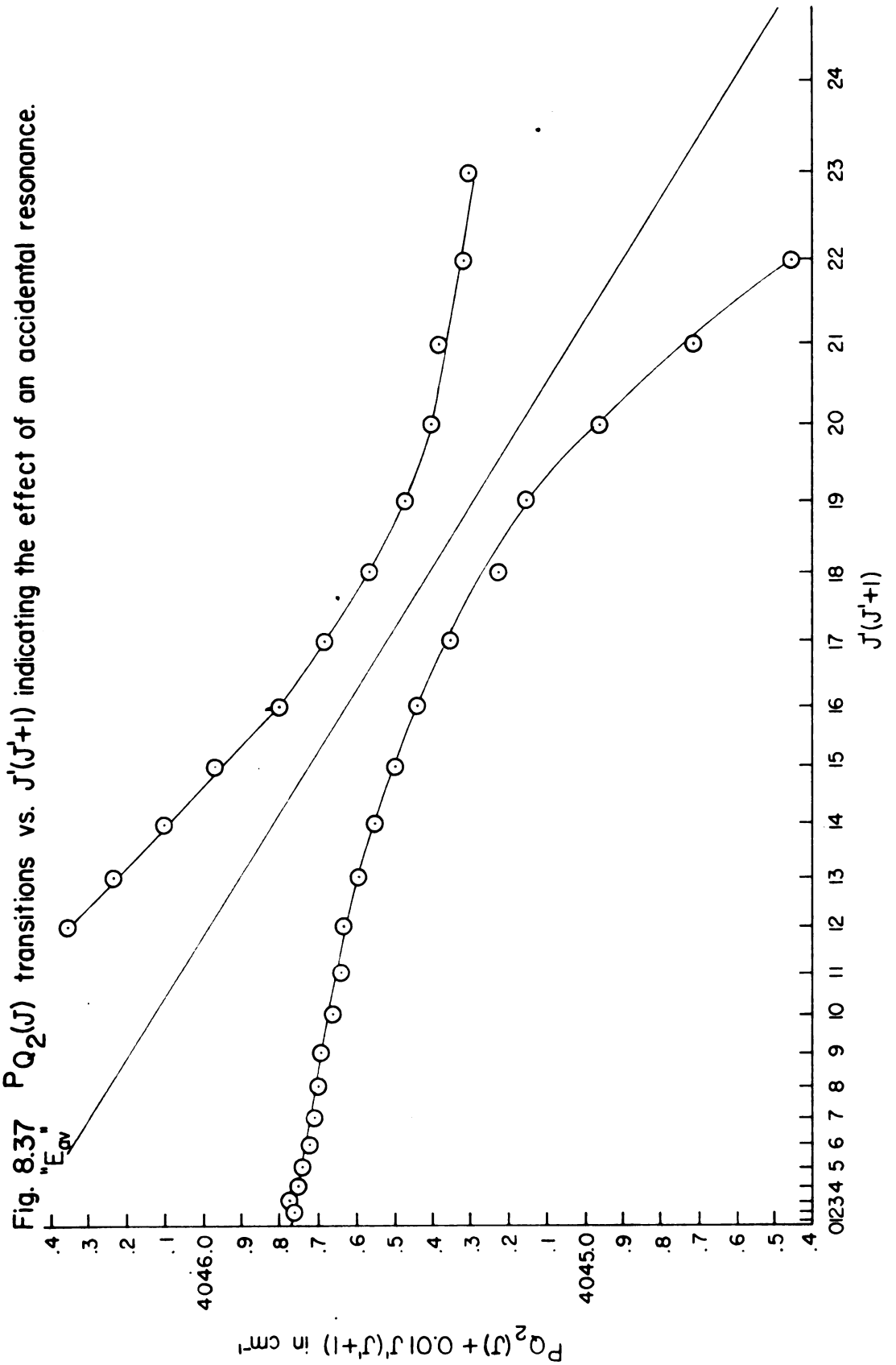


Fig. 8.37 $P_{Q_2}(J)$ transitions vs. J'(J'+1) indicating the effect of an accidental resonance.

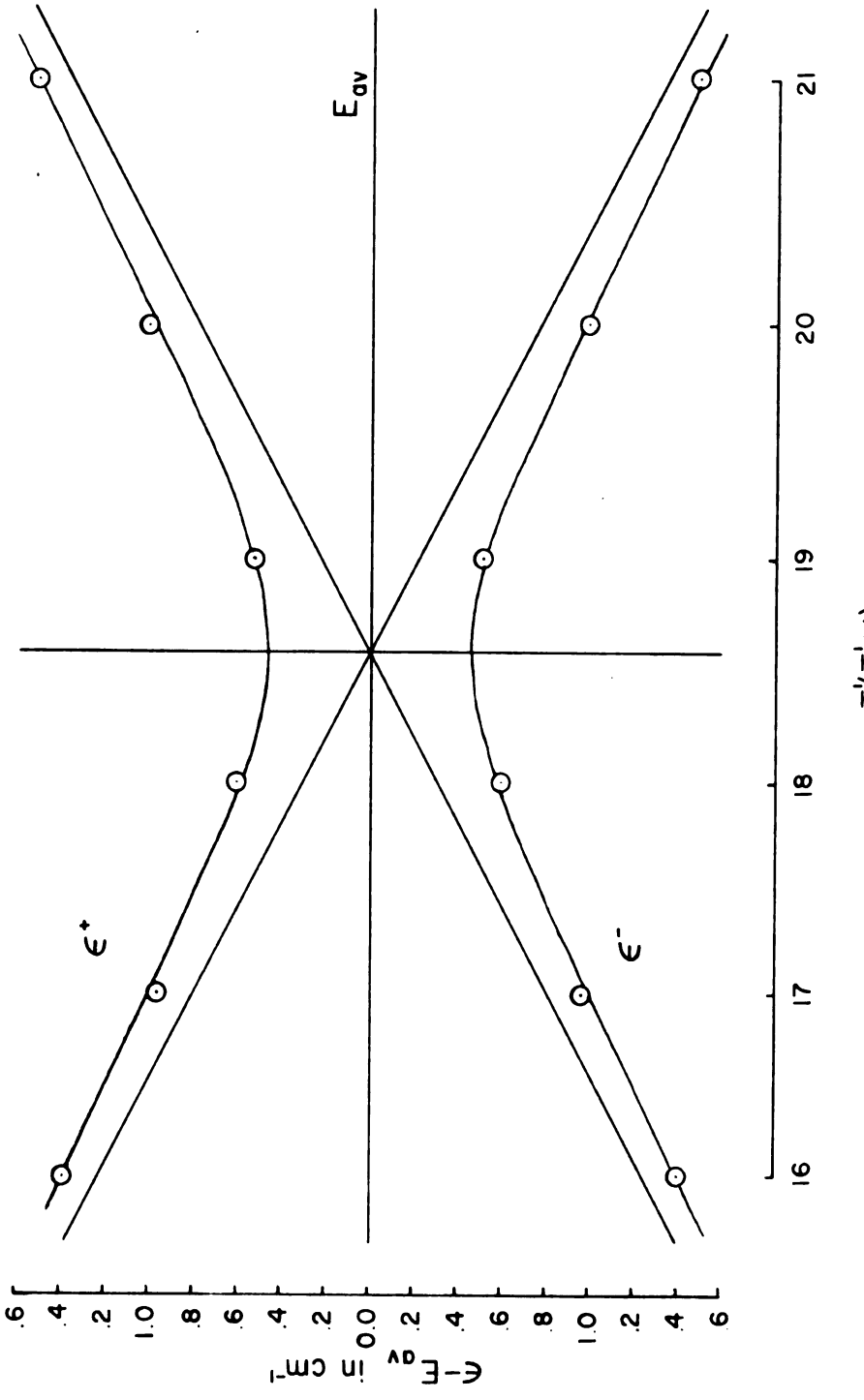


Fig. 8.38 Perturbation hyperbola for the $K'=\pm 2$, $\ell=\pm 1$ levels.

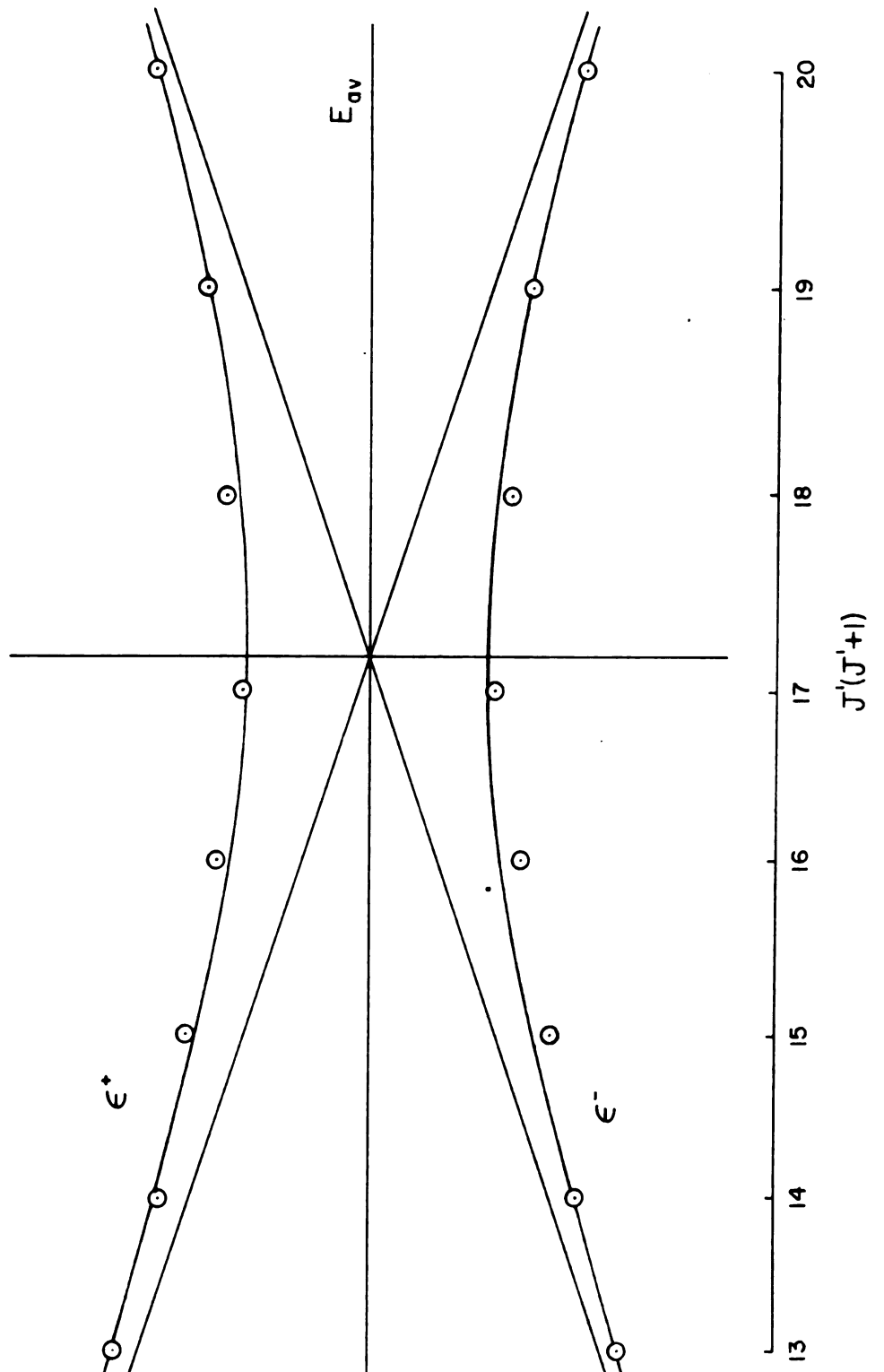


Fig. 8.39 Perturbation hyperbola for $K'=\pm 1$, $l=\mp 1$ levels.

Table 8.11 Summary of results of the analysis of the perturbations affecting the $K' = \pm 2$, $\ell = \pm 1$, and $K' = \pm 1$, $\ell = \mp 1$ levels of $\nu_3+\nu_4$.

Equation of the perturbation hyperbola

$$\frac{\epsilon^2}{c^2} - \frac{x(x+1)}{d^2} = 1$$

For $K' = \pm 2$, $\ell = \pm 1$ levels

$J'(J'+1) = 363$ at resonance

$c = 0.44\text{cm}^{-1}$

$d = 33$

$\epsilon_{asym} = \pm 0.0136x(x+1)$ (asymptotes)

$\delta = 9.081 - 0.0272\ J'(J'+1)\text{cm}^{-1}$

For $K' = \pm 1$, $\ell = \mp 1$ levels

$J'(J'+1) = 313$

$c = 0.155\text{cm}^{-1}$

$d = 66$

$\epsilon_{asym} = \pm 0.0023x(x+1)\text{cm}^{-1}$ (asymptotes)

$\delta = 1.44 - 0.0046\ J'(J'+1)\text{cm}^{-1}$

this second interpretation of the high J low K perturbation is made plausible by the transitions found for the +1 and -2 subbands.

In either case, we cannot at the present time decide between the two possible interpretations.

Weak Coriolis Resonance in the Negative Subbands

Figures 8.4-8.8 indicate the presence of a weak Coriolis type resonance, quite likely of the form $W\sqrt{J(J+1)-K(K\pm1)}$ which if the separation of the perturbing levels is large enough will give rise to an added term in E_{VR} for the upper state, of the form

$$\epsilon = \frac{W^2J'(J'+1) - W^2\left(K'(K'\pm1)\right)}{\delta} \qquad (8.28)$$

where, as before, δ is the energy separation of the perturbing levels. In general δ is a function of J and K as discussed in Chapter 6. From our analysis it is possible to obtain approximate values of (W^2/δ). We find:

subband (K"ΔK)	(W^2/δ)(cm-1)
-9	+0.0021 ± 0.0001
-8	+0.0012 ± 0.0003
-7	+0.0008 ± 0.0001
-5	+0.0018 ± 0.0004
-4	-0.0002 ± 0.0001

The uncertainties indicated above are the simultaneous confidence intervals of the type discussed in Chapter 5.

In the list above, no results are given for the -6 subband since it is perturbed quite strongly and the coefficient of $(J'(J'+1)$ is not well defined. This is easily verified by noting the form of the perturbation of -6 subband lines in Fig. 8.7. It appears quite likely that the -6 subband is perturbed by the same form of perturbation as the other negative subbands discussed above but the resonance is probably accidentally strong so that the energy levels have the added correction here of

$$\epsilon' = E_{av} \pm \sqrt{(\delta^2/4)+W^2[J'(J'+1)-K'(K'\pm1)]} \quad (8.30)$$

where δ is very small.

At this point we interject a word of caution concerning the analysis of subband origins.

For the purpose of comparison, the -9 to +9 subband origins were obtained graphically from expanded graphs of effective Q branch lines vs. $J'(J'+1)$ (cf. Fig.8.27, for example). The subband origins were also obtained by a computer analysis of the individual subband lines using the equation (for a fixed K and ΔK):

$$\begin{aligned}&\left\{{}^{\Delta K}(\Delta J)_K(J)\right\}_{obs} - B_o\left[(J+\Delta J)(J+1+\Delta J)-J(J+1)\right]+\\ &D_o^J\left[(J+\Delta J)^2(J+1+\Delta J)^2-J^2(J+1)^2\right]+\\ &D_o^{JK}\left[(K+\Delta K)^2(J+\Delta J)(J+1+\Delta J)-K^2J(J+1)\right]=\\ &\nu_{sub}(K)-\left[\alpha\tfrac{B}{3}+\alpha\tfrac{B}{4}-\eta\tfrac{J}{4}(K+\Delta K)\Delta K\right](J+\Delta J)(J+1+\Delta J),\end{aligned} \quad (8.31)$$

where the dependence of the lines on B_0, D_0^J, and D_0^{JK} is subtracted off using microwave values of B_0, D_0^J and D_0^{JK} (58). In both cases the obviously perturbed high J lines were ignored (graphical method) or not fit (computer method). The subband origins (ν_{sub}) obtained in the two methods agreed to $0.01 cm^{-1}$.

These subband origins were further analyzed graphically and those which were thought to be perturbed (+5,+1,-3,-4, -5,-6,-7,-8,-9) were not included in the subsequent least squares analysis. The results of a least squares analysis of the subband origins to the equation

$$\nu_{sub} = a + bK\Delta K + cK^2 + dK^3\Delta K \qquad (8.32)$$

are given in Table 8.12 where the coefficients a,b,c,d (assuming that the subband origins included in the analysis are unperturbed) are interpreted in that order in the table. Table 8.13 lists the results of the analysis for each subband origin. Those points enclosed in parenthesis were not included in the analysis since they were thought to be perturbed. We notice particularly that from -4 to -9 there appears to be a K dependent perturbation of the subbands. In this respect, remember that the subband origins used here are actually <u>apparent</u> subband origins obtained from an analysis based on Eq.(8.31). However Figs. 8.4-8.9 indicate that the low J lines ($J \approx K$) in the -4 to -9 subbands do indeed appear near their calculated values. The apparent discrepancy is due to the use of

Table 8.12 Subband origin analysis results (cm^{-1}).

$$\nu_o - 2A_e\zeta + A_o - B_o - \alpha^A + \alpha^B + \eta_4^K - D_o^K = 4060.99 \pm 0.015$$

$$2(A_o - A_e\zeta - B_o - \alpha^A + \alpha^B) + 3\eta_4^K = 7.5954 \pm 0.0067$$

$$-\alpha^A + \alpha^B + 3\eta_4^K - 6D_o^K = -0.0110 \pm 0.0029$$

$$-4D_o^K + \eta_4^K = -0.0089 \pm 0.0027$$

Std. dev. of observations = 0.0062

Table 3.13 Subband analysis results (cm^{-1}).

K	ν_{sub}(obs)	ν_{sub}(calc)	(obs-calc)
+9	4127.80	.80	0.00
+8	4120.59	.59	0.00
+7	4113.31	.31	+0.00
+6	4105.98	.97	+0.01
+5	(4098.11)	.58	(-0.47)
+4	4091.14	.14	0.00
+3	4083.65	.66	-0.01
+2	4076.14	.13	+0.01
+1	(4068.57)	.58	(-0.01)
0	4060.99	.99	0.00
-1	4053.39	.39	0.00
-2	4045.76	.76	0.00
-3	(4038.08)	.13	(-0.05)
-4	(4030.39)	.49	(-0.10)
-5	(4022.69)	.85	(-0.16)
-6	(not defined)	4015.22	
-7	(4007.30)	.59	(-0.29)
-8	(3999.48)	.98	(-0.50)
-9	(3991.64)	2.40	(-0.76)

extrapolated subband origins in the -4 to -9 subbands. However, there is no other way of obtaining the subband origins "accurately" on the basis of an analysis of lines only from a particular subband. Thus, there is the additional effect of a perturbation of the type $W\sqrt{J(J+1)-K(K\pm1)}$ which leads one to false subband origins, by changing the coefficient of the $J'(J'+1)$ term in the upper state energy expression.

Perturbation Affecting the +5 Subband

The final major perturbation affects the +5 subband as indicated in Fig. 8.18. Its principal effect is a shift of the subband lines to lower wave numbers by about $0.55cm^{-1}$ at the subband origin, plus a small change in the coefficient of $J'(J'+1)$ in the upper state energy expression. The first effect is probably due to a perturbation of type I or III, i.e., a coupling of the form W or WK while the second is probably due to a coupling of type II, i.e., $W\sqrt{J(J+1)-K(K\pm1)}$.

Conclusion

We have obtained, under high resolution ($\approx 0.04cm^{-1}$), a perpendicular band which has, in addition to the usual ^{R}R, ^{R}P, ^{P}R, and ^{P}P "fine structure", numerous resolved $^{R}Q_K(J)$ and $^{P}Q_K(J)$ transitions. In fact, this is the first example of such highly resolved structure in the molecules of the methyl halide family of which we are aware. We have

simultaneously analyzed 207 ground state combination differences according to the method of Chapter 4 and 156 "unperturbed" transitions according to the method described in Chapter 5 to find the molecular parameters for this rotation-vibration band.

In addition, we have observed several perturbations in this band. We have identified one as a Coriolis resonance which lifts the degeneracy of the $K' = \ell = \pm 1$ levels. Our observations are somewhat unique since we have here resolved the individual $^{R}Q_{0}(J)$ as well as the $^{R}R_{0}(J)$ and $^{R}P_{0}(J)$ transitions making possible a full analysis of this perturbation. Another interesting perturbation is the accidental resonance which shows up as a crossing of the $K' = \pm 2$, $\ell = \pm 1$ and $K' = \pm 2$, $\ell = \mp 1$ unperturbed energy levels of $\nu_3+\nu_4$ with those of another band. Due to our observation of the Q(J) lines involved in these resonances as well as the R(J) and P(J) lines, we have well substantiated data on these resonances. Using the method of Chapter 6 we have searched for a complete quantitative solution to the perturbation. However, we have not been able to assign the perturbing levels to a single rotation-vibration band and have reason to believe that the actual perturbation may involve the levels of two or more rotation-vibration bands. We have not been able to investigate this possibility due to the non-availability of anharmonic constants for CH_3F. We have however obtained some quantitative results because of the manner in which we

have treated the data from our observations of these perturbed transitions.

Several other perturbations were also observed and some information obtained from our observations.

We have treated this band according to the methods outlined in the first six chapters of this work and have carried the analysis as far as we believe it may be readily taken at the present time.

The analysis of unperturbed spectra itself is a complex problem when treated properly as described in Chapters 3,4 and 5, due in part to the huge volume of data one observes and the small effects which must be taken into account (conservatively, as small as $0.05cm^{-1}$ or $\approx 6.2x10^{-6}$ electron-volts). When one steps into the realm of perturbed spectra the problem is several times more complex, a point which is borne out by the large number of perturbed spectra which have been observed and the very few which have been completely solved.

Note added in proof - We have been able to recalibrate $\nu_3 + \nu_4$ against 17 Neon lines using the 300 li/mm grating. The results of this calibration indicate that the frequencies should be corrected according to the formula: $\nu_{new} = +0.2989 + 0.9999193\ \nu_{old}$. For the ground state constants, this leaves D_0^J and D_0^{JK} unchanged and gives the value $0.851872cm^{-1}$ for B_0 which differs from the microwave results by $0.000078cm^{-1}$ which lies within our simultaneous confidence interval of $\pm 0.000087cm^{-1}$.

CHAPTER 9

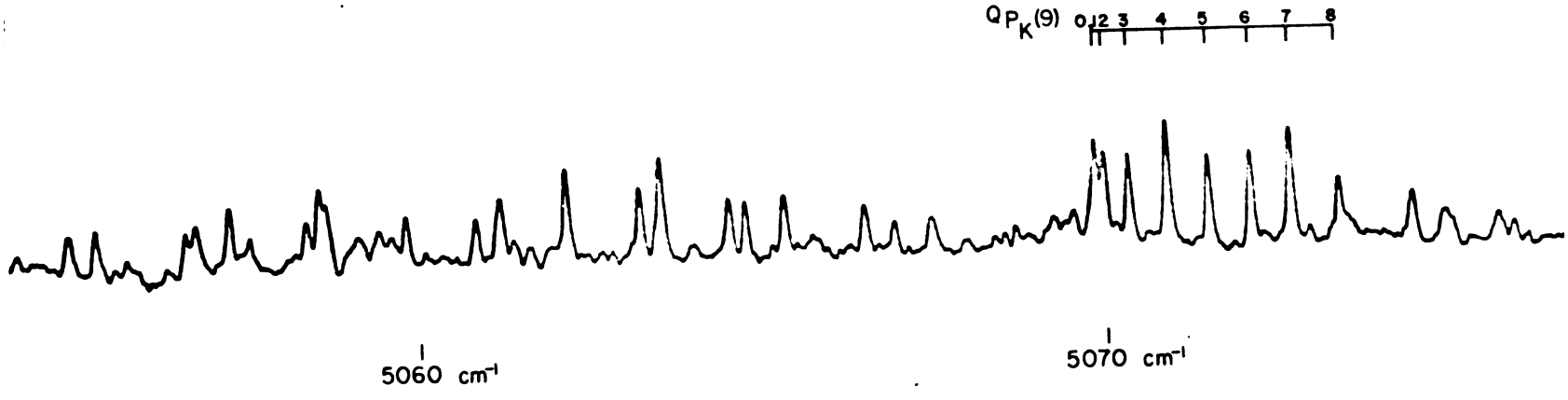
SIMULTANEOUS ANALYSIS OF COMBINATION DIFFERENCES APPLIED TO $\nu_1+\nu_2$ OF CHD_3 AND $\nu_2+\nu_3$ OF CH_3D

The high resolution spectra of two parallel bands, $\nu_1+\nu_2$ of CHD_3 and $\nu_2+\nu_3$ of CH_3D, were obtained as described in Chapter 7. Upon investigation both were found to be perturbed and we shall discuss this briefly in this chapter. However, the principal reason for this chapter is to illustrate the application of the results of Chapter 4 to two molecules whose pure rotation spectra have not been observed by microwave stpectroscopists because of the extremely small permanent dipole moments which these molecules possess. As a result of our work we have found good values for B_0, D_0^J and D_0^{JK} for both molecules, even though the upper levels are perturbed.

$\nu_1+\nu_2$ of CHD_3

The observed spectrum of CHD_3 which we have assigned to $\nu_1+\nu_2$ is shown in Fig. 9.1, with assignment of the principal transitions indicated. The $^QQ_K(J)$ transitions, in particular, are well resolved on the high resolution working records. Appendix XI lists the observed transitions for $\nu_1+\nu_2$. We observed, upon attempting to analyze the spectrum, that it is perturbed and have not definitely found any large subset of apparently unperturbed lines (as was the case for $\nu_3+\nu_4$ of CH_3F in Chapter 8). The first striking aspect of the perturbation, apart from an apparent J

Fig. 9.1 $\nu_1 + \nu_2$ of CHD_3.



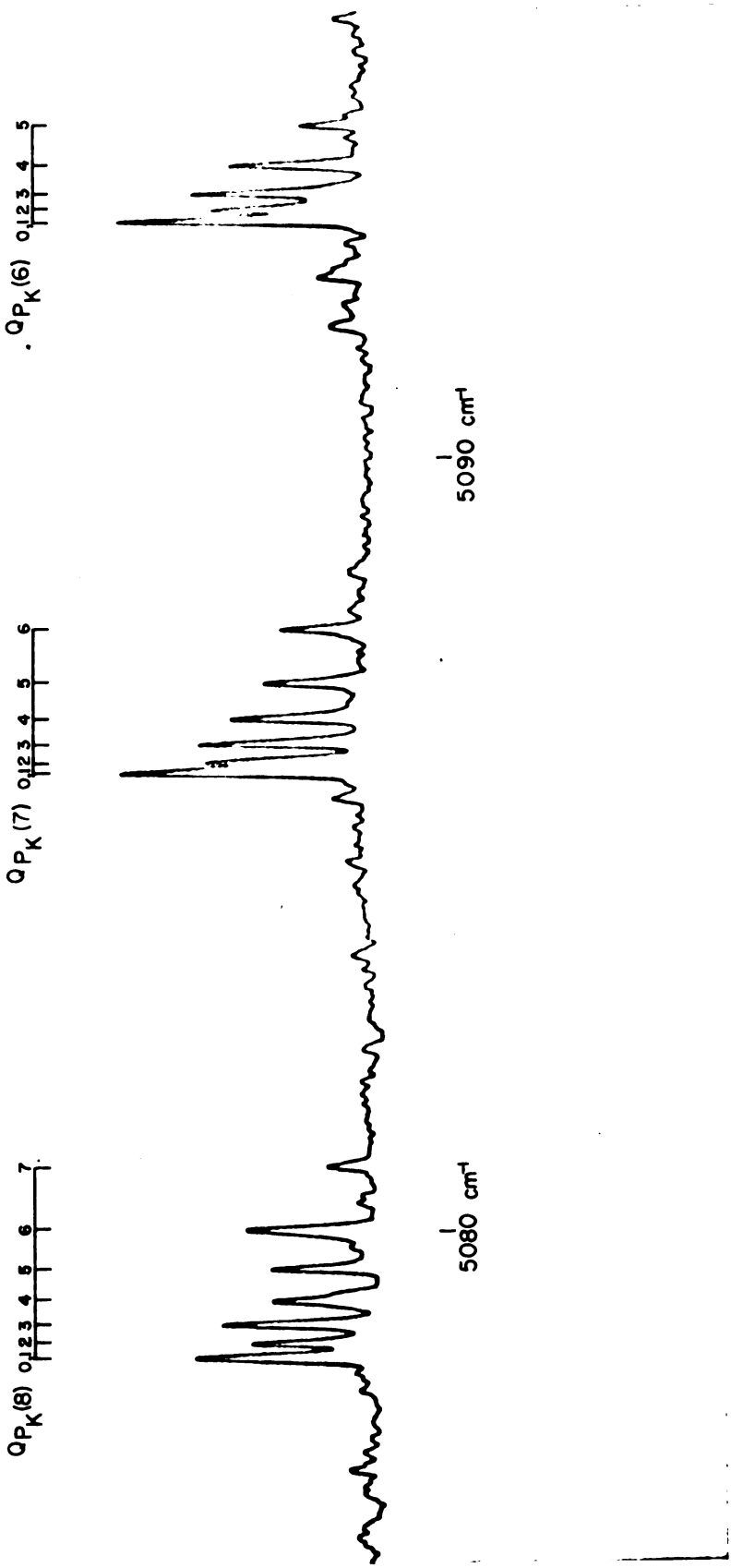


Fig. 9.1 Continued.

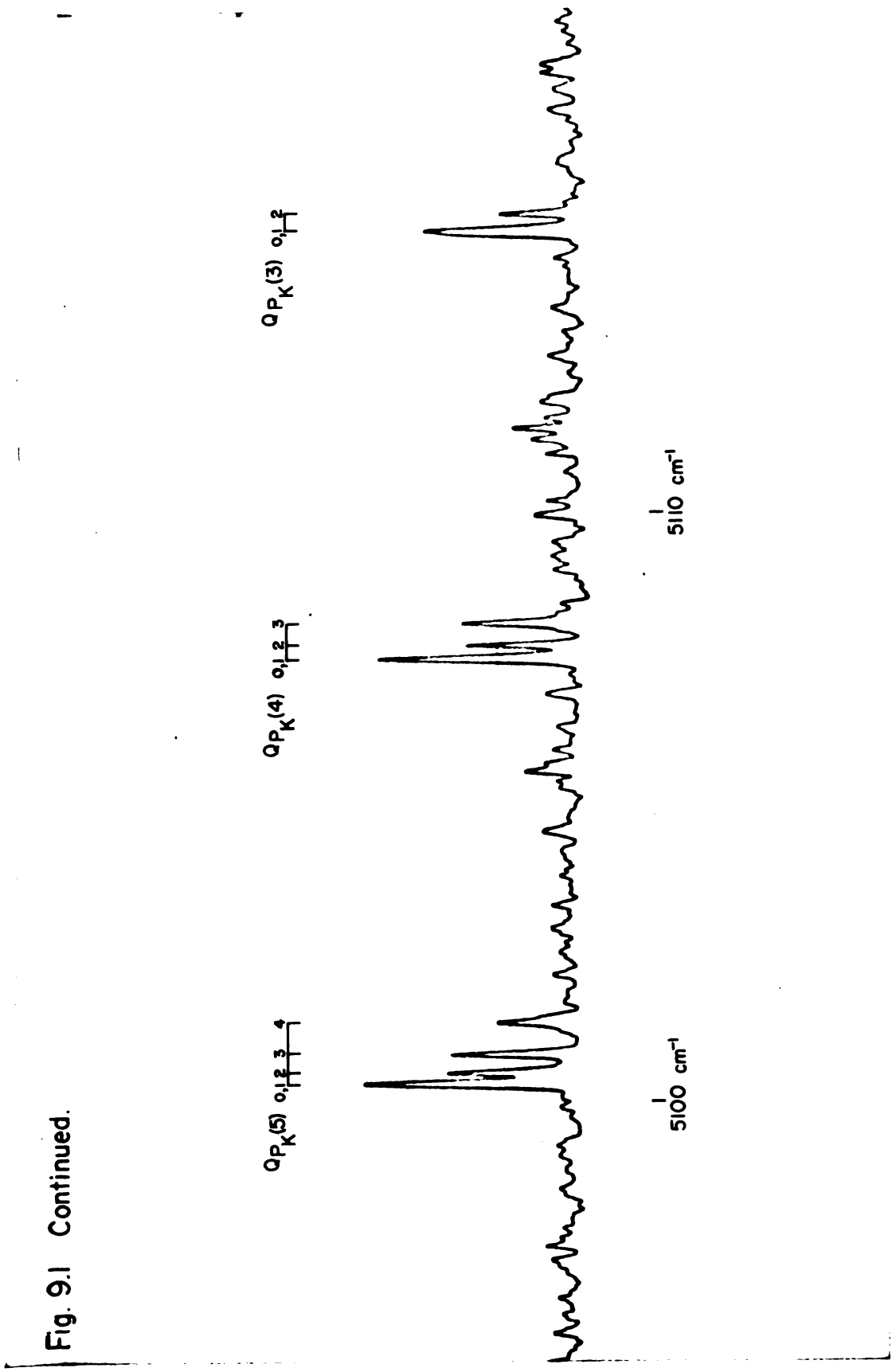


Fig. 9.1 Continued.

Fig. 9.1 Continued.

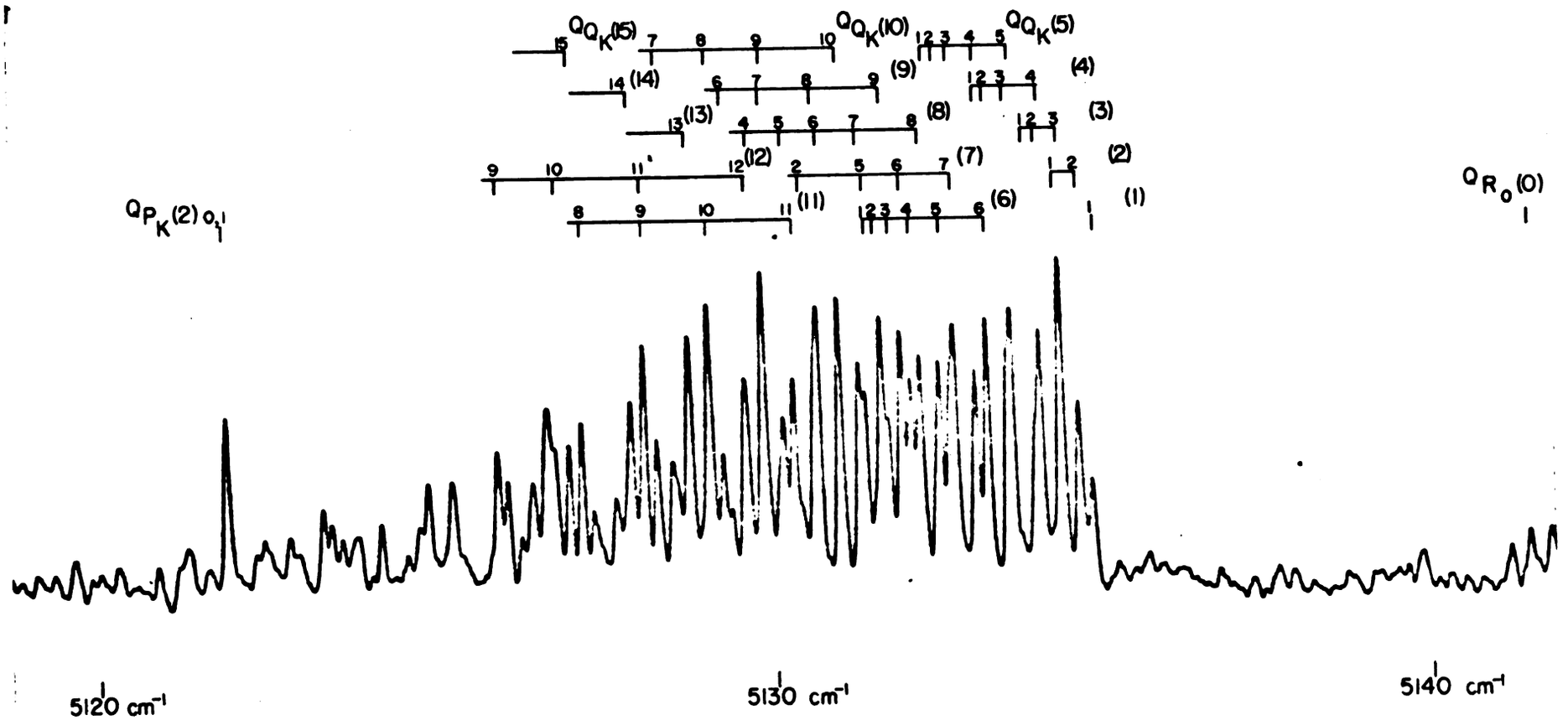
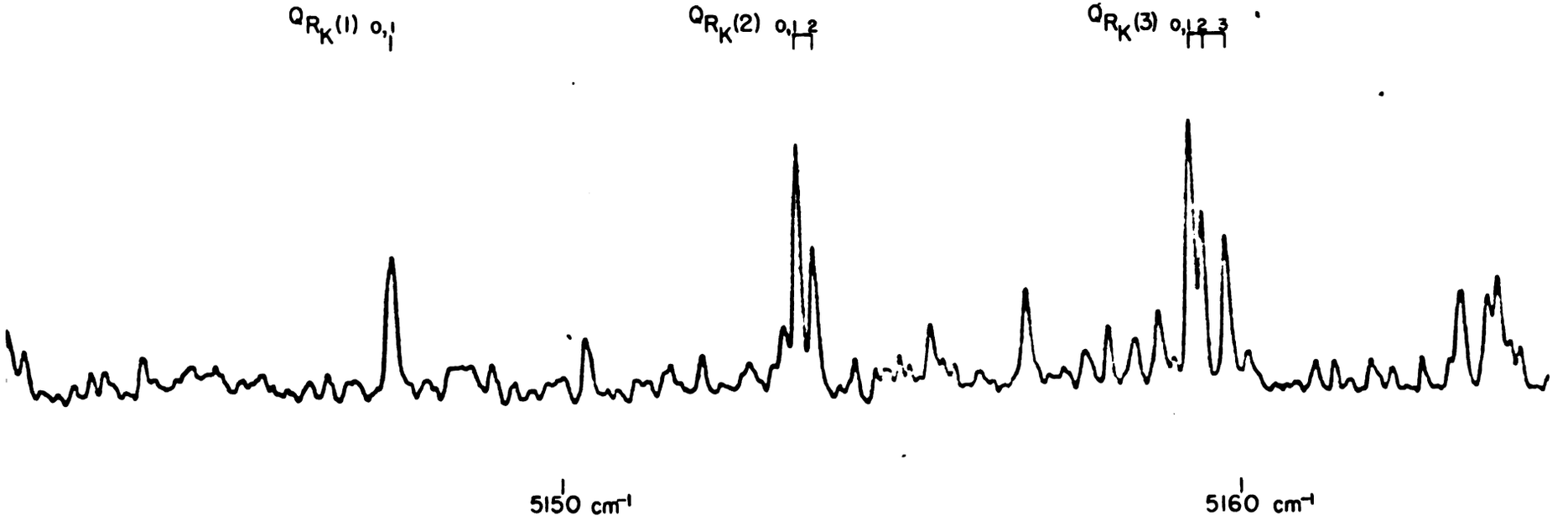


Fig. 9.1 Continued.



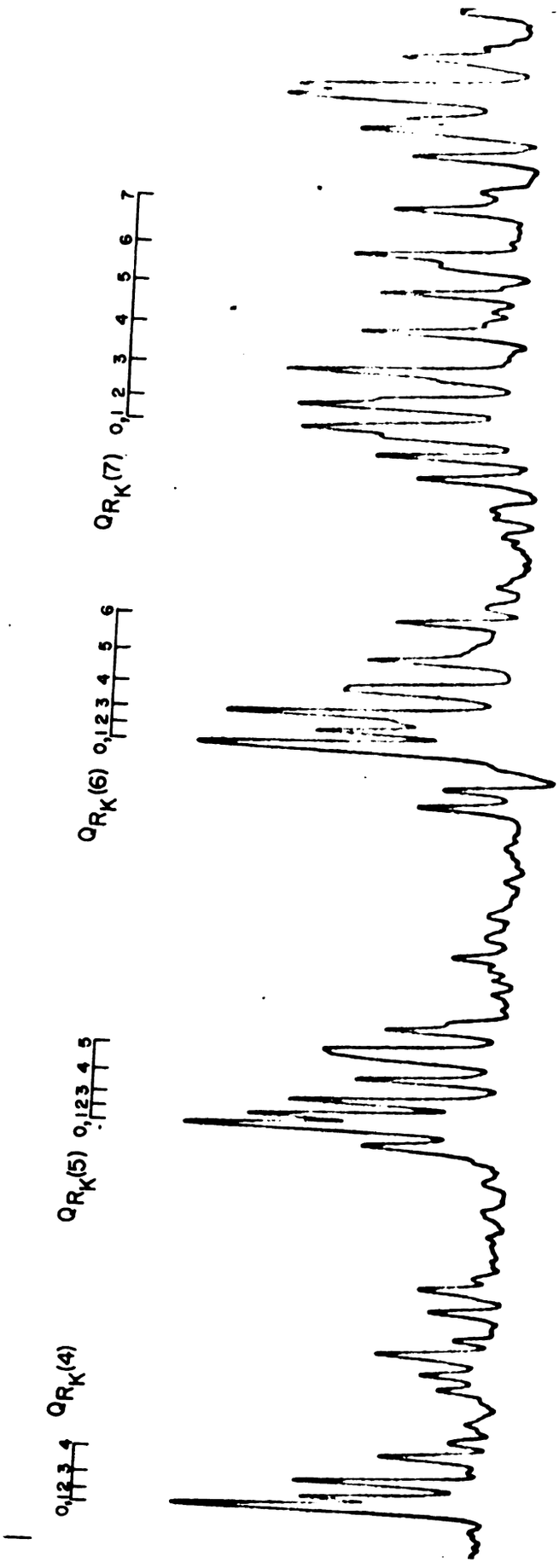


Fig. 9.1 Continued.

dependent perturbation, is that the J'=K' levels in the upper state appear to be displaced from their expected position (on the basis of other levels of the same J) by a nearly constant amount ($\approx$ 0.20cm^{-1} higher than expected). If one assumes that the K'=J' transitions are perturbed, while the others are not as strongly perturbed, then $\nu_0 \approx$ 5135.04cm^{-1} whereas if one assumes the K'=J' are unperturbed, then $\nu_0 \approx$ 5134.84cm^{-1}. In addition, an apparent J dependent perturbation shows up when one attempts to analyze a single K subband. We have not been able to find an explanation for the perturbation at this time.

Ground State Combination Differences of $\nu_1+\nu_2$

The ground state combination differences of $\nu_1+\nu_2$ were, however, analyzed simultaneously following the method described in Chapter 4. The perturbation affects only the upper state of $\nu_1+\nu_2$ and therefore the ground state combination differences give good values for B_0, D_0^J, and D_0^{JK}. Table 9.1 lists the results of this simultaneous analysis with the simultaneous confidence intervals [48] for each constant (cf. Chapter 5) from an analysis of 54 ground state

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[48] The more meaningful simultaneous confidence intervals used throughout differ by the factor $S = [pF_\alpha(p, n-p)]^{1/2}$ from those usually quoted (e.g. reference 107). In this work S ranged from 2.5 to 3.5. An α of 0.05 was used throughout this work.

Table 9.1 Ground state constants of CHD_3

$B_o = 3.27944 \pm 0.00062 cm^{-1}$

$D_o^{JK} = -4.8 \times 10^{-5} \pm 1.4 \times 10^{-5} cm^{-1}$

$D_o^{J} = 5.22 \times 10^{-5} \pm 0.61 \times 10^{-5} cm^{-1}$

$s = 0.010 cm^{-1}$ std. dev.

combination differences. The comparison of observed and calculated combination differences is given in Appendix XII. Table 9.2 compares the results of this study with results of analyses of several other infrared bands (2,3,104,105). We believe our values to be the best presently available for this molecule.

$\nu_2+\nu_3$ of CH_3D

The observed spectrum of $\nu_2+\nu_3$ of CH_3D is shown in Fig. 9.2. The structure of the band is similar to that of $\nu_1+\nu_2$ of CHD_3 due in part to the similarity of B_0 between the two bands and particularly due to the large α^A and α^B in both bands.

We find that $\nu_2+\nu_3$ is also perturbed, particularly for $J > 10$ or 12 and $K > 6$ or 7. Part of the perturbation shows up as a divergence to high wave numbers with large K and J.[49]

Ground State Combination Differences of $\nu_2+\nu_3$ of CH_3D

As with $\nu_1+\nu_2$ of CHD_3 we have simultaneously analyzed all observed ground state combination differences of $\nu_2+\nu_3$ of CH_3D following the method presented in Chapter 4. The

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[49] W.B. Olson (6) of the National Bureau of Standards (105) has communicated the information that $\nu_2+\nu_3$ also shows a perturbation in the K"=0 and 1 series of lines. He adds that the probable perturbing levels belong to $3\nu_6$, a band which is too weak to be observed.

Table 9.2 Comparison of available results for CHD_3 ground state constants·(cm^{-1})

	B_0	D_0^{JK}	D_0^{J}	ν_0
$\nu_1+\nu_2$ [a]	3.2794	-4.8×10^{-5}	5.2×10^{-5}	5134.84 or 5135.04 [b]
$2\nu_1$ [c]	3.2777	-4×10^{-5}	3.9×10^{-5}	5865.02
$3\nu_1$ [d]	3.2784		5×10^{-5}	8623.31
$4\nu_1$ [d]	3.2787	-3.5×10^{-5}	4.6×10^{-5}	11266.94
ν_1 [e]	3.2792		4.6×10^{-5}	2992.3
$2\nu_5$ [f]	3.278	4×10^{-5}		2592.6

[a] This Study.

[b] cf. text

[c] From an analysis of transitions (2).

[d] From an analysis of combination differences (104).

[e] From an analysis of combination differences (3).

[f] From an analysis of combination differences (105).

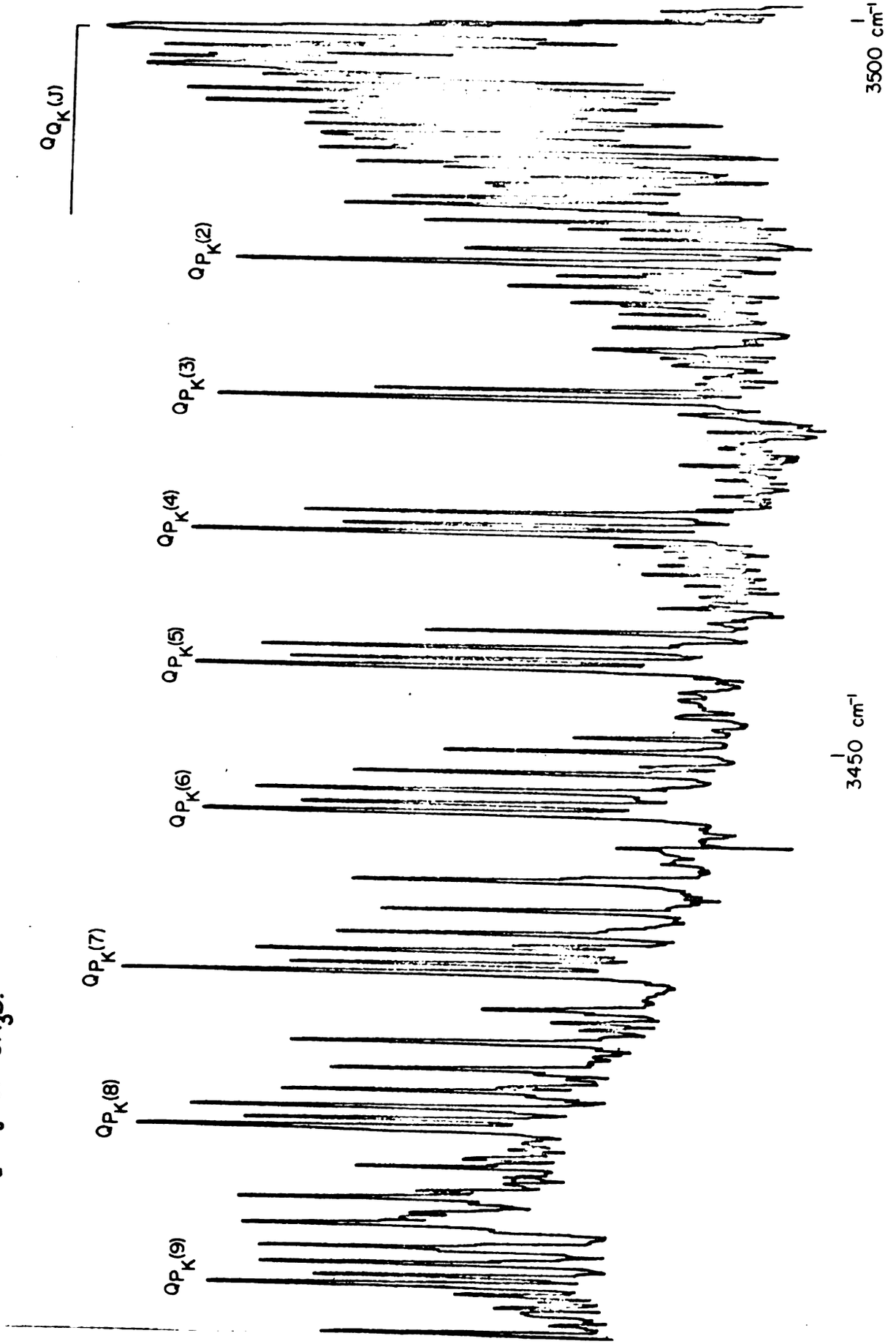


Fig. 9.2 $\nu_2+\nu_3$ of CH_3D.

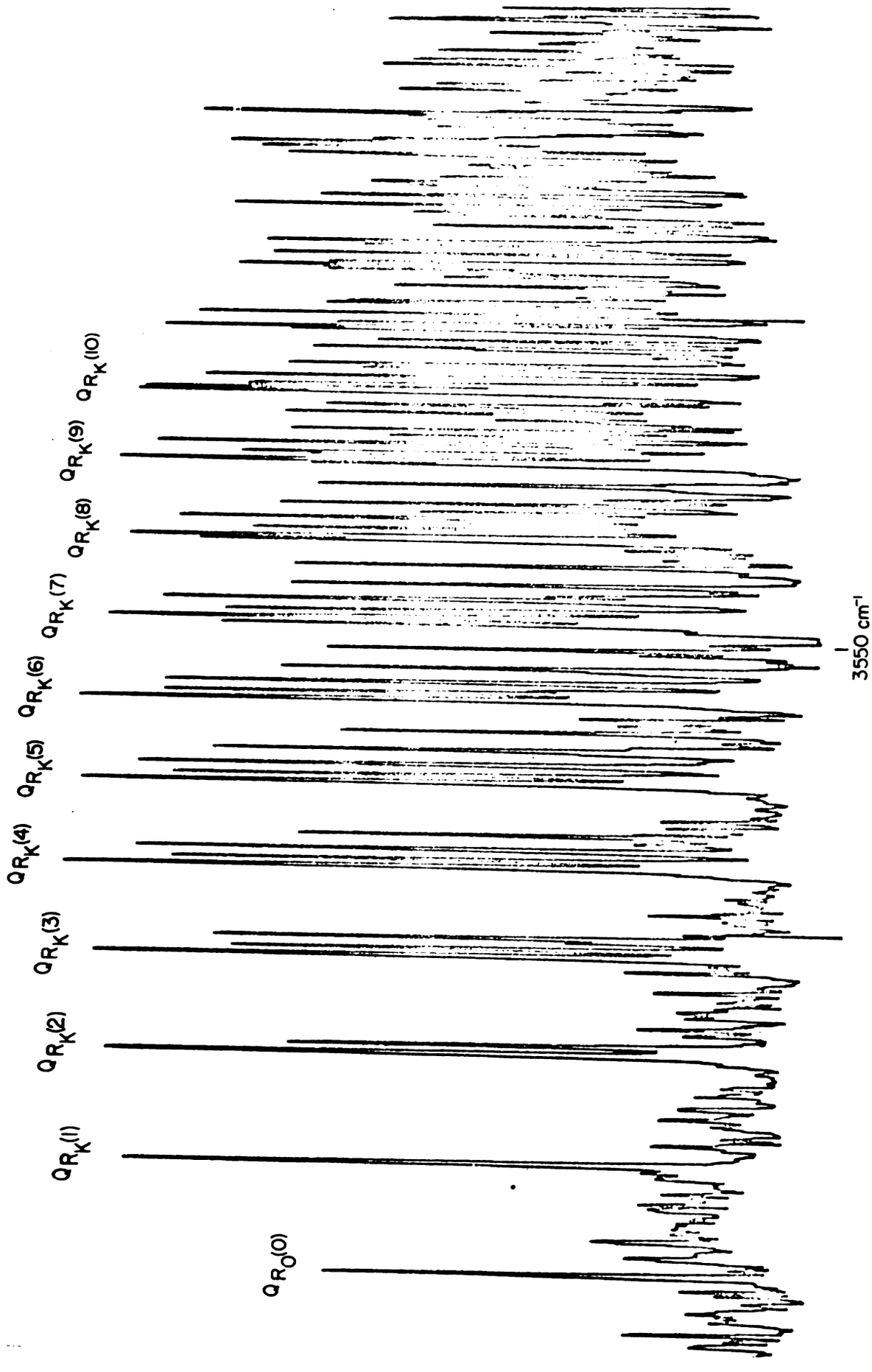


Fig. 5.2 Continued.

The results of our analysis of 108 ground state combination differences for $\nu_2+\nu_3$ are given with their simultaneous confidence intervals (cf.Chapter 5) in Table 9.3. The comparison of observed and calculated combination differences is given in Appendix XIII. Table 9.4 compares our results with two other studies of CH_3D, one infrared absorption study (105) and one Raman study (107).

Analysis of Upper State Combination Differences and Unperturbed Transitions of $\nu_2+\nu_3$

For those upper state levels which are not measureably perturbed, we have simultaneously analyzed 83 upper state combination differences involving these levels. The method of analysis is described in Chapter 4. The results are listed, with their simultaneous confidence intervals (cf. Chapter 5), in Table 9.3. The comparison of the observed and calculated upper state combination differences are listed in Appendix XIV.

Using the values of B_o, D_o^J, and D_o^{JK}, B_v, D_v^J, and D_v^{JK} from Table 9.3, 99 "unperturbed" transitions of $\nu_2+\nu_3$ were analyzed using the expression:

$$\left[\Delta K \Delta J_K(J)\right]_{obs} - B_o\left[(J+\Delta J)(J+1+\Delta J)-J(J+1)\right] +$$

$$(\alpha_2^B+\alpha_3^B)(J+\Delta J)(J+1+\Delta J) + D_o^J\left[(J+\Delta J)^2(J+1+\Delta J)^2-J^2(J+1)^2\right] +$$

$$D_o^{JK}\left[K^2(J+\Delta J)(J+1+\Delta J)-K^2J(J+1)\right] - (\beta_2^J+\beta_3^J)(J+\Delta J)^2(J+1+\Delta J)^2 -$$

$$(\beta_2^{JK}+\beta_3^{JK})K^2(J+\Delta J)(J+1+\Delta J) = \nu_o - (\alpha_2^A+\alpha_3^A)K^2$$

where $\beta_v^m = D_o^m - D_v^m$.

Table 9.3 Molecular constants for CH_3D (in cm^{-1}).

	From Ground State Combination Differences[a]	
B_0	3.88107	± 0.00031
D_0^{JK}	1.192×10^{-4}	± 0.070×10^{-4}
D_0^J	5.28×10^{-5}	± 0.18×10^{-5}
	From Upper State Combination Differences[b]	
B_v	3.74260	± 0.00035
D_v^{JK}	2.51×10^{-4}	± 0.16×10^{-4}
D_v^J	-1.52×10^{-5}	± 0.21×10^{-5}.
	From Analysis of Transition Frequencies[c]	
ν_0	3499.6291	± 0.0026
$\alpha^A - \alpha^B$	0.151718	± 0.00020

[a] Std. dev. = 0.012 cm^{-1} for 108 points included in the analysis.

[b] Std. dev. = 0.012 cm^{-1} for 83 points included in the analysis.

[c] Std. dev. = 0.007 cm^{-1} for 99 points included in the analysis.

Table 9.4 Comparison of ground state constants for CH_3D (in cm^{-1}).

	$\nu_2 + \nu_3$ [a]	ν_2 [b]	ν_4 [c]
ν_0	3499.63	2200.03	3016.59
B_0	3.88107	3.8800	3.877
D_0^{JK}	1.192×10^{-4}	1.2×10^{-4}	3×10^{-5}
D_0^{J}	5.28×10^{-5}	5×10^{-5}	4.7×10^{-5}

[a] This study, from 108 ground state combination differences.

[b] From an analysis of ground state combination differences (105).

[c] From an analysis of transitions (107).

The results are given with their simultaneous confidence intervals (cf. Chapter 5) in Table 9.3. The comparison of the observed and calculated frequencies of the lines included in the analysis make up the first part of Appendix XV. The second part of Appendix XV is a comparison of the calculated and observed frequencies of all other lines we have assigned but which were not included in the least squares analysis.

The effect of the perturbation may be seen by scanning the observed minus calculated column of Appendix XV.

Conclusion

Using the method of Chapter 4 we have obtained statistically favorable values of B_0, D_0^J and D_0^{JK}. This is especially valuable for molecules whose pure rotation spectra has not been observed in the microwave region. This was the case for the two molecules discussed in this chapter.

In addition, from our results for CH_3D, it appears - although not surprisingly - that if possible one should use combination differences to obtain the molecular constants which can be found from combination differences.

CHAPTER 10

CONCLUSION

In this work we have gathered together many facets of the theory of molecular spectras particularly as applicable to molecules belonging to the point group C_{3v}.

We have also set down a number of important considerations and practical methods, usable in the analysis of spectra, which have evolved over the four year period this work was in progress, particularly, the simultaneous representation of all possible transitions[50] (Chapter 3), the simultaneous analysis of all observable ground state combination differences (Chapter 4); and a reasonable approach to the analysis of the large quantities of data involved in molecular spectra[51] (Chapter 5).

We have also attempted to gather together many of the salient features of the remarkable work of Dr. G. Amat of the University of Paris on the semi-quantitative study of perturbations in molecular spectra (Chapter 6). Using all of the foregoing we have analyzed the perturbed band, $\nu_3+\nu_4$ of CH_3F, (Chapter 8) where we have found several perturbations and have come to a somewhat better understanding of

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[50] This result evolved from a rather extensive study of data analysis schemes applied to molecular spectra carried out in collaboration with J.W. Boyd. A similar result, although not carried as far was, obtained independently by Brodersen and Richardson (61).

[51] These results are in part taken from a thesis by Boyd (50) and in part the result of the data analysis studies carried out with J.W. Boyd.

several of these perturbations. However, the problem involving this single band is not completely solved although we feel that we have carried the problem about as far as it can readily be taken at present. We have found a good example of a Coriolis resonance which lifts the degeneracy of $K' = \pm 2$, $\ell = \pm 1$ levels. We have, in this case, resolved all of the K"=0 transitions involved in the resonance, i.e., ${}^{R}P_{0}(J)$, ${}^{R}Q_{0}(J)$, ${}^{R}R_{0}(J)$, and have obtained a value for the Coriolis constant q from a simultaneous analysis of all observed K"=0 transitions. Additionally, we have observed several accidentally strong resonances, and for at least two cases have well substantiated data on the effect of these resonances on the observed spectrum. These accidental resonances provide a fine example of applied quantum mechanical perturbation theory.

In Chapter 9 we have applied the method of Chapter 4 to two parallel bands (CH_3D and CHD_3) in order to demonstrate the principle and to obtain good values of B_0, D_0^J and D_0^{JK} for two molecules whose microwave spectra has not been observed. The upper states of both parallel bands are perturbed and we have not yet reached an understanding of those perturbations.

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APPENDIX I

SYMMETRY SPECIES OF ROTATION-VIBRATION LEVELS OF MOLECULES BELONGING TO THE POINT GROUP C_{3v}

In the systematic analysis of molecular spectra, it is helpful to know the symmetry species of the rotation-vibration levels of the absorption bands under study.

A simple, though not fundamental method of determining the symmetry species of the rotation-vibration levels of axially symmetric molecules belonging to the point group C_{3v} is presented in this appendix.

The point group C_{3v} has symmetry species A_1, A_2 and E_1; the latter is a two dimensional representation and for the axially symmetric molecule corresponds to an essential degeneracy of the levels which are of symmetry E_1(12). This degeneracy may only be lifted by a perturbation of lower symmetry than that of the Hamiltonian of the molecule. Levels of species A_1 and A_2 also occur in degenerate pairs; however the degeneracy of species A levels is not essential, i.e., the degeneracy may be lifted by a perturbation of symmetry equal to that of the Hamiltonian, i.e., a term contained in the Hamiltonian of the molecule may lift such a degeneracy(12).

Since A_1 and A_2 levels occur in degenerate pairs, we shall only speak of levels of symmetry A and we shall drop the subscript on the E.

Amat has found a convenient rule (49) that allows one to determine which matrix elements of the transformed Hamiltonian

h' or h^+ are not necessarily zero due to symmetry considerations. Specialized to the case of the C_{3v} axially symmetric molecule the rule may be written

$$\Delta K - \Sigma_t \Delta \ell_t = 3p \qquad \text{(AI.1)}$$

where p is an interger 0, ±1, ±2,...and where the matrix elements may be written as

$$(\ldots K, \ldots \ell_t \ldots | h_m^+ | \ldots K+\Delta K, \ldots \ell_t + \Delta \ell_t \ldots) \qquad \text{(AI.2)}$$

Since only levels of species A may be split, i.e., may have their degeneracy lifted, consider a generic segment of the Hamiltonian matrix for a given vibrational state as shown below.

	$-\Sigma \ell_t$ $-K$	$+\Sigma \ell_t$ $+K$
$-\Sigma \ell_t$ $-K$	$Q(h^+)$	$P(h^+)$
$+\Sigma \ell_t$ $+K$	$P(h^+)$	$Q(h^+)$

In the matrix, the $Q(h^+)$ elements are the diagonal elements of h^+ corresponding, in the absence of off diagonal elements, to the energy of the level with $K = K$ and $\Sigma \ell_t = \Sigma \ell_t$. The two diagonal elements shown form a degenerate pair either of species E or A. If the level is of species A it may have its degeneracy lifted by a perturbing term indicated by $P(h^+)$; if the level if of species E, the element $P(h^+)$ will necessarily be identically zero due to the symmetry of the Hamiltonian.

Therefore, if $P(h^+)$ is identically zero the level K, $\Sigma \ell_t$ is of species E, whereas if $P(h^+)$ is not <u>necessarily</u> zero due to symmetry the level is of species A.

Applying Amat's rule to the matrix element

$$(\ldots -K\ldots -\Sigma \ell_t \ldots | P(h^+) | \ldots +K\ldots +\Sigma \ell_t \ldots) \qquad (AI.3)$$

it is apparent that in this instance $\Delta K = 2K$ and $\Sigma \ell_t = 2\Sigma \ell_t$. Therefore if $P(h^+)$ is not <u>necessarily</u> zero then

$$2K - 2\Sigma \ell_t = 3p = 0, \pm 3, \pm 6, \pm 9, \pm 12, \ldots$$

or, after dividing by 2 and recalling that K and ℓ_t must necessarily be intergers,

$$K - \Sigma \ell_t = 3n = 0, \pm 3, \pm 6, \ldots$$

where n may take on the values $0, \pm 1, \pm 2, \pm 3, \ldots$.

Quite generally for a C_{3v} molecule the A species level are those which satisfy the relation

$$K - \Sigma \ell_t = 3p; \; p = 0, \pm 1, \pm 2, \ldots \qquad (AI.4)$$

Consequently the E species levels are those which satisfy the relation

$$K - \Sigma \ell_t = 3p \pm 1 \qquad (AI.5)$$

This approach may also be used for molecules belonging to other point groups and in fact the results obtained here depend only upon the fact that the top axis is a three fold axis.

APPENDIX II

LIST OF CALCULATED GROUND STATE COMBINATION DIFFERENCES FOR CH_3F

The following pages contain ground state combination differences (in cm^{-1}) computed on the Michigan State University Digital Computer, MISTIC. The values of the constants used are (in cm^{-1}):

$$B_o = 0.851793$$

$$D_o^{JK} = 1.48 \times 10^{-5}$$

$$D_o^{J} = 1.98 \times 10^{-6}$$

These constants are taken from the results of the pure rotation spectra observed in the microwave region (58).

In order to use the tables one should note that the designation of the combination differences in this appendix is that used in Chapter 4. Note also that

$$QPK,J = RQK,J+1.$$

ASSIGNMENT	CALCULATED GSCD
RQ 0, 1	1.7036
RQ 0, 2	3.4071
RQ 0, 3	5.1105
RQ 0, 4	6.8138
RQ 0, 5	8.5169
RQ 0, 6	10.2198
RQ 0, 7	11.9224
RQ 0, 8	13.6246
RQ 0, 9	15.3265
RQ 0,10	17.0279
RQ 0,11	18.7289
RQ 0,12	20.4293
RQ 0,13	22.1292
RQ 0,14	23.8285
RQ 0,15	25.5271
RQ 0,16	27.2250
RQ 0,17	28.9221
RQ 0,18	30.6185
RQ 0,19	32.3139
RQ 0,20	34.0085
RQ 0,21	35.7022
RQ 0,22	37.3948
RQ 0,23	39.0864
RQ 0,24	40.7769
RQ 0,25	42.4663
RQ 0,26	44.1545
RQ 0,27	45.8415
RQ 0,28	47.5272
RQ 0,29	49.2115
RQ 0,30	50.8945
RQ 0,31	52.5761
RQ 0,32	54.2562
RQ 0,33	55.9348
RQ 0,34	57.6118
RQ 0,35	59.2873
RQ 0,36	60.9610
RQ 0,37	62.6331
RQ 0,38	64.3034
RQ 0,39	65.9719
RQ 0,40	67.6386
RQ 1, 2	3.4070
RQ 1, 3	5.1104
RQ 1, 4	6.8137
RQ 1, 5	8.5168
RQ 1, 6	10.2196
RQ 1, 7	11.9221
RQ 1, 8	13.6244
RQ 1, 9	15.3262
RQ 1,10	17.0276
RQ 1,11	18.7286

ASSIGN-MENT	CALCULATED GSCD
RQ 1,12	20.4290
RQ 1,13	22.1288
RQ 1,14	23.8281
RQ 1,15	25.5266
RQ 1,16	27.2245
RQ 1,17	28.9216
RQ 1,18	30.6179
RQ 1,19	32.3134
RQ 1,20	34.0079
RQ 1,21	35.7015
RQ 1,22	37.3942
RQ 1,23	39.0857
RQ 1,24	40.7762
RQ 1,25	42.4656
RQ 1,26	44.1537
RQ 1,27	45.8407
RQ 1,28	47.5263
RQ 1,29	49.2107
RQ 1,30	50.8936
RQ 1,31	52.5752
RQ 1,32	54.2553
RQ 1,33	55.9338
RQ 1,34	57.6108
RQ 1,35	59.2862
RQ 1,36	60.9600
RQ 1,37	62.6320
RQ 1,38	64.3023
RQ 1,39	65.9708
RQ 1,40	67.6374
RQ 2, 3	5.1102
RQ 2, 4	6.8133
RQ 2, 5	8.5163
RQ 2, 6	10.2191
RQ 2, 7	11.9215
RQ 2, 8	13.6237
RQ 2, 9	15.3254
RQ 2,10	17.0267
RQ 2,11	18.7276
RQ 2,12	20.4279
RQ 2,13	22.1277
RQ 2,14	23.8268
RQ 2,15	25.5253
RQ 2,16	27.2231
RQ 2,17	28.9201
RQ 2,18	30.6163
RQ 2,19	32.3117
RQ 2,20	34.0062
RQ 2,21	35.6997
RQ 2,22	37.3922
RQ 2,23	39.0837

ASSIGN-MENT	CALCULATED GSCD
RQ 2,24	40.7741
RQ 2,25	42.4633
RQ 2,26	44.1514
RQ 2,27	45.8383
RQ 2,28	47.5238
RQ 2,29	49.2081
RQ 2,30	50.8910
RQ 2,31	52.5724
RQ 2,32	54.2524
RQ 2,33	55.9309
RQ 2,34	57.6078
RQ 2,35	59.2831
RQ 2,36	60.9568
RQ 2,37	62.6287
RQ 2,38	64.2989
RQ 2,39	65.9673
RQ 2,40	67.6339
RQ 3, 4	6.8127
RQ 3, 5	8.5156
RQ 3, 6	10.2182
RQ 3, 7	11.9205
RQ 3, 8	13.6225
RQ 3, 9	15.3241
RQ 3,10	17.0252
RQ 3,11	18.7259
RQ 3,12	20.4261
RQ 3,13	22.1257
RQ 3,14	23.8247
RQ 3,15	25.5231
RQ 3,16	27.2207
RQ 3,17	28.9176
RQ 3,18	30.6137
RQ 3,19	32.3089
RQ 3,20	34.0032
RQ 3,21	35.6966
RQ 3,22	37.3889
RQ 3,23	39.0803
RQ 3,24	40.7705
RQ 3,25	42.4596
RQ 3,26	44.1476
RQ 3,27	45.8343
RQ 3,28	47.5197
RQ 3,29	49.2038
RQ 3,30	50.8865
RQ 3,31	52.5678
RQ 3,32	54.2477
RQ 3,33	55.9260
RQ 3,34	57.6028
RQ 3,35	59.2779
RQ 3,36	60.9514

ASSIGN-MENT	CALCULATED GSCD
RQ 3,37	62.6232
RQ 3,38	64.2933
RQ 3,39	65.9615
RQ 3,40	67.6279
RQ 4, 5	8.5145
RQ 4, 6	10.2169
RQ 4, 7	11.9190
RQ 4, 8	13.6208
RQ 4, 9	15.3222
RQ 4,10	17.0232
RQ 4,11	18.7237
RQ 4,12	20.4236
RQ 4,13	22.1230
RQ 4,14	23.8218
RQ 4,15	25.5200
RQ 4,16	27.2174
RQ 4,17	28.9141
RQ 4,18	30.6099
RQ 4,19	32.3049
RQ 4,20	33.9990
RQ 4,21	35.6922
RQ 4,22	37.3844
RQ 4,23	39.0755
RQ 4,24	40.7655
RQ 4,25	42.4544
RQ 4,26	44.1422
RQ 4,27	45.8287
RQ 4,28	47.5139
RQ 4,29	49.1978
RQ 4,30	50.8803
RQ 4,31	52.5614
RQ 4,32	54.2410
RQ 4,33	55.9191
RQ 4,34	57.5957
RQ 4,35	59.2706
RQ 4,36	60.9439
RQ 4,37	62.6155
RQ 4,38	64.2854
RQ 4,39	65.9534
RQ 4,40	67.6196
RQ 5, 6	10.2153
RQ 5, 7	11.9172
RQ 5, 8	13.6187
RQ 5, 9	15.3198
RQ 5,10	17.0205
RQ 5,11	18.7207
RQ 5,12	20.4204
RQ 5,13	22.1196
RQ 5,14	23.8181
RQ 5,15	25.5160

ASSIGN-MENT	CALCULATED GSCD
RQ 5,16	27.2131
RQ 5,17	28.9095
RQ 5,18	30.6051
RQ 5,19	32.2998
RQ 5,20	33.9937
RQ 5,21	35.6866
RQ 5,22	37.3785
RQ 5,23	39.0693
RQ 5,24	40.7591
RQ 5,25	42.4478
RQ 5,26	44.1352
RQ 5,27	45.8214
RQ 5,28	47.5064
RQ 5,29	49.1900
RQ 5,30	50.8723
RQ 5,31	52.5531
RQ 5,32	54.2325
RQ 5,33	55.9103
RQ 5,34	57.5866
RQ 5,35	59.2613
RQ 5,36	60.9343
RQ 5,37	62.6056
RQ 5,38	64.2752
RQ 5,39	65.9430
RQ 5,40	67.6089
RQ 6, 7	11.9149
RQ 6, 8	13.6161
RQ 6, 9	15.3169
RQ 6,10	17.0172
RQ 6,11	18.7171
RQ 6,12	20.4165
RQ 6,13	22.1153
RQ 6,14	23.8135
RQ 6,15	25.5111
RQ 6,16	27.2079
RQ 6,17	28.9040
RQ 6,18	30.5992
RQ 6,19	32.2936
RQ 6,20	33.9872
RQ 6,21	35.6797
RQ 6,22	37.3713
RQ 6,23	39.0618
RQ 6,24	40.7513
RQ 6,25	42.4396
RQ 6,26	44.1267
RQ 6,27	45.8126
RQ 6,28	47.4972
RQ 6,29	49.1805
RQ 6,30	50.8625
RQ 6,31	52.5430

ASSIGN-MENT	CALCULATED GSCD
RQ 6,32	54.2220
RQ 6,33	55.8995
RQ 6,34	57.5755
RQ 6,35	59.2499
RQ 6,36	60.9226
RQ 6,37	62.5936
RQ 6,38	64.2628
RQ 6,39	65.9303
RQ 6,40	67.5959
RQ 7, 8	13.6130
RQ 7, 9	15.3134
RQ 7,10	17.0134
RQ 7,11	18.7129
RQ 7,12	20.4119
RQ 7,13	22.1103
RQ 7,14	23.8081
RQ 7,15	25.5053
RQ 7,16	27.2017
RQ 7,17	28.8974
RQ 7,18	30.5923
RQ 7,19	32.2863
RQ 7,20	33.9794
RQ 7,21	35.6716
RQ 7,22	37.3628
RQ 7,23	39.0530
RQ 7,24	40.7420
RQ 7,25	42.4300
RQ 7,26	44.1167
RQ 7,27	45.8022
RQ 7,28	47.4864
RQ 7,29	49.1694
RQ 7,30	50.8509
RQ 7,31	52.5310
RQ 7,32	54.2097
RQ 7,33	55.8868
RQ 7,34	57.5624
RQ 7,35	59.2364
RQ 7,36	60.9087
RQ 7,37	62.5793
RQ 7,38	64.2481
RQ 7,39	65.9152
RQ 7,40	67.5804
RQ 8, 9	15.3094
RQ 8,10	17.0089
RQ 8,12	20.4065
RQ 8,11	18.7080
RQ 8,13	22.1045
RQ 8,14	23.8019
RQ 8,15	25.4986
RQ 8,16	27.1946

ASSIGN-MENT	CALCULATED GSCD
RQ 8,17	28.8898
RQ 8,18	30.5843
RQ 8,19	32.2779
RQ 8,20	33.9705
RQ 8,21	35.6623
RQ 8,22	37.3530
RQ 8,23	39.0427
RQ 8,24	40.7313
RQ 8,25	42.4188
RQ 8,26	44.1051
RQ 8,27	45.7902
RQ 8,28	47.4740
RQ 8,29	49.1564
RQ 8,30	50.8375
RQ 8,31	52.5172
RQ 8,32	54.1954
RQ 8,33	55.8721
RQ 8,34	57.5473
RQ 8,35	59.2208
RQ 8,36	60.8926
RQ 8,37	62.5628
RQ 8,38	64.2312
RQ 8,39	65.8978
RQ 8,40	67.5626
RQ 9,10	17.0039
RQ 9,11	18.7024
RQ 9,12	20.4005
RQ 9,13	22.0980
RQ 9,14	23.7948
RQ 9,15	25.4910
RQ 9,16	27.1865
RQ 9,17	28.8813
RQ 9,18	30.5752
RQ 9,19	32.2683
RQ 9,20	33.9604
RQ 9,21	35.6517
RQ 9,22	37.3419
RQ 9,23	39.0311
RQ 9,24	40.7192
RQ 9,25	42.4062
RQ 9,26	44.0920
RQ 9,27	45.7766
RQ 9,28	47.4599
RQ 9,29	49.1418
RQ 9,30	50.8224
RQ 9,31	52.5016
RQ 9,32	54.1793
RQ 9,33	55.8555
RQ 9,34	57.5301
RQ 9,35	59.2031

ASSIGN-MENT	CALCULATED GSCD
RQ 9,36	60.8745
RQ 9,37	62.5441
RQ 9,38	64.2121
RQ 9,39	65.8782
RQ 9,40	67.5424
RP 0, 0	1.7036
RP 0, 1	5.1107
RP 0, 2	8.5176
RP 0, 3	11.9243
RP 0, 4	15.3307
RP 0, 5	18.7367
RP 0, 6	22.1421
RP 0, 7	25.5470
RP 0, 8	28.9511
RP 0, 9	32.3544
RP 0,10	35.7568
RP 0,11	39.1582
RP 0,12	42.5586
RP 0,13	45.9577
RP 0,14	49.3556
RP 0,15	52.7521
RP 0,16	56.1471
RP 0,17	59.5406
RP 0,18	62.9324
RP 0,19	66.3225
RP 0,20	69.7107
RP 0,21	73.0970
RP 0,22	76.4812
RP 0,23	79.8633
RP 0,24	83.2432
RP 0,25	86.6208
RP 0,26	89.9960
RP 0,27	93.3686
RP 0,28	96.7387
RP 0,29	100.1061
RP 0,30	103.4706
RP 0,31	106.8323
RP 0,32	110.1910
RP 0,33	113.5466
RP 0,34	116.8991
RP 0,35	120.2483
RP 0,36	123.5941
RP 0,37	126.9365
RP 0,38	130.2753
RP 0,39	133.6105
RP 0,40	136.9420
RP 1, 1	5.1106
RP 1, 2	8.5175
RP 1, 3	11.9241
RP 1, 4	15.3305

ASSIGNMENT	CALCULATED GSCD
RP 1, 5	18.7364
RP 1, 6	22.1417
RP 1, 7	25.5465
RP 1, 8	28.9506
RP 1, 9	32.3538
RP 1,10	35.7562
RP 1,12	42.5578
RP 1,13	45.9569
RP 1,14	49.3547
RP 1,15	52.7512
RP 1,16	56.1461
RP 1,17	59.5396
RP 1,18	62.9313
RP 1,19	66.3213
RP 1,20	69.7095
RP 1,21	73.0957
RP 1,22	76.4799
RP 1,23	79.8619
RP 1,24	83.2418
RP 1,25	86.6193
RP 1,26	89.9944
RP 1,27	93.3670
RP 1,28	96.7370
RP 1,29	100.1043
RP 1,30	103.4688
RP 1,31	106.8304
RP 1,32	110.1891
RP 1,33	113.5446
RP 1,34	116.8970
RP 1,35	120.2462
RP 1,36	123.5920
RP 1,37	126.9343
RP 1,38	130.2731
RP 1,39	133.6082
RP 1,40	136.9396
RP 2, 2	8.5170
RP 2, 3	11.9235
RP 2, 4	15.3297
RP 2, 5	18.7354
RP 2, 6	22.1406
RP 2, 7	25.5452
RP 2, 8	28.9491
RP 2, 9	32.3521
RP 2,10	35.7543
RP 2,11	39.1555
RP 2,12	42.5556
RP 2,13	45.9545
RP 2,14	49.3521
RP 2,15	52.7484
RP 2,16	56.1432

ASSIGN-MENT	CALCULATED GSCD
RP 2,17	59.5364
RP 2,18	62.9280
RP 2,19	66.3178
RP 2,20	69.7058
RP 2,21	73.0919
RP 2,22	76.4759
RP 2,23	79.8578
RP 2,24	83.2374
RP 2,25	86.6148
RP 2,26	89.9897
RP 2,27	93.3621
RP 2,28	96.7319
RP 2,29	100.0991
RP 2,30	103.4634
RP 2,31	106.8248
RP 2,32	110.1833
RP 2,33	113.5387
RP 2,34	116.8909
RP 2,35	120.2399
RP 2,36	123.5855
RP 2,37	126.9276
RP 2,38	130.2662
RP 2,39	133.6011
RP 2,40	136.9324
RP 3, 3	11.9225
RP 3, 4	15.3283
RP 3, 5	18.7338
RP 3, 6	22.1387
RP 3, 7	25.5430
RP 3, 8	28.9465
RP 3, 9	32.3493
RP 3,10	35.7512
RP 3,11	39.1521
RP 3,12	42.5519
RP 3,13	45.9505
RP 3,14	49.3478
RP 3,15	52.7438
RP 3,16	56.1383
RP 3,17	59.5312
RP 3,18	62.9225
RP 3,19	66.3121
RP 3,20	69.6997
RP 3,21	73.0855
RP 3,22	76.4692
RP 3,23	79.8508
RP 3,24	83.2302
RP 3,25	86.6072
RP 3,26	89.9818
RP 3,27	93.3539
RP 3,28	96.7235

ASSIGN-MENT	CALCULATED GSCD
RP 3,29	100.0903
RP 3,30	103.4543
RP 3,31	106.8155
RP 3,32	110.1736
RP 3,33	113.5287
RP 3,34	116.8807
RP 3,35	120.2293
RP 3,36	123.5746
RP 3,37	126.9165
RP 3,38	130.2548
RP 3,39	133.5894
RP 3,40	136.9203
RP 4, 4	15.3265
RP 4, 5	18.7315
RP 4, 6	22.1360
RP 4, 7	25.5398
RP 4, 8	28.9430
RP 4, 9	32.3454
RP 4,10	35.7468
RP 4,11	39.1473
RP 4,12	42.5467
RP 4,13	45.9449
RP 4,14	49.3418
RP 4,15	52.7374
RP 4,16	56.1314
RP 4,17	59.5240
RP 4,18	62.9148
RP 4,19	66.3040
RP 4,20	69.6912
RP 4,21	73.0766
RP 4,22	76.4599
RP 4,23	79.8410
RP 4,24	83.2200
RP 4,25	86.5966
RP 4,26	89.9708
RP 4,27	93.3425
RP 4,28	96.7116
RP 4,29	100.0780
RP 4,30	103.4417
RP 4,31	106.8024
RP 4,32	110.1601
RP 4,33	113.5148
RP 4,34	116.8663
RP 4,35	120.2146
RP 4,36	123.5595
RP 4,37	126.9009
RP 4,38	130.2388
RP 4,39	133.5730
RP 4,40	136.9035
RP 5, 5	18.7285

ASSIGN-MENT	CALCULATED GSCD
RP 5, 6	22.1325
RP 5, 7	25.5358
RP 5, 8	28.9385
RP 5, 9	32.3403
RP 5,10	35.7412
RP 5,11	39.1412
RP 5,12	42.5400
RP 5,13	45.9377
RP 5,14	49.3341
RP 5,15	52.7291
RP 5,16	56.1226
RP 5,17	59.5146
RP 5,18	62.9050
RP 5,19	66.2935
RP 5,20	69.6803
RP 5,21	73.0651
RP 5,22	76.4478
RP 5,23	79.8285
RP 5,24	83.2069
RP 5,25	86.5830
RP 5,26	89.9567
RP 5,27	93.3278
RP 5,28	96.6964
RP 5,29	100.0623
RP 5,30	103.4254
RP 5,31	106.7856
RP 5,32	110.1428
RP 5,33	113.4969
RP 5,34	116.8479
RP 5,35	120.1956
RP 5,36	123.5400
RP 5,37	126.8809
RP 5,38	130.2182
RP 5,39	133.5519
RP 5,40	136.8819
RP 6, 6	22.1282
RP 6, 7	25.5309
RP 6, 8	28.9329
RP 6, 9	32.3341
RP 6,10	35.7344
RP 6,11	39.1337
RP 6,12	42.5318
RP 6,13	45.9289
RP 6,14	49.3246
RP 6,15	52.7190
RP 6,16	56.1119
RP 6,17	59.5032
RP 6,18	62.8929
RP 6,19	66.2808
RP 6,20	69.6669

ASSIGN-MENT	CALCULATED GSCD
RP 6,21	73.0510
RP 6,22	76.4331
RP 6,23	79.8131
RP 6,24	83.1909
RP 6,25	86.5663
RP 6,26	89.9394
RP 6,27	93.3099
RP 6,28	96.6778
RP 6,29	100.0430
RP 6,30	103.4054
RP 6,31	106.7650
RP 6,32	110.1216
RP 6,33	113.4750
RP 6,34	116.8254
RP 6,35	120.1724
RP 6,36	123.5161
RP 6,37	126.8564
RP 6,38	130.1931
RP 6,39	133.5261
RP 6,40	136.8554
RP 7, 7	25.5251
RP 7, 8	28.9264
RP 7, 9	32.3268
RP 7,10	35.7263
RP 7,11	39.1248
RP 7,12	42.5222
RP 7,13	45.9184
RP 7,14	49.3134
RP 7,15	52.7070
RP 7,16	56.0991
RP 7,17	59.4897
RP 7,18	62.8786
RP 7,19	66.2658
RP 7,20	69.6511
RP 7,21	73.0344
RP 7,22	76.4158
RP 7,23	79.7950
RP 7,24	83.1720
RP 7,25	86.5466
RP 7,26	89.9189
RP 7,27	93.2887
RP 7,28	96.6558
RP 7,29	100.0203
RP 7,30	103.3819
RP 7,31	106.7407
RP 7,32	110.0965
RP 7,33	113.4492
RP 7,34	116.7987
RP 7,35	120.1450
RP 7,36	123.4880

ASSIGN-MENT	CALCULATED GSCD
RP 7,37	126.8274
RP 7,38	130.1634
RP 7,39	133.4956
RP 7,40	136.8242
RP 8, 8	28.9188
RP 8, 9	32.3183
RP 8,10	35.7169
RP 8,11	39.1145
RP 8,12	42.5111
RP 8,13	45.9064
RP 8,14	49.3005
RP 8,15	52.6932
RP 8,16	56.0844
RP 8,17	59.4741
RP 8,18	62.8621
RP 8,19	66.2484
RP 8,20	69.6328
RP 8,21	73.0153
RP 8,22	76.3957
RP 8,23	79.7741
RP 8,24	83.1502
RP 8,25	86.5239
RP 8,26	89.8953
RP 8,27	93.2642
RP 8,28	96.6304
RP 8,29	99.9940
RP 8,30	103.3548
RP 8,31	106.7126
RP 8,32	110.0675
RP 8,33	113.4194
RP 8,34	116.7680
RP 8,35	120.1134
RP 8,36	123.4555
RP 8,37	126.7940
RP 8,38	130.1291
RP 8,39	133.4605
RP 8,40	136.7881
RP 9, 9	32.3087
RP 9,10	35.7063
RP 9,11	39.1029
RP 9,12	42.4985
RP 9,13	45.8928
RP 9,14	49.2859
RP 9,15	52.6776
RP 9,16	56.0678
RP 9,17	59.4564
RP 9,18	62.8435
RP 9,19	66.2287
RP 9,20	69.6121
RP 9,21	72.9936

ASSIGN-MENT	CALCULATED GSCD
RP 9,22	76.3730
RP 9,23	79.7504
RP 9,24	83.1254
RP 9,25	86.4982
RP 9,26	89.8686
RP 9,27	93.2364
RP 9,28	96.6017
RP 9,29	99.9642
RP 9,30	103.3240
RP 9,31	106.6809
RP 9,32	110.0347
RP 9,33	113.3856
RP 9,34	116.7332
RP 9,35	120.0776
RP 9,36	123.4186
RP 9,37	126.7562
RP 9,38	130.0902
RP 9,39	133.4206
RP 9,40	136.7473

APPENDIX III

LIST OF CALCULATED GROUND STATE COMBINATION DIFFERENCES FOR CHD_3

The following pages contain calculated ground state combination differences (in cm^{-1}) computed on the Michigan State University Digital Computer, MISTIC. The values of the constants used are (in cm^{-1}):

$$B_o = 3.27944$$

$$D_o^{JK} = -4.8 \times 10^{-5}$$

$$D_o^{J} = 5.22 \times 10^{-5}$$

These constants were obtained from an analysis of $\nu_1+\nu_2$ of CHD_3 discussed in Chapter 9.

In order to use the tables one should note that the designation of the combination differences in this appendix is that used in Chapter 4. Note also that

$$QRK,J = RQK,J+1.$$

ASSIGN-MENT	CALCULATED GSCD
RQ 0, 1	6.5587
RQ 0, 2	13.1161
RQ 0, 3	19.6710
RQ 0, 4	26.2222
RQ 0, 5	32.7683
RQ 0, 6	39.3082
RQ 0, 7	45.8406
RQ 0, 8	52.3642
RQ 0, 9	58.8777
RQ 0,10	65.3801
RQ 0,11	71.8699
RQ 0,12	78.3459
RQ 0,13	84.8069
RQ 0,14	91.2516
RQ 0,15	97.6788
RQ 0,16	104.0871
RQ 0,17	110.4755
RQ 0,18	116.8426
RQ 0,19	123.1871
RQ 0,20	129.5078
RQ 0,21	135.8035
RQ 0,22	142.0729
RQ 0,23	148.3147
RQ 0,24	154.5278
RQ 0,25	160.7107
RQ 0,26	166.8624
RQ 0,27	172.9815
RQ 0,28	179.0668
RQ 0,29	185.1171
RQ 0,30	191.1310
RQ 0,31	197.1073
RQ 0,32	203.0449
RQ 0,33	208.9423
RQ 0,34	214.7984
RQ 0,35	220.6120
RQ 0,36	226.3817
RQ 0,37	232.1063
RQ 0,38	237.7846
RQ 0,39	243.4154
RQ 0,40	248.9972
RQ 1, 2	13.1163
RQ 1, 3	19.6713
RQ 1, 4	26.2225
RQ 1, 5	32.7688
RQ 1, 6	39.3088
RQ 1, 7	45.8412
RQ 1, 8	52.3649
RQ 1, 9	58.8786
RQ 1,10	65.3810
RQ 1,11	71.8709

ASSIGN-MENT	CALCULATED GSCD
RQ 1,12	78.3470
RQ 1,13	84.8081
RQ 1,14	91.2529
RQ 1,15	97.6802
RQ 1,16	104.0887
RQ 1,17	110.4771
RQ 1,18	116.8443
RQ 1,19	123.1889
RQ 1,20	129.5098
RQ 1,21	135.8055
RQ 1,22	142.0750
RQ 1,23	148.3170
RQ 1,24	154.5301
RQ 1,25	160.7132
RQ 1,26	166.8649
RQ 1,27	172.9841
RQ 1,28	179.0695
RQ 1,29	185.1199
RQ 1,30	191.1339
RQ 1,31	197.1103
RQ 1,32	203.0480
RQ 1,33	208.9455
RQ 1,34	214.8017
RQ 1,35	220.6154
RQ 1,36	226.3852
RQ 1,37	232.1099
RQ 1,38	237.7883
RQ 1,39	243.4191
RQ 1,40	249.0011
RQ 2, 3	19.6722
RQ 2, 4	26.2237
RQ 2, 5	32.7702
RQ 2, 6	39.3105
RQ 2, 7	45.8433
RQ 2, 8	52.3673
RQ 2, 9	58.8812
RQ 2,10	65.3839
RQ 2,11	71.8741
RQ 2,12	78.3505
RQ 2,13	84.8119
RQ 2,14	91.2570
RQ 2,15	97.6846
RQ 2,16	104.0933
RQ 2,17	110.4821
RQ 2,18	116.8495
RQ 2,19	123.1945
RQ 2,20	129.5156
RQ 2,21	135.8116
RQ 2,22	142.0814
RQ 2,23	148.3236

ASSIGN-MENT	CALCULATED GSCD
RQ 2,24	154.5371
RQ 2,25	160.7204
RQ 2,26	166.8725
RQ 2,27	172.9920
RQ 2,28	179.0777
RQ 2,29	185.1283
RQ 2,30	191.1426
RQ 2,31	197.1193
RQ 2,32	203.0573
RQ 2,33	208.9551
RQ 2,34	214.8116
RQ 2,35	220.6255
RQ 2,36	226.3957
RQ 2,37	232.1207
RQ 2,38	237.7994
RQ 2,39	243.4305
RQ 2,40	249.0127
RQ 3, 4	26.2256
RQ 3, 5	32.7727
RQ 3, 6	39.3134
RQ 3, 7	45.8467
RQ 3, 8	52.3711
RQ 3, 9	58.8856
RQ 3,10	65.3888
RQ 3,11	71.8794
RQ 3,12	78.3563
RQ 3,13	84.8182
RQ 3,14	91.2638
RQ 3,15	97.6918
RQ 3,16	104.1011
RQ 3,17	110.4903
RQ 3,18	116.8583
RQ 3,19	123.2037
RQ 3,20	129.5253
RQ 3,21	135.8218
RQ 3,22	142.0921
RQ 3,23	148.3348
RQ 3,24	154.5487
RQ 3,25	160.7325
RQ 3,26	166.8851
RQ 3,27	173.0051
RQ 3,28	179.0912
RQ 3,29	185.1423
RQ 3,30	191.1571
RQ 3,31	197.1344
RQ 3,32	203.0728
RQ 3,33	208.9711
RQ 3,34	214.8281
RQ 3,35	220.6425
RQ 3,36	226.4131

ASSIGN-MENT	CALCULATED GSCD
RQ 3,37	232.1386
RQ 3,38	237.8173
RQ 3,39	243.4494
RQ 3,40	249.0321
RQ 4, 5	32.7761
RQ 4, 6	39.3175
RQ 4, 7	45.8514
RQ 4, 8	52.3766
RQ 4, 9	58.8917
RQ 4,10	65.3956
RQ 4,11	71.8869
RQ 4,12	78.3645
RQ 4,13	84.8270
RQ 4,14	91.2733
RQ 4,15	97.7020
RQ 4,16	104.1119
RQ 4,17	110.5019
RQ 4,18	116.8705
RQ 4,19	123.2165
RQ 4,20	129.5388
RQ 4,21	135.8361
RQ 4,22	142.1070
RQ 4,23	148.3504
RQ 4,24	154.5650
RQ 4,25	160.7495
RQ 4,26	166.9027
RQ 4,27	173.0234
RQ 4,28	179.1102
RQ 4,29	185.1620
RQ 4,30	191.1775
RQ 4,31	197.1554
RQ 4,32	203.0945
RQ 4,33	208.9935
RQ 4,34	214.8511
RQ 4,35	220.6662
RQ 4,36	226.4375
RQ 4,37	232.1637
RQ 4,38	237.8435
RQ 4,39	243.4758
RQ 4,40	249.0592
RQ 5, 6	39.3227
RQ 5, 7	45.8575
RQ 5, 8	52.3835
RQ 5, 9	58.8995
RQ 5,10	65.4043
RQ 5,11	71.8965
RQ 5,12	78.3749
RQ 5,13	84.8384
RQ 5,14	91.2855
RQ 5,15	97.7151

ASSIGN-MENT	CALCULATED GSCD
RQ 5,16	104.1259
RQ 5,17	110.5167
RQ 5,18	116.8862
RQ 5,19	123.2331
RQ 5,20	129.5563
RQ 5,21	135.8544
RQ 5,22	142.1262
RQ 5,23	148.3704
RQ 5,24	154.5859
RQ 5,25	160.7713
RQ 5,26	166.9254
RQ 5,27	173.0469
RQ 5,28	179.1346
RQ 5,29	185.1873
RQ 5,30	191.2036
RQ 5,31	197.1824
RQ 5,32	203.1224
RQ 5,33	209.0222
RQ 5,34	214.8808
RQ 5,35	220.6968
RQ 5,36	226.4689
RQ 5,37	232.1960
RQ 5,38	237.8767
RQ 5,39	243.5098
RQ 5,40	249.0941
RQ 6, 7	45.8650
RQ 6, 8	52.3921
RQ 6, 9	58.9091
RQ 6,10	65.4149
RQ 6,11	71.9082
RQ 6,12	78.3877
RQ 6,13	84.8522
RQ 6,14	91.3004
RQ 6,15	97.7311
RQ 6,16	104.1429
RQ 6,17	110.5348
RQ 6,18	116.9053
RQ 6,19	123.2534
RQ 6,20	129.5776
RQ 6,21	135.8768
RQ 6,22	142.1496
RQ 6,23	148.3950
RQ 6,24	154.6115
RQ 6,25	160.7979
RQ 6,26	166.9531
RQ 6,27	173.0757
RQ 6,28	179.1645
RQ 6,29	185.2182
RQ 6,30	191.2356
RQ 6,31	197.2155

ASSIGN-MENT	CALCULATED GSCD
RQ 6,32	203.1565
RQ 6,33	209.0574
RQ 6,34	214.9170
RQ 6,35	220.7341
RQ 6,36	226.5073
RQ 6,37	232.2354
RQ 6,38	237.9172
RQ 6,39	243.5514
RQ 6,40	249.1367
RQ 7, 8	52.4021
RQ 7, 9	58.9205
RQ 7,10	65.4275
RQ 7,11	71.9221
RQ 7,12	78.4028
RQ 7,13	84.8686
RQ 7,14	91.3180
RQ 7,15	97.7500
RQ 7,16	104.1631
RQ 7,17	110.5562
RQ 7,18	116.9280
RQ 7,19	123.2773
RQ 7,20	129.6028
RQ 7,21	135.9032
RQ 7,22	142.1773
RQ 7,23	148.4239
RQ 7,24	154.6417
RQ 7,25	160.8294
RQ 7,26	166.9858
RQ 7,27	173.1097
RQ 7,28	179.1998
RQ 7,29	185.2547
RQ 7,30	191.2734
RQ 7,31	197.2545
RQ 7,32	203.1968
RQ 7,33	209.0990
RQ 7,34	214.9598
RQ 7,35	220.7781
RQ 7,36	226.5526
RQ 7,37	232.2820
RQ 7,38	237.9650
RQ 7,39	243.6005
RQ 7,40	249.1871
RQ 8, 9	58.9336
RQ 8,10	65.4421
RQ 8,12	78.4203
RQ 8,11	71.9381
RQ 8,13	84.8875
RQ 8,14	91.3384
RQ 8,15	97.7718
RQ 8,16	104.1864

ASSIGN-MENT	CALCULATED GSCD
RQ 8,17	110.5809
RQ 8,18	116.9542
RQ 8,19	123.3049
RQ 8,20	129.6318
RQ 8,21	135.9337
RQ 8,22	142.2093
RQ 8,23	148.4573
RQ 8,24	154.6766
RQ 8,25	160.8658
RQ 8,26	167.0236
RQ 8,27	173.1489
RQ 8,28	179.2404
RQ 8,29	185.2969
RQ 8,30	191.3170
RQ 8,31	197.2995
RQ 8,32	203.2433
RQ 8,33	209.1469
RQ 8,34	215.0093
RQ 8,35	220.8290
RQ 8,36	226.6049
RQ 8,37	232.3358
RQ 8,38	238.0203
RQ 8,39	243.6572
RQ 8,40	249.2453
RQ 9,10	65.4585
RQ 9,11	71.9562
RQ 9,12	78.4400
RQ 9,13	84.9089
RQ 9,14	91.3614
RQ 9,15	97.7965
RQ 9,16	104.2127
RQ 9,17	110.6089
RQ 9,18	116.9838
RQ 9,19	123.3362
RQ 9,20	129.6648
RQ 9,21	135.9683
RQ 9,22	142.2455
RQ 9,23	148.4952
RQ 9,24	154.7161
RQ 9,25	160.9069
RQ 9,26	167.0665
RQ 9,27	173.1934
RQ 9,28	179.2866
RQ 9,29	185.3446
RQ 9,30	191.3664
RQ 9,31	197.3506
RQ 9,32	203.2960
RQ 9,33	209.2013
RQ 9,34	215.0653
RQ 9,35	220.8867

ASSIGN-MENT	CALCULATED GSCD
RQ 9,36	226.6642
RQ 9,37	232.3967
RQ 9,38	238.0829
RQ 9,39	243.7214
RQ 9,40	249.3111
RP 0, 0	6.5587
RP 0, 1	19.6748
RP 0, 2	32.7871
RP 0, 3	45.8932
RP 0, 4	58.9905
RP 0, 5	72.0765
RP 0, 6	85.1487
RP 0, 7	98.2047
RP 0, 8	111.2419
RP 0, 9	124.2578
RP 0,10	137.2499
RP 0,11	150.2157
RP 0,12	163.1527
RP 0,13	176.0584
RP 0,14	188.9303
RP 0,15	201.7659
RP 0,16	214.5626
RP 0,17	227.3181
RP 0,18	240.0297
RP 0,19	252.6949
RP 0,20	265.3113
RP 0,21	277.8764
RP 0,22	290.3876
RP 0,23	302.8425
RP 0,24	315.2385
RP 0,25	327.5732
RP 0,26	339.8439
RP 0,27	352.0484
RP 0,28	364.1839
RP 0,29	376.2480
RP 0,30	388.2383
RP 0,31	400.1522
RP 0,32	411.9872
RP 0,33	423.7407
RP 0,34	435.4104
RP 0,35	446.9937
RP 0,36	458.4880
RP 0,37	469.8910
RP 0,38	481.2000
RP 0,39	492.4126
RP 0,40	503.5262
RP 1, 1	19.6750
RP 1, 2	32.7876
RP 1, 3	45.8938
RP 1, 4	58.9913

ASSIGNMENT	CALCULATED GSCD
RP 1, 5	72.0776
RP 1, 6	85.1500
RP 1, 7	98.2062
RP 1, 8	111.2436
RP 1, 9	124.2597
RP 1,10	137.2520
RP 1,12	163.1552
RP 1,13	176.0611
RP 1,14	188.9331
RP 1,15	201.7689
RP 1,16	214.5658
RP 1,17	227.3215
RP 1,18	240.0332
RP 1,19	252.6987
RP 1,20	265.3153
RP 1,21	277.8806
RP 1,22	290.3920
RP 1,23	302.8471
RP 1,24	315.2433
RP 1,25	327.5781
RP 1,26	339.8491
RP 1,27	352.0537
RP 1,28	364.1894
RP 1,29	376.2538
RP 1,30	388.2442
RP 1,31	400.1583
RP 1,32	411.9935
RP 1,33	423.7472
RP 1,34	435.4171
RP 1,35	447.0006
RP 1,36	458.4951
RP 1,37	469.8982
RP 1,38	481.2075
RP 1,39	492.4202
RP 1,40	503.5341
RP 2, 2	32.7890
RP 2, 3	45.8959
RP 2, 4	58.9939
RP 2, 5	72.0807
RP 2, 6	85.1538
RP 2, 7	98.2105
RP 2, 8	111.2485
RP 2, 9	124.2652
RP 2,10	137.2581
RP 2,11	150.2246
RP 2,12	163.1624
RP 2,13	176.0689
RP 2,14	188.9416
RP 2,15	201.7779
RP 2,16	214.5754

ASSIGN-MENT	CALCULATED GSCD
RP 2,17	227.3316
RP 2,18	240.0440
RP 2,19	252.7100
RP 2,20	265.3272
RP 2,21	277.8931
RP 2,22	290.4051
RP 2,23	302.8607
RP 2,24	315.2575
RP 2,25	327.5929
RP 2,26	339.8645
RP 2,27	352.0697
RP 2,28	364.2060
RP 2,29	376.2709
RP 2,30	388.2619
RP 2,31	400.1766
RP 2,32	412.0124
RP 2,33	423.7667
RP 2,34	435.4372
RP 2,35	447.0212
RP 2,36	458.5163
RP 2,37	469.9200
RP 2,38	481.2298
RP 2,39	492.4432
RP 2,40	503.5576
RP 3, 3	45.8993
RP 3, 4	58.9983
RP 3, 5	72.0861
RP 3, 6	85.1601
RP 3, 7	98.2178
RP 3, 8	111.2567
RP 3, 9	124.2744
RP 3,10	137.2682
RP 3,11	150.2358
RP 3,12	163.1745
RP 3,13	176.0820
RP 3,14	188.9556
RP 3,15	201.7929
RP 3,16	214.5914
RP 3,17	227.3486
RP 3,18	240.0619
RP 3,19	252.7289
RP 3,20	265.3471
RP 3,21	277.9139
RP 3,22	290.4269
RP 3,23	302.8835
RP 3,24	315.2812
RP 3,25	327.6176
RP 3,26	339.8902
RP 3,27	352.0963

ASSIGN-MENT	CALCULATED GSCD
RP 3,28	364.2336
RP 3,29	376.2995
RP 3,30	388.2915
RP 3,31	400.2071
RP 3,32	412.0438
RP 3,33	423.7992
RP 3,34	435.4706
RP 3,35	447.0556
RP 3,36	458.5517
RP 3,37	469.9564
RP 3,38	481.2671
RP 3,39	492.4815
RP 3,40	503.5969
RP 4, 4	59.0044
RP 4, 5	72.0935
RP 4, 6	85.1689
RP 4, 7	98.2280
RP 4, 8	111.2683
RP 4, 9	124.2873
RP 4,10	137.2825
RP 4,11	150.2514
RP 4,12	163.1915
RP 4,13	176.1003
RP 4,14	188.9753
RP 4,15	201.8139
RP 4,16	214.6138
RP 4,17	227.3723
RP 4,18	240.0870
RP 4,19	252.7554
RP 4,20	265.3749
RP 4,21	277.9431
RP 4,22	290.4574
RP 4,23	302.9154
RP 4,24	315.3145
RP 4,25	327.6522
RP 4,26	339.9261
RP 4,27	352.1336
RP 4,28	364.2722
RP 4,29	376.3395
RP 4,30	388.3329
RP 4,31	400.2498
RP 4,32	412.0879
RP 4,33	423.8446
RP 4,34	435.5174
RP 4,35	447.1037
RP 4,36	458.6012
RP 4,37	470.0072
RP 4,38	481.3194
RP 4,39	492.5350
RP 4,40	503.6518

ASSIGN-MENT	CALCULATED GSCD
RP 5, 5	72.1031
RP 5, 6	85.1802
RP 5, 7	98.2410
RP 5, 8	111.2831
RP 5, 9	124.3038
RP 5,10	137.3008
RP 5,11	150.2714
RP 5,12	163.2133
RP 5,13	176.1238
RP 5,14	189.0006
RP 5,15	201.8410
RP 5,16	214.6426
RP 5,17	227.4028
RP 5,18	240.1193
RP 5,19	252.7894
RP 5,20	265.4106
RP 5,21	277.9806
RP 5,22	290.4966
RP 5,23	302.9563
RP 5,24	315.3572
RP 5,25	327.6967
RP 5,26	339.9723
RP 5,27	352.1816
RP 5,28	364.3219
RP 5,29	376.3909
RP 5,30	388.3861
RP 5,31	400.3048
RP 5,32	412.1446
RP 5,33	423.9030
RP 5,34	435.5775
RP 5,35	447.1657
RP 5,36	458.6649
RP 5,37	470.0726
RP 5,38	481.3865
RP 5,39	492.6039
RP 5,40	503.7224
RP 6, 6	85.1941
RP 6, 7	98.2570
RP 6, 8	111.3012
RP 6, 9	124.3241
RP 6,10	137.3232
RP 6,11	150.2960
RP 6,12	163.2399
RP 6,13	176.1526
RP 6,14	189.0315
RP 6,15	201.8740
RP 6,16	214.6777
RP 6,17	227.4401
RP 6,18	240.1587
RP 6,19	252.8309

ASSIGN-MENT	CALCULATED GSCD
RP 6,20	265.4543
RP 6,21	278.0264
RP 6,22	290.5446
RP 6,23	303.0064
RP 6,24	315.4094
RP 6,25	327.7510
RP 6,26	340.0288
RP 6,27	352.2402
RP 6,28	364.3827
RP 6,29	376.4538
RP 6,30	388.4511
RP 6,31	400.3719
RP 6,32	412.2139
RP 6,33	423.9744
RP 6,34	435.6511
RP 6,35	447.2413
RP 6,36	458.7427
RP 6,37	470.1526
RP 6,38	481.4686
RP 6,39	492.6881
RP 6,40	503.8087
RP 7, 7	98.2759
RP 7, 8	111.3226
RP 7, 9	124.3480
RP 7,10	137.3496
RP 7,11	150.3249
RP 7,12	163.2714
RP 7,13	176.1866
RP 7,14	189.0680
RP 7,15	201.9131
RP 7,16	214.7193
RP 7,17	227.4842
RP 7,18	240.2053
RP 7,19	252.8801
RP 7,20	265.5060
RP 7,21	278.0805
RP 7,22	290.6013
RP 7,23	303.0656
RP 7,24	315.4711
RP 7,25	327.8153
RP 7,26	340.0956
RP 7,27	352.3095
RP 7,28	364.4545
RP 7,29	376.5281
RP 7,30	388.5279
RP 7,31	400.4513
RP 7,32	412.2957
RP 7,33	424.0588
RP 7,34	435.7380
RP 7,35	447.3308

ASSIGN-MENT	CALCULATED GSCD
RP 7,36	458.8346
RP 7,37	470.2470
RP 7,38	481.5655
RP 7,39	492.7876
RP 7,40	503.9108
RP 8, 8	111.3473
RP 8, 9	124.3756
RP 8,10	137.3801
RP 8,11	150.3583
RP 8,12	163.3078
RP 8,13	176.2259
RP 8,14	189.1101
RP 8,15	201.9581
RP 8,16	214.7673
RP 8,17	227.5351
RP 8,18	240.2591
RP 8,19	252.9367
RP 8,20	265.5656
RP 8,21	278.1430
RP 8,22	290.6667
RP 8,23	303.1339
RP 8,24	315.5423
RP 8,25	327.8894
RP 8,26	340.1726
RP 8,27	352.3894
RP 8,28	364.5373
RP 8,29	376.6139
RP 8,30	388.6165
RP 8,31	400.5428
RP 8,32	412.3902
RP 8,33	424.1562
RP 8,34	435.8383
RP 8,35	447.4339
RP 8,36	458.9407
RP 8,37	470.3560
RP 8,38	481.6774
RP 8,39	492.9024
RP 8,40	504.0285
RP 9, 9	124.4069
RP 9,10	137.4147
RP 9,11	150.3962
RP 9,12	163.3489
RP 9,13	176.2703
RP 9,14	189.1579
RP 9,15	202.0092
RP 9,16	214.8216
RP 9,17	227.5927
RP 9,18	240.3200
RP 9,19	253.0010
RP 9,20	265.6331

ASSIGN-MENT	CALCULATED GSCD
RP 9,21	278.2139
RP 9,22	290.7408
RP 9,23	303.2113
RP 9,24	315.6231
RP 9,25	327.9734
RP 9,26	340.2599
RP 9,27	352.4800
RP 9,28	364.6312
RP 9,29	376.7111
RP 9,30	388.7170
RP 9,31	400.6466
RP 9,32	412.4973
RP 9,33	424.2665
RP 9,34	435.9519
RP 9,35	447.5509
RP 9,36	459.0609
RP 9,37	470.4796
RP 9,38	481.8043
RP 9,39	493.0325
RP 9,40	504.1619

APPENDIX IV

LIST OF CALCULATED GROUND STATE COMBINATION DIFFERENCES FOR CH_3D

The following pages contain calculated ground state combination differences (in cm^{-1}) computed on the Michigan State University Digital Computer, MISTIC. The values of the constants used are

$$B_0 = 3.88107$$

$$D_0^{JK} = 1.192 \times 10^{-4}$$

$$D_0^{J} = 5.28 \times 10^{-5}$$

These constants were obtained from an analysis of $\nu_2+\nu_3$ of CH_3D discussed in Chapter 9.

In order to use the tables one should note that the designation of the combination differences in this appendix is that used in Chapter 4. Note also that

$$QPK,J = RQK,J+1.$$

ASSIGN-MENT	CALCULATED GSCD
RQ 0, 1	7.7619
RQ 0, 2	15.5226
RQ 0, 3	23.2807
RQ 0, 4	31.0350
RQ 0, 5	38.7843
RQ 0, 6	46.5272
RQ 0, 7	54.2624
RQ 0, 8	61.9888
RQ 0, 9	69.7051
RQ 0,10	77.4099
RQ 0,11	85.1020
RQ 0,12	92.7802
RQ 0,13	100.4432
RQ 0,14	108.0896
RQ 0,15	115.7183
RQ 0,16	123.3279
RQ 0,17	130.9173
RQ 0,18	138.4850
RQ 0,19	146.0300
RQ 0,20	153.5508
RQ 0,21	161.0462
RQ 0,22	168.5150
RQ 0,23	175.9559
RQ 0,24	183.3676
RQ 0,25	190.7488
RQ 0,26	198.0983
RQ 0,27	205.4148
RQ 0,28	212.6970
RQ 0,29	219.9437
RQ 0,30	227.1536
RQ 0,31	234.3255
RQ 0,32	241.4580
RQ 0,33	248.5499
RQ 0,34	255.5999
RQ 0,35	262.6067
RQ 0,36	269.5692
RQ 0,37	276.4859
RQ 0,38	283.3558
RQ 0,39	290.1773
RQ 0,40	296.9494
RQ 1, 2	15.5221
RQ 1, 3	23.2800
RQ 1, 4	31.0341
RQ 1, 5	38.7831
RQ 1, 6	46.5257
RQ 1, 7	54.2608
RQ 1, 8	61.9869
RQ 1, 9	69.7029
RQ 1,10	77.4075
RQ 1,11	85.0994

ASSIGN-MENT	CALCULATED GSCD
RQ 1,12	92.7773
RQ 1,13	100.4401
RQ 1,14	108.0863
RQ 1,15	115.7147
RQ 1,16	123.3241
RQ 1,17	130.9132
RQ 1,18	138.4808
RQ 1,19	146.0254
RQ 1,20	153.5460
RQ 1,21	161.0412
RQ 1,22	168.5098
RQ 1,23	175.9504
RQ 1,24	183.3618
RQ 1,25	190.7428
RQ 1,26	198.0921
RQ 1,27	205.4083
RQ 1,28	212.6903
RQ 1,29	219.9368
RQ 1,30	227.1465
RQ 1,31	234.3181
RQ 1,32	241.4503
RQ 1,33	248.5420
RQ 1,34	255.5918
RQ 1,35	262.5984
RQ 1,36	269.5606
RQ 1,37	276.4771
RQ 1,38	283.3467
RQ 1,39	290.1680
RQ 1,40	296.9399
RQ 2, 3	23.2779
RQ 2, 4	31.0312
RQ 2, 5	38.7795
RQ 2, 6	46.5214
RQ 2, 7	54.2558
RQ 2, 8	61.9812
RQ 2, 9	69.6965
RQ 2,10	77.4004
RQ 2,11	85.0915
RQ 2,12	92.7688
RQ 2,13	100.4308
RQ 2,14	108.0763
RQ 2,15	115.7040
RQ 2,16	123.3127
RQ 2,17	130.9011
RQ 2,18	138.4679
RQ 2,19	146.0119
RQ 2,20	153.5317
RQ 2,21	161.0262
RQ 2,22	168.4940
RQ 2,23	175.9339

ASSIGN-MENT	CALCULATED GSCD
RQ 2,24	183.3447
RQ 2,25	190.7249
RQ 2,26	198.0735
RQ 2,27	205.3890
RQ 2,28	212.6703
RQ 2,29	219.9161
RQ 2,30	227.1250
RQ 2,31	234.2959
RQ 2,32	241.4275
RQ 2,33	248.5184
RQ 2,34	255.5675
RQ 2,35	262.5734
RQ 2,36	269.5349
RQ 2,37	276.4507
RQ 2,38	283.3195
RQ 2,39	290.1402
RQ 2,40	296.9113
RQ 3, 4	31.0264
RQ 3, 5	38.7735
RQ 3, 6	46.5143
RQ 3, 7	54.2474
RQ 3, 8	61.9717
RQ 3, 9	69.6858
RQ 3,10	77.3885
RQ 3,11	85.0784
RQ 3,12	92.7545
RQ 3,13	100.4153
RQ 3,14	108.0596
RQ 3,15	115.6861
RQ 3,16	123.2936
RQ 3,17	130.8808
RQ 3,18	138.4464
RQ 3,19	145.9892
RQ 3,20	153.5079
RQ 3,21	161.0012
RQ 3,22	168.4678
RQ 3,23	175.9065
RQ 3,24	183.3161
RQ 3,25	190.6952
RQ 3,26	198.0425
RQ 3,27	205.3569
RQ 3,28	212.6370
RQ 3,29	219.8815
RQ 3,30	227.0893
RQ 3,31	234.2590
RQ 3,32	241.3893
RQ 3,33	248.4791
RQ 3,34	255.5269
RQ 3,35	262.5317
RQ 3,36	269.4920

ASSIGN-MENT	CALCULATED GSCD
RQ 3,37	276.4066
RQ 3,38	283.2742
RQ 3,39	290.0937
RQ 3,40	296.8636
RQ 4, 5	38.7652
RQ 4, 6	46.5043
RQ 4, 7	54.2357
RQ 4, 8	61.9583
RQ 4, 9	69.6708
RQ 4,10	77.3718
RQ 4,11	85.0601
RQ 4,12	92.7344
RQ 4,13	100.3936
RQ 4,14	108.0362
RQ 4,15	115.6611
RQ 4,16	123.2669
RQ 4,17	130.8524
RQ 4,18	138.4164
RQ 4,19	145.9575
RQ 4,20	153.4745
RQ 4,21	160.9661
RQ 4,22	168.4311
RQ 4,23	175.8682
RQ 4,24	183.2760
RQ 4,25	190.6534
RQ 4,26	197.9991
RQ 4,27	205.3118
RQ 4,28	212.5903
RQ 4,29	219.8331
RQ 4,30	227.0392
RQ 4,31	234.2073
RQ 4,32	241.3359
RQ 4,33	248.4240
RQ 4,34	255.4702
RQ 4,35	262.4733
RQ 4,36	269.4319
RQ 4,37	276.3449
RQ 4,38	283.2109
RQ 4,39	290.0286
RQ 4,40	296.7969
RQ 5, 6	46.4914
RQ 5, 7	54.2207
RQ 5, 8	61.9412
RQ 5, 9	69.6515
RQ 5,10	77.3503
RQ 5,11	85.0365
RQ 5,12	92.7087
RQ 5,13	100.3657
RQ 5,14	108.0062
RQ 5,15	115.6289

ASSIGN-MENT	CALCULATED GSCD
RQ 5,16	123.2326
RQ 5,17	130.8160
RQ 5,18	138.3778
RQ 5,19	145.9168
RQ 5,20	153.4316
RQ 5,21	160.9211
RQ 5,22	168.3839
RQ 5,23	175.8188
RQ 5,24	183.2246
RQ 5,25	190.5998
RQ 5,26	197.9434
RQ 5,27	205.2539
RQ 5,28	212.5302
RQ 5,29	219.7709
RQ 5,30	226.9749
RQ 5,31	234.1408
RQ 5,32	241.2673
RQ 5,33	248.3532
RQ 5,34	255.3973
RQ 5,35	262.3982
RQ 5,36	269.3547
RQ 5,37	276.2655
RQ 5,38	283.1294
RQ 5,39	289.9450
RQ 5,40	296.7111
RQ 6, 7	54.2024
RQ 6, 8	61.9202
RQ 6, 9	69.6279
RQ 6,10	77.3241
RQ 6,11	85.0077
RQ 6,12	92.6773
RQ 6,13	100.3316
RQ 6,14	107.9695
RQ 6,15	115.5896
RQ 6,16	123.1907
RQ 6,17	130.7714
RQ 6,18	138.3306
RQ 6,19	145.8670
RQ 6,20	153.3792
RQ 6,21	160.8660
RQ 6,22	168.3263
RQ 6,23	175.7585
RQ 6,24	183.1616
RQ 6,25	190.5343
RQ 6,26	197.8752
RQ 6,27	205.1831
RQ 6,28	212.4568
RQ 6,29	219.6949
RQ 6,30	226.8963
RQ 6,31	234.0595

ASSIGN-MENT	CALCULATED GSCD
RQ 6,32	241.1834
RQ 6,33	248.2667
RQ 6,34	255.3082
RQ 6,35	262.3064
RQ 6,36	269.2603
RQ 6,37	276.1685
RQ 6,38	283.0297
RQ 6,39	289.8427
RQ 6,40	296.6063
RQ 7, 8	61.8954
RQ 7, 9	69.6000
RQ 7,10	77.2931
RQ 7,11	84.9736
RQ 7,12	92.6401
RQ 7,13	100.2913
RQ 7,14	107.9261
RQ 7,15	115.5431
RQ 7,16	123.1411
RQ 7,17	130.7188
RQ 7,18	138.2748
RQ 7,19	145.8081
RQ 7,20	153.3172
RQ 7,21	160.8010
RQ 7,22	168.2581
RQ 7,23	175.6873
RQ 7,24	183.0873
RQ 7,25	190.4568
RQ 7,26	197.7947
RQ 7,27	205.0995
RQ 7,28	212.3700
RQ 7,29	219.6051
RQ 7,30	226.8033
RQ 7,31	233.9635
RQ 7,32	241.0843
RQ 7,33	248.1645
RQ 7,34	255.2028
RQ 7,35	262.1980
RQ 7,36	269.1488
RQ 7,37	276.0539
RQ 7,38	282.9120
RQ 7,39	289.7219
RQ 7,40	296.4823
RQ 8, 9	69.5678
RQ 8,10	77.2574
RQ 8,12	92.5972
RQ 8,11	84.9343
RQ 8,13	100.2449
RQ 8,14	107.8761
RQ 8,15	115.4895
RQ 8,16	123.0839

ASSIGN-MENT	CALCULATED GSCD
RQ 8,17	130.6580
RQ 8,18	138.2105
RQ 8,19	145.7402
RQ 8,20	153.2457
RQ 8,21	160.7259
RQ 8,22	168.1795
RQ 8,23	175.6051
RQ 8,24	183.0015
RQ 8,25	190.3675
RQ 8,26	197.7017
RQ 8,27	205.0030
RQ 8,28	212.2700
RQ 8,29	219.5014
RQ 8,30	226.6961
RQ 8,31	233.8526
RQ 8,32	240.9699
RQ 8,33	248.0465
RQ 8,34	255.0813
RQ 8,35	262.0729
RQ 8,36	269.0201
RQ 8,37	275.9216
RQ 8,38	282.7762
RQ 8,39	289.5825
RQ 8,40	296.3393
RQ 9,10	77.2169
RQ 9,11	84.8897
RQ 9,12	92.5486
RQ 9,13	100.1922
RQ 9,14	107.8193
RQ 9,15	115.4287
RQ 9,16	123.0191
RQ 9,17	130.5891
RQ 9,18	138.1376
RQ 9,19	145.6632
RQ 9,20	153.1647
RQ 9,21	160.6408
RQ 9,22	168.0903
RQ 9,23	175.5119
RQ 9,24	182.9043
RQ 9,25	190.2662
RQ 9,26	197.5964
RQ 9,27	204.8936
RQ 9,28	212.1565
RQ 9,29	219.3839
RQ 9,30	226.5745
RQ 9,31	233.7271
RQ 9,32	240.8402
RQ 9,33	247.9128
RQ 9,34	254.9435
RQ 9,35	261.9311

ASSIGNMENT	CALCULATED GSCD
RQ 9,36	268.8742
RQ 9,37	275.7717
RQ 9,38	282.6222
RQ 9,39	289.4245
RQ 9,40	296.1773
RP 0, 0	7.7619
RP 0, 1	23.2845
RP 0, 2	38.8033
RP 0, 3	54.3157
RP 0, 4	69.8193
RP 0, 5	85.3114
RP 0, 6	100.7896
RP 0, 7	116.2513
RP 0, 8	131.6939
RP 0, 9	147.1150
RP 0,10	162.5119
RP 0,11	177.8822
RP 0,12	193.2234
RP 0,13	208.5328
RP 0,14	223.8079
RP 0,15	239.0462
RP 0,16	254.2452
RP 0,17	269.4023
RP 0,18	284.5150
RP 0,19	299.5808
RP 0,20	314.5970
RP 0,21	329.5612
RP 0,22	344.4709
RP 0,23	359.3234
RP 0,24	374.1163
RP 0,25	388.8471
RP 0,26	403.5131
RP 0,27	418.1118
RP 0,28	432.6407
RP 0,29	447.0974
RP 0,30	461.4791
RP 0,31	475.7834
RP 0,32	490.0078
RP 0,33	504.1497
RP 0,34	518.2066
RP 0,35	532.1759
RP 0,36	546.0551
RP 0,37	559.8417
RP 0,38	573.5331
RP 0,39	587.1268
RP 0,40	600.6202
RP 1, 1	23.2838
RP 1, 2	38.8021
RP 1, 3	54.3141
RP 1, 4	69.8171

ASSIGN-MENT	CALCULATED GSCD
RP 1, 5	85.3088
RP 1, 6	100.7865
RP 1, 7	116.2477
RP 1, 8	131.6899
RP 1, 9	147.1104
RP 1,10	162.5069
RP 1,12	193.2174
RP 1,13	208.5263
RP 1,14	223.8010
RP 1,15	239.0388
RP 1,16	254.2373
RP 1,17	269.3940
RP 1,18	284.5062
RP 1,19	299.5715
RP 1,20	314.5872
RP 1,21	329.5510
RP 1,22	344.4602
RP 1,23	359.3122
RP 1,24	374.1047
RP 1,25	388.8349
RP 1,26	403.5004
RP 1,27	418.0987
RP 1,28	432.6272
RP 1,29	447.0833
RP 1,30	461.4646
RP 1,31	475.7684
RP 1,32	489.9923
RP 1,33	504.1338
RP 1,34	518.1902
RP 1,35	532.1590
RP 1,36	546.0377
RP 1,37	559.8238
RP 1,38	573.5147
RP 1,39	587.1080
RP 1,40	600.6009
RP 2, 2	38.7985
RP 2, 3	54.3091
RP 2, 4	69.8107
RP 2, 5	85.3009
RP 2, 6	100.7772
RP 2, 7	116.2370
RP 2, 8	131.6777
RP 2, 9	147.0969
RP 2,10	162.4919
RP 2,11	177.8603
RP 2,12	193.1995
RP 2,13	208.5070
RP 2,14	223.7802
RP 2,15	239.0167

ASSIGN-MENT	CALCULATED GSCD
RP 2,16	254.2137
RP 2,17	269.3689
RP 2,18	284.4797
RP 2,19	299.5436
RP 2,20	314.5579
RP 2,21	329.5202
RP 2,22	344.4280
RP 2,23	359.2786
RP 2,24	374.0696
RP 2,25	388.7984
RP 2,26	403.4625
RP 2,27	418.0594
RP 2,28	432.5864
RP 2,29	447.0411
RP 2,30	461.4210
RP 2,31	475.7234
RP 2,32	489.9459
RP 2,33	504.0859
RP 2,34	518.1408
RP 2,35	532.1082
RP 2,36	545.9855
RP 2,37	559.7702
RP 2,38	573.4597
RP 2,39	587.0515
RP 2,40	600.5430
RP 3, 3	54.3007
RP 3, 4	69.8000
RP 3, 5	85.2878
RP 3, 6	100.7617
RP 3, 7	116.2191
RP 3, 8	131.6574
RP 3, 9	147.0742
RP 3,10	162.4669
RP 3,11	177.8329
RP 3,12	193.1697
RP 3,13	208.4748
RP 3,14	223.7457
RP 3,15	238.9797
RP 3,16	254.1744
RP 3,17	269.3272
RP 3,18	284.4356
RP 3,19	299.4971
RP 3,20	314.5091
RP 3,21	329.4690
RP 3,22	344.3744
RP 3,23	359.2226
RP 3,24	374.0112
RP 3,25	388.7377
RP 3,26	403.3994
RP 3,27	417.9938

ASSIGN-MENT	CALCULATED GSCD
RP 3,28	432.5185
RP 3,29	446.9708
RP 3,30	461.3483
RP 3,31	475.6483
RP 3,32	489.8684
RP 3,33	504.0060
RP 3,34	518.0586
RP 3,35	532.0236
RP 3,36	545.8985
RP 3,37	559.6808
RP 3,38	573.3679
RP 3,39	586.9573
RP 3,40	600.4465
RP 4, 4	69.7850
RP 4, 5	85.2695
RP 4, 6	100.7400
RP 4, 7	116.1941
RP 4, 8	131.6291
RP 4, 9	147.0425
RP 4,10	162.4319
RP 4,11	177.7945
RP 4,12	193.1280
RP 4,13	208.4298
RP 4,14	223.6973
RP 4,15	238.9280
RP 4,16	254.1194
RP 4,17	269.2689
RP 4,18	284.3739
RP 4,19	299.4320
RP 4,20	314.4407
RP 4,21	329.3973
RP 4,22	344.2993
RP 4,23	359.1442
RP 4,24	373.9295
RP 4,25	388.6526
RP 4,26	403.3110
RP 4,27	417.9021
RP 4,28	432.4234
RP 4,29	446.8724
RP 4,30	461.2465
RP 4,31	475.5432
RP 4,32	489.7600
RP 4,33	503.8942
RP 4,34	517.9435
RP 4,35	531.9052
RP 4,36	545.7768
RP 4,37	559.5557
RP 4,38	573.2395
RP 4,39	586.8255
RP 4,40	600.3113

ASSIGN-MENT	CALCULATED GSCD
RP 5, 5	85.2459
RP 5, 6	100.7121
RP 5, 7	116.1619
RP 5, 8	131.5926
RP 5, 9	147.0018
RP 5,10	162.3868
RP 5,11	177.7452
RP 5,12	193.0744
RP 5,13	208.3719
RP 5,14	223.6351
RP 5,15	238.8615
RP 5,16	254.0486
RP 5,17	269.1938
RP 5,18	284.2946
RP 5,19	299.3484
RP 5,20	314.3527
RP 5,21	329.3050
RP 5,22	344.2028
RP 5,23	359.0434
RP 5,24	373.8244
RP 5,25	388.5432
RP 5,26	403.1973
RP 5,27	417.7841
RP 5,28	432.3011
RP 5,29	446.7458
RP 5,30	461.1157
RP 5,31	475.4081
RP 5,32	489.6206
RP 5,33	503.7505
RP 5,34	517.7955
RP 5,35	531.7529
RP 5,36	545.6202
RP 5,37	559.3948
RP 5,38	573.0743
RP 5,39	586.6561
RP 5,40	600.1376
RP 6, 6	100.6781
RP 6, 7	116.1226
RP 6, 8	131.5481
RP 6, 9	146.9520
RP 6,10	162.3318
RP 6,11	177.6849
RP 6,12	193.0089
RP 6,13	208.3011
RP 6,14	223.5591
RP 6,15	238.7802
RP 6,16	253.9621
RP 6,17	269.1020
RP 6,18	284.1976
RP 6,19	299.2462

ASSIGN-MENT	CALCULATED GSCD
RP 6,20	314.2452
RP 6,21	329.1923
RP 6,22	344.0848
RP 6,23	358.9202
RP 6,24	373.6959
RP 6,25	388.4095
RP 6,26	403.0583
RP 6,27	417.6399
RP 6,28	432.1517
RP 6,29	446.5912
RP 6,30	460.9558
RP 6,31	475.2429
RP 6,32	489.4502
RP 6,33	503.5749
RP 6,34	517.6146
RP 6,35	531.5668
RP 6,36	545.4288
RP 6,37	559.1982
RP 6,38	572.8725
RP 6,39	586.4490
RP 6,40	599.9253
RP 7, 7	116.0761
RP 7, 8	131.4954
RP 7, 9	146.8931
RP 7,10	162.2667
RP 7,11	177.6137
RP 7,12	192.9314
RP 7,13	208.2175
RP 7,14	223.4692
RP 7,15	238.6842
RP 7,16	253.8598
RP 7,17	268.9936
RP 7,18	284.0829
RP 7,19	299.1253
RP 7,20	314.1182
RP 7,21	329.0591
RP 7,22	343.9454
RP 7,23	358.7746
RP 7,24	373.5441
RP 7,25	388.2515
RP 7,26	402.8941
RP 7,27	417.4695
RP 7,28	431.9751
RP 7,29	446.4084
RP 7,30	460.7668
RP 7,31	475.0477
RP 7,32	489.2488
RP 7,33	503.3673
RP 7,34	517.4008
RP 7,35	531.3468

ASSIGN-MENT	CALCULATED GSCD
RP 7,36	545.2027
RP 7,37	558.9659
RP 7,38	572.6339
RP 7,39	586.2042
RP 7,40	599.6743
RP 8, 8	131.4346
RP 8, 9	146.8252
RP 8,10	162.1916
RP 8,11	177.5314
RP 8,12	192.8420
RP 8,13	208.1209
RP 8,14	223.3656
RP 8,15	238.5734
RP 8,16	253.7419
RP 8,17	268.8685
RP 8,18	283.9507
RP 8,19	298.9859
RP 8,20	313.9717
RP 8,21	328.9054
RP 8,22	343.7845
RP 8,23	358.6066
RP 8,24	373.3690
RP 8,25	388.0692
RP 8,26	402.7047
RP 8,27	417.2729
RP 8,28	431.7714
RP 8,29	446.1975
RP 8,30	460.5487
RP 8,31	474.8225
RP 8,32	489.0164
RP 8,33	503.1278
RP 8,34	517.1542
RP 8,35	531.0930
RP 8,36	544.9417
RP 8,37	558.6978
RP 8,38	572.3587
RP 8,39	585.9218
RP 8,40	599.3848
RP 9, 9	146.7482
RP 9,10	162.1066
RP 9,11	177.4383
RP 9,12	192.7408
RP 9,13	208.0115
RP 9,14	223.2481
RP 9,15	238.4478
RP 9,16	253.6082
RP 9,17	268.7267
RP 9,18	283.8008
RP 9,19	298.8279
RP 9,20	313.8055

ASSIGN-MENT	CALCULATED GSCD
RP 9,21	328.7312
RP 9,22	343.6022
RP 9,23	358.4161
RP 9,24	373.1704
RP 9,25	387.8626
RP 9,26	402.4900
RP 9,27	417.0501
RP 9,28	431.5404
RP 9,29	445.9584
RP 9,30	460.3016
RP 9,31	474.5673
RP 9,32	488.7531
RP 9,33	502.8564
RP 9,34	516.8746
RP 9,35	530.8053
RP 9,36	544.6459
RP 9,37	558.3939
RP 9,38	572.0467
RP 9,39	585.6018
RP 9,40	599.0566

APPENDIX V

LIST OF ASSIGNMENTS AND FREQUENCIES OF OBSERVED TRANSITIONS FOR $\nu_3+\nu_4$ OF CH_3F

The following pages contain a list of the observed transitions of $\nu_3+\nu_4$ of CH_3F. The columns of the list, left to right, are: the assignment ($\Delta K,\Delta J,K,J$); the observed frequency (in cm^{-1}); the observed fringe number (from which the frequency may be calculated - cf. Chapter 7); the $\Delta\nu$ (weight = $(NORM)^2/(\Delta\nu)^2$); the weight; observed line height; and the line number.

ASSIGN-MENT	OBSERVED FREQUENCY	FRINGE NUMBER	DELTA NU	WEIGHT	INT	LINE NO
PP 9, 9	3975.7390	89.6480	.0140	.50	14	90
PP 9,10	3973.9180	83.9030	.0200	.25	14	83
PP 9,11	3972.0460	78.0810	.0140	.50	14	75
PP 9,12	3970.1670	72.2410	.0140	.50	13	68
PP 9,13	3968.2650	66.3250	.0140	.50	8	62
PP 9,14	3966.3600	60.4010	.0200	.25	9	54
PP 9,15	3964.4370	54.4200	.0140	.50	10	46
PP 9,16	3962.5090	48.4220	.0140	.50	7	39
PP 9,17	3960.5590	42.3600	.0140	.50	8	32
PP 9,18	3958.5740	36.1870	.0140	.50	9	26
PP 9,19	3956.6220	30.1150	.0200	.25	5	19
PP 9,20	3954.6280	23.9150	.0200	.25	7	15
PP 9,21	3952.6370	17.7230	.0200	.25	4	8
PQ 9, 9	3990.9020	136.7210	.9999	.00	12	166A
PQ 9,12	3990.3650	135.0540	.0200	.25	4	164
PQ 9,13	3990.1840	134.4910	.0200	.25	4	163A
PQ 9,15	3989.7250	133.0610	.9999	.00	4	161
PQ 9,16	3989.4280	132.1390	.9999	.00	12	160
PQ 9,17	3989.1880	131.3910	.9999	.00	4	159
PQ 9,18	3988.8710	130.4050	.9999	.00	10	157A
PQ 9,19	3988.6090	129.5930	.0200	.25	4	155
PQ 9,20	3988.3020	128.6370	.0200	.25	3	154
PR 9, 9	4007.7510	189.1220	.0200	.25	6	236A
PR 9,10	4009.2680	193.8380	.9999	.00	5	244
PR 9,11	4010.7750	198.5260	.9999	.00	5	252A
PR 9,15	4016.6630	216.8370	.9999	.00	4	289
PR 9,16	4018.0390	221.1160	.9999	.00	15	295A
PR 9,19	4022.2300	234.1490	.9999	.00	22	316
PP 8, 8	3985.3710	119.5230	.0200	.25	7	139
PP 8, 8	3985.4280	119.7000	.0200	.25	5	139A
PP 8, 9	3983.5320	113.8020	.0200	.25	8	130
PP 8,10	3981.6630	107.9890	.0100	1.00	9	119
PP 8,11	3979.7830	102.1430	.0140	.50	10	109
PP 8,12	3977.8700	96.1930	.0140	.50	9	100
PP 8,13	3975.9650	90.2710	.0200	.25	6	91
PP 8,14	3974.0370	84.2750	.0140	.50	7	84
PP 8,15	3972.1070	78.2270	.0200	.25	12	75A
PP 8,16	3970.1670	72.2410	.0200	.25	13	68
PP 8,17	3968.1290	65.9020	.9999	.00	6	61
PQ 8, 8	3998.8380	161.4020	.9999	.00	6	200
PQ 8, 9	3998.6570	160.8410	.9999	.00	10	199
PQ 8,10	3998.4980	160.3460	.9999	.00	14	198
PQ 8,12	3998.0590	158.9790	.0200	.25	4	195C
PQ 8,13	3997.8610	158.3640	.9999	.00	7	195A
PQ 8,13	3997.8190	158.2340	.9999	.00	7	195
PQ 8,14	3997.5970	157.5420	.9999	.00	6	194
PR 8, 8	4013.8630	208.1280	.9999	.00	11	275A
PR 8,12	4019.9400	227.0290	.9999	.00	13	304
PR 8,13	4021.3310	231.3550	.9999	.00	5	311A
PR 8,14	4022.8340	236.0270	.9999	.00	5	318

ASSIGN-MENT	OBSERVED FREQUENCY	FRINGE NUMBER	DELTA NU	WEIGHT	INT	LINE NO
PP 7, 7	3994.9820	149.4120	.0140	.50	12	182
PP 7, 8	3993.1480	143.7070	.0140	.50	9	174
PP 7, 9	3991.2950	137.9460	.0200	.25	8	168
PP 7,10	3989.4280	132.1390	.0200	.25	12	160
PP 7,11	3987.5260	126.2250	.0140	.50	8	150
PP 7,12	3985.6180	120.2900	.0140	.50	6	140
PP 7,13	3983.7050	114.3420	.0200	.25	6	131
PP 7,14	3981.7930	108.3930	.0140	.50	9	120
PP 7,15	3979.7830	102.1430	.0200	.25	10	109
PP 7,16	3977.8700	96.1930	.0200	.25	9	100
PQ 7, 7	4006.7690	186.0670	.9999	.00	8	231
PQ 7, 8	4006.6130	185.5820	.9999	.00	3	230A
PQ 7,10	4006.2430	184.4320	.9999	.00	6	229A
PQ 7,11	4006.0280	183.7630	.9999	.00	9	228
PQ 7,12	4005.8010	183.0580	.9999	.00	9	227
PQ 7,13	4005.5980	182.4250	.9999	.00	8	226A
PQ 7,14	4005.2870	181.4590	.9999	.00	8	225
PQ 7,15	4005.0850	180.8300	.9999	.00	8	224
PR 7, 8	4021.7430	232.6340	.9999	.00	11	313
PR 7,10	4024.7560	242.0040	.0200	.25	3	327
PP 6, 7	4003.0220	174.4150	.0100	1.00	14	216
PP 6, 8	4001.1710	168.6570	.0140	.50	15	208
PP 6, 9	3999.3010	162.8430	.0140	.50	14	201
PP 6,10	3997.4220	156.9990	.0200	.25	15	193
PP 6,11	3995.5440	151.1580	.0100	1.00	15	184
PP 6,12	3993.6510	145.2720	.0140	.50	14	176
PP 6,13	3991.7530	139.3680	.0140	.50	12	169
PP 6,14	3989.8440	133.4310	.0100	1.00	14	162
PP 6,15	3987.9340	127.4920	.0100	1.00	13	151
PP 6,16	3986.0300	121.5710	.0200	.25	10	142
PP 6,17	3984.1220	115.6360	.0140	.50	9	134
PP 6,18	3982.2340	109.7660	.0200	.25	8	123
PP 6,19	3980.3740	103.9810	.0200	.25	7	112
PP 6,20	3978.5640	98.3540	.9999	.00	4	103
PP 6,21	3976.7650	92.7570	.9999	.00	6	94
PQ 6, 6	4014.9440	211.4900	.0140	.50	5	281
PQ 6, 8	4014.6200	210.4840	.0100	1.00	7	279
PQ 6, 9	4014.4420	209.9300	.0100	1.00	10	278
PQ 6,10	4014.2570	209.3540	.0200	.25	14	276A
PQ 6,12	4013.8630	208.1280	.0100	1.00	11	275
PQ 6,13	4013.6530	207.4770	.0100	1.00	11	273
PQ 6,14	4013.4420	206.8190	.0140	.50	12	272
PQ 6,15	4013.2310	206.1640	.0140	.50	10	271
PQ 6,16	4013.0320	205.5440	.0140	.50	12	270
PQ 6,17	4012.8340	204.9300	.0200	.25	9	260
PQ 6,18	4012.6790	204.4480	.0140	.50	11	259
PQ 6,19	4012.5400	204.0140	.0140	.50	9	258
PQ 6,20	4012.4480	203.7280	.0140	.50	13	257
PR 6, 7	4028.2280	252.9040	.9999	.00	13	348A
PR 6, 8	4029.7830	257.6380	.9999	.00	14	356

ASSIGN-MENT	OBSERVED FREQUENCY	FRINGE NUMBER	DELTA NU	WEIGHT	INT	LINE NO
PR 6,11	4034.2790	271.6210	.9999	.00	8	379A
PR 6,15	4040.2360	290.1490	.9999	.00	11	408A
PR 6,16	4041.7400	294.8280	.0200	.25	6	414A
PP 5, 6	4012.2110	202.9920	.0200	.25	11	256
PP 5, 7	4010.4360	197.4720	.9999	.00	20	251
PP 5, 8	4008.5470	191.8380	.9999	.00	15	241
PP 5, 9	4006.7690	186.0670	.0200	.25	8	231
PP 5,10	4004.8930	180.2340	.9999	.00	12	223A
PP 5,11	4003.0220	174.4150	.0100	1.00	14	216
PP 5,12	4001.1710	168.6570	.0140	.50	15	208
PP 5,13	3999.3010	162.8430	.9999	.00	14	201
PP 5,14	3997.3130	156.6600	.0200	.25	5	192
PQ 5, 5	4022.4230	234.7490	.9999	.00	5	316B
PQ 5, 6	4022.3420	234.4990	.0200	.25	7	316A
PQ 5, 7	4022.2300	234.1490	.9999	.00	22	316
PQ 5, 8	4022.1060	233.7630	.9999	.00	14	315
PQ 5, 9	4021.9500	233.2780	.9999	.00	25	314
PQ 5,10	4021.7430	232.6340	.9999	.00	11	313
PQ 5,12	4021.3310	231.3550	.9999	.00	5	311A
PQ 5,13	4021.1540	230.8040	.9999	.00	3	310
PR 5, 6	4034.1820	271.3180	.9999	.00	4	378B
PR 5, 7	4035.7000	276.0390	.9999	.00	17	385A
PR 5, 8	4037.2290	280.7960	.9999	.00	17	392A
PR 5, 9	4038.7750	285.6070	.9999	.00	15	401
PR 5,12	4043.2440	299.5050	.9999	.00	8	423
PP 4, 6	4019.8560	226.7660	.0140	.50	10	303
PP 4, 7	4018.0390	221.1160	.0200	.25	15	295A
PP 4, 8	4016.1740	215.3170	.0140	.50	14	288
PP 4, 9	4014.2960	209.4730	.0100	1.00	16	277
PP 4,10	4012.3880	203.5420	.0140	.50	12	256A
PP 4,12	4008.5470	191.5960	.0200	.25	9	240A
PP 4,13	4006.6130	185.5820	.0200	.25	3	230A
PP 4,14	4004.6070	179.3450	.0200	.25	6	222
PQ 4, 6	4029.9260	258.0830	.9999	.00	10	356A
PQ 4, 7	4029.7830	257.6380	.9999	.00	14	356
PQ 4, 8	4029.5890	257.0360	.9999	.00	21	355
PQ 4, 9	4029.4020	256.4550	.0100	1.00	22	354A
PQ 4,10	4029.1570	255.6910	.9999	.00	19	353
PQ 4,11	4028.9140	254.9350	.0200	.25	8	351
PQ 4,12	4028.6740	254.1890	.9999	.00	9	350A
PQ 4,13	4028.4000	253.3370	.0200	.25	5	349
PR 4, 6	4041.7400	294.8280	.0200	.25	6	414A
PR 4, 7	4043.2440	299.5050	.9999	.00	8	423
PR 4,10	4047.7390	313.4800	.9999	.00	7	444
PR 4,12	4050.5770	322.3060	.0200	.25	5	459B
PP 3, 4	4031.1380	261.8530	.0200	.25	23	363
PP 3, 5	4029.3500	256.2930	.0100	1.00	25	354
PP 3, 6	4027.5470	250.6840	.0140	.50	17	343
PP 3, 7	4025.7030	244.9510	.0140	.50	18	333
PP 3, 8	4023.8420	239.1640	.0100	1.00	18	323

ASSIGN-MENT	OBSERVED FREQUENCY	FRINGE NUMBER	DELTA NU	WEIGHT	INT	LINE NO
PP 3, 9	4021.9500	233.2780	.0200	.25	25	314
PP 3,10	4020.0340	227.3210	.0140	.50	21	305
PP 3,11	4018.0890	221.2700	.0140	.50	21	296
PP 3,12	4016.1020	215.0920	.9999	.00	17	287
PP 3,13	4014.0600	208.7430	.9999	.00	26	276
PP 3,14	4012.0740	202.5660	.9999	.00	4	255A
PP 3,16	4006.7690	186.0670	.9999	.00	8	231
PP 3,15	4010.7750	198.5260	.9999	.00	5	252A
PP 3,17	4006.0280	183.7630	.0140	.50	9	228
PP 3,18	4004.0010	177.4590	.0200	.25	9	220A
PP 3,19	4001.8540	170.7810	.9999	.00	12	210
PP 3,20	3999.6990	164.0800	.9999	.00	4	202
PP 3,21	3997.5970	157.5420	.9999	.00	6	194
PQ 3, 3	4037.9480	283.0340	.0200	.25	9	397
PQ 3, 4	4037.8670	282.7830	.0140	.50	16	396B
PQ 3, 5	4037.7630	282.4550	.0140	.50	18	396
PQ 3, 6	4037.6290	282.0380	.0200	.25	19	395
PQ 3, 7	4037.4650	281.5300	.0140	.50	23	394
PQ 3, 8	4037.2830	280.9640	.0140	.50	26	393
PQ 3, 9	4037.0760	280.3190	.0100	1.00	26	392
PQ 3,10	4036.8240	279.5350	.0140	.50	23	391
PQ 3,11	4036.5260	278.6090	.9999	.00	19	389
PQ 3,12	4036.1900	277.5630	.9999	.00	30	388
PQ 3,13	4035.9000	276.6610	.9999	.00	10	387A
PQ 3,14	4035.2440	474.6200	.9999	.00	27	384
PQ 3,15	4033.9860	270.7100	.9999	.00	7	378
PQ 3,13	4037.7940	282.5560	.9999	.00	17	396A
PQ 3,14	4036.5470	278.6740	.9999	.00	18	388A
PQ 3,15	4035.4300	275.2010	.0140	.50	11	385
PQ 3,16	4034.9350	273.6600	.0200	.25	11	382A
PQ 3,17	4034.5960	272.6060	.0200	.25	11	381
PQ 3,18	4034.1820	271.3180	.9999	.00	4	378B
PQ 3,19	4033.7560	269.9950	.0140	.50	14	376
PQ 3,20	4033.3000	268.5770	.9999	.00	19	373A
PR 3, 3	4044.6600	303.9070	.9999	.00	15	429B
PR 3, 4	4046.2720	308.9220	.0200	.25	5	438A
PR 3, 5	4047.8400	313.7950	.0140	.50	7	445
PR 3, 6	4049.3880	318.6090	.0140	.50	6	453
PR 3, 7	4050.9090	323.3380	.0140	.50	8	461
PR 3, 8	4052.4190	328.0350	.9999	.00	23	469
PR 3, 9	4053.8390	332.4610	.0200	.25	9	477
PR 3,10	4055.2530	336.8470	.9999	.00	13	484
PR 3,11	4056.6080	341.0600	.9999	.00	9	490
PR 3,12	4058.0270	345.4730	.0200	.25	8	497
PR 3,16	4063.5110	362.5280	.0200	.25	9	525A
PR 3,17	4064.8150	366.5350	.0200	.25	13	531
PR 3,18	4066.0540	370.4360	.9999	.00	9	538B
PR 3,19	4067.2860	374.2700	.9999	.00	10	544
PP 2, 3	4040.5950	291.2620	.0200	.25	13	410
PP 2, 4	4038.8620	285.8720	.0100	1.00	18	402

ASSIGN-MENT	OBSERVED FREQUENCY	FRINGE NUMBER	DELTA NU	WEIGHT	INT	LINE NO
PP 2, 5	4037.0240	280.1570	.9999	.00	15	391A
PP 2, 6	4035.2120	274.5220	.9999	.00	24	383B
PP 2, 7	4033.4080	268.9110	.0200	.25	20	374A
PP 2, 8	4031.5420	263.1080	.9999	.00	13	365
PP 2, 9	4029.6390	257.1910	.9999	.00	22	355B
PP 2,10	4027.7610	251.3500	.0200	.25	13	344
PP 2,11	4025.8330	245.3540	.0100	1.00	14	334
PP 2,12	4023.8900	239.3130	.0140	.50	16	323A
PP 2,13	4021.9500	233.2780	.9999	.00	25	314
PP 2,14	4019.9400	227.0290	.0200	.25	13	304
PP 2,15	4017.7220	220.7520	.0100	1.00	12	295
PP 2,16	4015.8750	214.3850	.9999	.00	12	286
PP 2,17	4013.7990	207.9290	.0140	.50	9	274
PP 2,18	4011.6660	201.2960	.0200	.25	8	253
PQ 2, 2	4045.7000	307.1400	.9999	.00	10	436A
PQ 2, 3	4045.6510	306.9860	.9999	.00	12	436
PQ 2, 4	4045.5450	306.6560	.0140	.50	11	435
PQ 2, 5	4045.4280	306.2930	.0100	1.00	13	434
PQ 2, 6	4045.3070	305.9160	.9999	.00	12	433
PQ 2, 7	4045.1510	305.4300	.0200	.25	14	432
PQ 2, 8	4044.9740	304.8800	.0100	1.00	19	431A
PQ 2, 9	4044.7890	304.3040	.0200	.25	18	430
PQ 2,10	4044.5630	303.6040	.0140	.50	14	429
PQ 2,11	4044.3210	302.8490	.0100	1.00	17	427
PQ 2,12	4044.0670	302.0600	.0200	.25	16	426
PQ 2,13	4043.7710	301.1400	.0140	.50	15	425
PQ 2,14	4043.4370	300.1000	.9999	.00	5	423A
PQ 2,15	4043.0900	299.0230	.0140	.50	16	422A
PQ 2,16	4042.6880	297.7730	.9999	.00	14	420
PQ 2,17	4042.2870	296.5230	.9999	.00	17	417B
PQ 2,18	4041.8060	295.0290	.0100	1.00	14	415
PQ 2,19	4041.2050	293.1590	.9999	.00	16	412A
PR 2, 2	4050.7960	322.9870	.9999	.00	15	460
PR 2, 3	4052.3450	327.8050	.9999	.00	12	468B
PR 2, 4	4054.0640	333.1510	.9999	.00	10	478B
PR 2, 5	4055.5200	337.6770	.0200	.25	4	485
PR 2, 6	4057.0800	342.5300	.0140	.50	9	493
PR 2, 9	4061.5950	356.5710	.0200	.25	9	516
PR 2,10	4063.0570	361.1170	.0200	.25	7	522A
PR 2,11	4064.4900	365.5750	.9999	.00	10	529
PR 2,12	4065.8990	369.9560	.0140	.50	15	537
PR 2,13	4067.2860	374.2700	.0200	.25	10	544
PR 2,14	4068.6260	378.4370	.0200	.25	8	553
PR 2,15	4069.9360	382.5100	.9999	.00	5	559
PR 2,16	4071.2160	386.4900	.0200	.25	6	563
PR 2,17	4072.4280	390.2590	.9999	.00	11	568A
PP 1, 2	4049.9580	320.3790	.0200	.25	8	456B
PP 1, 3	4048.2090	314.9400	.0140	.50	9	448
PP 1, 4	4046.4410	309.4470	.9999	.00	10	439A
PP 1, 5	4044.6240	303.7950	.0200	.25	14	429A

ASSIGN-MENT	OBSERVED FREQUENCY	FRINGE NUMBER	DELTA NU	WEIGHT	INT	LINE NO
PP 1, 6	4042.8460	298.2630	.9999	.00	12	421
PP 1, 7	4041.0140	292.5700	.9999	.00	12	411
PP 1, 8	4039.1840	286.8770	.9999	.00	19	403
PP 1, 9	4037.6050	281.9640	.9999	.00	26	393
PP 1,10	4035.4300	275.2010	.0200	.25	17	385
PP 1,11	4033.4880	269.1600	.9999	.00	23	375
PP 1,12	4031.5420	263.1080	.9999	.00	13	365
PP 1,13	4029.5890	257.0360	.9999	.00	21	355
PP 1,14	4027.6020	250.8570	.0200	.25	15	343A
PP 1,15	4025.5990	244.6260	.0200	.25	14	332
PP 1,16	4023.5780	238.3430	.9999	.00	15	321
PP 1,17	4021.5030	231.8880	.0100	1.00	9	312
PP 1,18	4019.4290	225.4390	.9999	.00	11	301
PP 1,19	4017.3010	218.8220	.9999	.00	9	292
PP 1,20	4015.1410	212.1020	.9999	.00	11	282
PP 1,21	4012.9550	205.3060	.0200	.25	7	260B
PQ 1, 1	4053.3730	331.0000	.9999	.00	11	475A
PQ 1, 2	4053.3240	330.8490	.0140	.50	15	475
PQ 1, 3	4053.2570	330.6390	.0140	.50	17	474A
PQ 1, 5	4053.4730	330.0690	.0100	1.00	13	473
PQ 1, 6	4052.9400	329.6530	.0100	1.00	15	472
PQ 1, 7	4052.7960	329.2070	.0140	.50	13	471
PQ 1, 8	4052.6260	328.6780	.0140	.50	15	470
PQ 1, 9	4052.4190	328.0550	.0200	.25	23	469
PQ 1,10	4052.2080	327.3790	.0200	.25	18	468
PQ 1,11	4051.9790	326.6670	.0100	1.00	12	467
PQ 1,12	4051.7190	325.8570	.0100	1.00	18	465
PQ 1,13	4051.4330	324.9680	.0100	1.00	15	464
PQ 1,14	4051.1260	324.0120	.0140	.50	14	462
PQ 1,15	4050.7950	322.9820	.0100	1.00	15	460
PQ 1,16	4050.4350	321.9650	.9999	.00	22	459
PQ 1,17	4050.0430	320.6440	.0100	1.00	15	457
PQ 1,18	4049.6170	319.3200	.0140	.50	12	455
PQ 1,19	4049.1530	317.8780	.0140	.50	15	452
PQ 1,20	4048.6790	316.4030	.9999	.00	17	450A
PR 1, 4	4061.5950	356.5710	.0200	.25	9	516
PR 1, 5	4063.1630	361.4460	.0140	.50	5	523
PR 1, 6	4063.7220	366.2940	.0200	.25	8	530
PR 1, 7	4066.2550	371.0620	.0200	.25	11	539
PR 1, 8	4067.7490	375.7100	.9999	.00	21	547
PR 1, 9	4069.2400	380.3470	.9999	.00	17	555A
PR 1,12	4073.5730	393.8200	.9999	.00	21	571
PR 1,13	4074.9500	398.1040	.9999	.00	14	576
PR 1,14	4076.3270	402.3860	.0140	.50	8	586
PR 1,15	4077.6610	406.5340	.0100	1.00	5	592
PR 1,16	4078.9610	410.5760	.0140	.50	9	596
PR 1,17	4080.2430	414.5630	.9999	.00	14	603
PR 1,18	4081.4630	418.3570	.9999	.00	23	606
PR 1,19	4082.7010	422.2090	.9999	.00	25	612
RP 0, 3	4055.8510	338.7070	.0200	.25	11	487

ASSIGN-MENT	OBSERVED FREQUENCY	FRINGE NUMBER	DELTA NU	WEIGHT	INT	LINE NO
RP 0, 4	4054.1170	333.3150	.0200	1.00	16	479
RP 0, 5	4052.2620	327.5470	.0140	.50	21	468A
RP 0, 6	4050.4670	321.9630	.0200	.25	24	459A
RP 0, 7	4048.6530	316.3230	.9999	.00	19	450
RP 0, 8	4046.7950	310.5450	.0200	.25	18	441
RP 0, 9	4044.9240	304.7270	.0100	1.00	17	431
RP 0,10	4043.0280	298.8330	.0140	.50	15	422
RP 0,11	4041.1330	292.9380	.0200	.25	23	412
RP 0,12	4039.1840	286.8770	.0140	.50	19	403
RP 0,13	4037.2290	280.7960	.0200	.25	17	392A
RP 0,14	4035.2440	274.6200	.9999	.00	27	384
RP 0,15	4033.2500	268.4190	.9999	.00	22	373
RP 0,16	4031.1990	262.0420	.0200	.25	20	363A
RP 0,17	4029.1570	255.6910	.0200	.25	19	353
RP 0,18	4027.0120	249.0200	.0140	.50	17	340
RP 0,19	4024.9160	242.5010	.9999	.00	19	328
RP 0,20	4022.6290	235.3890	.0140	.53	11	317
RP 0,21	4020.2660	228.0410	.0140	.50	16	306
RP 0,22	4017.7510	220.2190	.0140	.50	19	
RP 0,22	4017.7510	220.2190	.0140	.50	10	294
RP 0,23	4015.1410	212.1020	.9999	.00	11	282
RQ 0, 1	4060.9780	354.6520	.0140	.50	16	514A
RQ 0, 2	4060.9320	354.5090	.0100	1.00	18	514
RQ 0, 3	4060.8640	354.2970	.0100	1.00	20	513
RQ 0, 4	4060.7830	354.0450	.0100	1.00	21	512
RQ 0, 5	4060.6730	353.7040	.0100	1.00	21	511
RQ 0, 6	4060.5440	353.3010	.0100	1.00	21	510
RQ 0, 7	4060.3890	352.8190	.0070	2.00	20	509
RQ 0, 8	4060.2170	352.2640	.0070	2.00	22	508
RQ 0, 9	4060.0320	351.7110	.9999	.00	25	507
RQ 0,10	4059.8000	350.9870	.0140	.50	23	505
RQ 0,11	4059.5520	350.2160	.0140	.50	20	504
RQ 0,12	4059.2880	349.3970	.0100	1.00	25	503
RQ 0,13	4058.9860	348.4580	.0100	1.00	21	501
RQ 0,14	4058.6650	347.4590	.0140	.50	24	500
RQ 0,15	4058.3040	346.3350	.0140	.50	21	499
RQ 0,16	4057.9020	345.0840	.0200	.25	29	496
RQ 0,17	4057.4660	343.7290	.0100	1.00	19	495
RQ 0,18	4056.9640	342.1680	.0140	.50	18	492
RQ 0,19	4056.3900	340.3840	.0100	1.00	19	489
RQ 0,20	4055.7240	338.3130	.0100	1.00	19	486
RQ 0,21	4054.9590	335.9320	.0100	1.00	14	483
RR 0, 0	4062.6880	359.9700	.0200	.25	5	521
RR 0, 1	4064.3420	365.1140	.0100	1.00	8	528
RR 0, 2	4065.9860	370.2260	.0140	.50	14	538
RR 0, 3	4067.6000	375.2460	.0200	.25	18	546
RR 0, 4	4069.2100	380.2520	.0200	.25	16	555
RR 0, 5	4070.7860	385.1520	.9999	.00	19	561
RR 0, 6	4072.3550	390.0340	.9999	.00	20	568
RR 0, 7	4073.8920	394.8120	.0200	.25	24	572

ASSIGN-MENT	OBSERVED FREQUENCY	FRINGE NUMBER	DELTA NU	WEIGHT	INT	LINE NO
RR 0, 8	4075.3920	399.4790	.0200	.25	21	579
RR 0, 9	4076.8840	404.1180	.0140	.50	58	9
RR 0, 9	4076.8840	404.1180	.0140	.50	18	589
RR 0,10	4078.3470	408.6670	.9999	.00	23	594
RR 0,11	4079.7900	413.1540	.0140	.50	19	599
RR 0,12	4081.2070	417.5620	.0200	.25	23	600A
RR 0,13	4082.6070	421.9150	.0140	.50	18	611
RR 0,14	4083.9640	426.1360	.0100	1.00	16	619
RR 0,15	4085.2930	430.2690	.0140	.50	15	624
RR 0,16	4086.5860	434.2910	.0100	1.00	14	630
RR 0,17	4087.8150	438.1110	.0140	.50	16	635
RR 0,18	4088.9520	441.6490	.0200	.25	19	642
RR 0,19	4089.9720	444.8200	.0100	1.00	16	646
RR 0,20	4090.8480	447.5450	.0100	1.00	8	552
RP 1, 3	4063.3910	362.1550	.9999	.00	5	524
RP 1, 4	4064.8580	356.7180	.9999	.00	6	516A
RP 1, 5	4059.8680	351.2000	.9999	.00	15	506
RP 1, 6	4058.0260	345.4730	.0140	.50	8	497
RP 1, 7	4056.1960	339.7970	.9999	.00	8	488
RP 1, 8	4054.3270	333.9690	.9999	.00	11	480
RP 1, 9	4052.4190	328.0350	.9999	.00	23	469
RP 1,10	4050.4670	321.9630	.9999	.00	24	459A
RP 1,11	4048.3710	315.4460	.0200	.25	12	449
RP 1,12	4045.9480	307.9110	.0200	.25	2	437A
RP 1,13	4042.9430	298.5640	.0200	.25	7	421B
RP 1,11	4049.6190	319.3260	.0140	.50	12	455
RP 1,12	4047.0840	311.4440	.9999	.00	6	442
RP 1,13	4044.9740	304.8300	.0200	.25	19	431A
RP 1,14	4042.9430	298.5640	.0200	.25	7	421B
RP 1,15	4040.9630	292.4080	.0200	.25	9	410E
RP 1,17	4036.8240	279.5350	.9999	.00	23	391
RP 1,18	4034.7350	273.0400	.9999	.00	6	381A
RP 1,19	4032.4990	266.0860	.9999	.00	6	370B
RP 1,20	4029.2970	258.2390	.9999	.00	11	357
RP 1,21	4026.8500	248.5180	.0200	.25	10	339
RQ 1, 2	4068.5160	378.0950	.9999	.00	11	552A
RQ 1, 3	4068.4550	377.9030	.0200	.25	16	552
RQ 1, 4	4068.3630	377.6170	.0200	.25	20	551
RQ 1, 5	4068.2570	377.2880	.0200	.25	19	550
RQ 1, 6	4068.1170	376.8520	.0200	.25	19	549
RQ 1, 7	4067.9460	376.3220	.0140	.50	18	548
RQ 1, 8	4067.7490	375.7100	.0140	.50	21	547
RQ 1, 9	4067.5110	374.9700	.0200	.25	22	545
RQ 1,10	4067.1180	373.7450	.0200	.25	24	543
RQ 1,11	4066.3630	371.3970	.0200	.25	12	540
RQ 1,12	4065.0520	367.3210	.9999	.00	9	532
RQ 1,10	4068.3630	377.6170	.9999	.00	20	551
RQ 1,11	4067.5110	374.9700	.0200	.25	22	545
RQ 1,12	4067.1180	373.7450	.0200	.25	24	543
RQ 1,13	4066.7390	372.7240	.9999	.00	16	542

ASSIGN-MENT	OBSERVED FREQUENCY	FRINGE NUMBER	DELTA NU	WEIGHT	INT	LINE NO
RQ 1,14	4066.4960	371.8130	.0140	.50	13	541
RQ 1,15	4066.1400	370.7060	.0140	.50	14	538C
RQ 1,16	4065.7590	369.5200	.0140	.50	15	536
RQ 1,17	4065.3440	368.2280	.0140	.50	14	533
RQ 1,18	4064.8150	366.5850	.0140	.50	13	531
RQ 1,19	4063.9680	363.9490	.0200	.25	10	527
RQ 1,20	4062.5260	359.4670	.9999	.00	4	520A
RR 1, 1	4071.9250	388.6950	.0100	1.00	11	566
RR 1, 2	4073.5730	393.8200	.0100	1.00	21	571
RR 1, 3	4075.1820	398.8240	.0200	.25	17	578
RR 1, 4	4076.7700	403.7640	.0140	.50	15	588
RR 1, 5	4078.3470	408.6670	.9999	.00	23	594
RR 1, 6	4079.8720	413.4100	.0200	.25	13	600
RR 1, 7	4081.3830	418.1100	.0200	.25	13	605B
RR 1, 8	4082.8250	422.5930	.0140	.50	14	612B
RR 1, 9	4084.1260	426.6390	.0140	.50	9	620
RR 1,11	4085.4920	430.8370	.0200	.25	5	626
RR 1, 9	4085.4150	430.6490	.9999	.00	7	625
RR 1,10	4086.2500	433.2450	.0200	.25	10	628
RR 1,11	4087.5540	437.2990	.0140	.50	16	634
RR 1,12	4088.9520	441.6490	.0140	.50	19	642
RR 1,13	4090.3220	445.9080	.0140	.50	13	647
RR 1,14	4091.6440	450.0320	.0100	1.00	12	655
RR 1,15	4092.9930	454.2160	.0200	.25	10	659
RR 1,16	4094.2750	458.2020	.0200	.25	7	663
RR 1,17	4095.4330	461.8180	.0140	.50	7	668
RR 1,18	4096.2860	464.4400	.0200	.25	11	671B
RR 1,19	4096.5320	465.2220	.9999	.00	24	673
RP 2, 4	4069.2090	380.2520	.9999	.00	16	555
RP 2, 5	4067.4080	374.6490	.9999	.00	6	544B
RP 2, 7	4063.7640	363.3160	.0200	.25	9	526
RP 2, 8	4061.9170	357.5720	.0140	.50	6	518
RP 2,10	4058.1590	345.8850	.9999	.00	7	498
RP 2,11	4056.2010	339.7970	.9999	.00	8	488
RP 2,12	4054.3270	333.9690	.0200	.25	11	480
RP 2,13	4052.3450	327.8050	.0200	.25	12	468B
RP 2,15	4048.3710	315.4460	.0140	.50	12	449
RP 2,16	4046.3620	309.2000	.0200	.25	4	439
RP 2,17	4044.3210	302.8490	.9999	.00	17	427
RP 2,18	4042.2120	269.2910	.0200	.25	16	417A
RP 2,20	4037.9490	283.0340	.9999	.00	9	397
RP 2,21	4035.7380	276.1590	.9999	.00	22	386
RP 2,22	4033.5220	269.2650	.9999	.00	19	375A
RP 2,24	4029.0100	255.2340	.0200	.25	6	352
RQ 2, 3	4076.0200	401.4300	.9999	.00	7	584
RQ 2, 4	4075.9250	401.1360	.0140	.50	9	583
RQ 2, 5	4075.8190	400.8070	.9999	.00	9	582
RQ 2, 6	4075.6900	400.4290	.0100	1.00	11	581
RQ 2, 7	4075.5460	399.9560	.0140	.50	11	580
RQ 2, 8	4075.3920	399.4790	.9999	.00	21	579

ASSIGN-MENT	OBSERVED FREQUENCY	FRINGE NUMBER	DELTA NU	WEIGHT	INT	LINE NO
RQ 2, 9	4075.1820	398.8240	.0200	.25	17	578
RQ 2,10	4074.9500	398.1040	.9999	.00	14	576
RQ 2,11	4074.7530	397.4950	.0140	.50	13	575
RQ 2,12	4074.4910	396.6740	.0200	.25	13	574
RQ 2,13	4074.2060	395.7900	.0140	.50	11	573
RQ 2,14	4073.8920	394.8120	.9999	.00	24	572
RQ 2,15	4073.5730	343.8200	.9999	.00	21	571
RQ 2,16	4073.2250	392.7370	.0100	1.00	14	570
RQ 2,17	4072.8260	391.4960	.0140	.50	12	569
RQ 2,18	4072.3710	390.0340	.9999	.00	11	568A
RQ 2,19	4071.9250	388.6950	.0100	1.00	11	566
RQ 2,20	4071.4210	387.1290	.0200	.25	7	564
RQ 2,21	4070.8930	385.4870	.0200	.25	9	562
RQ 2,22	4070.3470	383.7370	.0200	.25	7	560
RQ 2,23	4069.7930	382.0650	.0200	.25	5	558A
RR 2, 2	4081.1510	417.3880	.9999	.00	25	605
RR 2, 3	4082.7390	422.3250	.0200	.25	25	612A
RR 2, 4	4084.2340	427.2870	.0100	1.00	13	621
RR 2, 5	4085.9180	432.2000	.0140	.50	16	627
RR 2, 6	4087.4740	437.0500	.0140	.50	14	633
RR 2, 7	4088.9970	441.7880	.0140	.50	18	642A
RR 2, 9	4091.9640	451.0150	.0140	.50	11	656A
RR 2,10	4093.4790	455.7260	.0140	.50	21	661A
RR 2,11	4094.9150	460.1910	.0200	.25	16	665B
RR 2,12	4096.3370	464.6140	.0140	.50	16	672
RR 2,13	4097.7360	468.9650	.0140	.50	11	678
RR 2,14	4099.1060	473.2250	.0140	.50	11	683
RR 2,15	4100.4460	477.3730	.0200	.25	9	689
RR 2,16	4101.7460	481.4350	.0140	.50	11	695
RR 2,17	4102.9980	485.3280	.0200	.25	8	699
RR 2,18	4104.2330	489.1690	.9999	.00	11	704A
RR 2,20	4106.5830	496.4780	.0200	.25	7	714
RR 2,21	4107.7360	500.0650	.9999	.00	4	719D
RP 3, 5	4074.9500	398.1040	.9999	.00	14	576
RP 3, 7	4071.2840	386.7030	.0200	.25	7	563B
RP 3, 8	4069.3680	380.7440	.0200	.25	6	556
RP 3, 9	4067.5500	375.0890	.9999	.00	18	545A
RP 3,10	4065.6880	369.3000	.9999	.00	13	535
RP 3,11	4063.7640	363.3160	.0200	.25	9	526
RP 3,12	4061.8270	357.2930	.0140	.50	9	517
RP 3,13	4059.8680	351.2000	.9999	.00	15	506
RP 3,14	4057.9020	345.0840	.9999	.00	29	496
RP 3,15	4055.9240	338.9350	.0140	.50	11	487A
RP 3,16	4053.9170	332.6940	.9999	.00	10	478
RP 3,17	4051.8960	326.4080	.0140	.50	11	466
RP 3,18	4049.8850	320.1530	.9999	.00	10	456A
RP 3,19	4047.7390	313.4800	.0140	.50	7	444
RP 3,20	4045.6510	306.9860	.9999	.00	12	436
RP 3,21	4043.4770	300.2240	.9999	.00	21	424
RP 3,22	4041.1340	292.9380	.9999	.00	23	412

ASSIGN-MENT	OBSERVED FREQUENCY	FRINGE NUMBER	DELTA NU	WEIGHT	INT	LINE NO
RQ 3, 4	4083.4400	424.5050	.0140	.50	10	617
RQ 3, 5	4083.3370	424.1860	.0140	.50	14	616
RQ 3, 6	4083.2120	423.7960	.0140	.50	17	615
RQ 3, 7	4083.0620	423.3290	.0100	1.00	17	614
RQ 3, 8	4082.8980	422.7900	.0100	1.00	21	613
RQ 3, 9	4082.7010	422.2090	.0140	.50	25	612
RQ 3,10	4082.4910	421.5540	.0140	.50	19	610
RQ 3,11	4082.2630	420.8470	.0140	.50	18	609
RQ 3,12	4082.0120	420.0660	.0140	.50	19	608
RQ 3,13	4081.7330	419.1970	.0140	.50	19	607
RQ 3,14	4081.4630	418.3570	.9999	.00	23	606
RQ 3,15	4081.1510	417.3880	.0200	.25	25	605
RQ 3,16	4080.8200	416.3590	.0100	1.00	8	604
RQ 3,17	4080.5000	415.3630	.9999	.00	14	603
RQ 3,18	4080.0870	414.0790	.9999	.00	15	601A
RQ 3,19	4079.6560	412.7380	.0140	.50	16	598
RQ 3,20	4079.1700	411.2260	.0140	.50	13	597
RQ 3,21	4078.5310	409.2390	.9999	.00	12	595
RQ 3,22	4077.4940	406.0140	.9999	.00	5	591
RR 3, 3	4090.2560	445.7030	.0100	1.00	20	648
RR 3, 4	4091.8650	450.7080	.0200	.25	21	656
RR 3, 5	4093.4320	455.5810	.0100	1.00	20	661
RR 3, 6	4094.9790	460.3920	.0100	1.00	24	666
RR 3, 7	4096.5320	465.2220	.0200	.25	24	673
RR 3, 8	4098.0350	469.8940	.9999	.00	23	679
RR 3, 9	4099.5150	474.4970	.0140	.50	21	686
RR 3,10	4100.9910	479.0870	.0100	1.00	22	692
RR 3,11	4102.4710	483.6890	.9999	.00	30	697
RR 3,13	4105.2760	492.4150	.0100	1.00	19	710
RR 3,14	4106.6720	496.7550	.0140	.50	16	715
RR 3,15	4108.0440	501.0210	.0140	.50	16	721
RR 3,16	4109.4260	505.3200	.9999	.00	21	728
RR 3,17	4110.6690	509.1860	.9999	.00	15	732
RR 3,18	4111.9590	513.1970	.0100	1.00	14	737
RR 3,20	4114.2250	520.2430	.0100	1.00	12	745
RP 4, 9	4075.0540	398.4250	.9999	.00	11	577
RP 4,11	4071.2530	386.6050	.9999	.00	6	563A
RP 4,13	4067.3400	374.4360	.0200	.25	8	544A
RP 4,14	4065.3440	368.2280	.9999	.00	14	533
RP 4,16	4061.1420	355.1630	.9999	.00	4	515
RP 4,17	4059.0920	348.7870	.0140	.50	7	502
RQ 4, 6	4090.6900	447.0530	.0140	.50	7	651
RQ 4, 7	4090.5400	446.5850	.9999	.00	15	650A
RQ 4, 8	4090.3740	446.0700	.0140	.50	14	649A
RQ 4, 9	4090.1840	445.4800	.0140	.50	13	647
RQ 4,10	4089.9720	444.8200	.0200	.25	16	646
RQ 4,11	4089.7250	444.0530	.0200	.25	9	645
RQ 4,12	4089.4620	443.2330	.9999	.00	12	644
RQ 4,13	4089.1630	442.3030	.0140	.50	13	643
RQ 4,14	4088.8140	441.2200	.0100	1.00	10	641

ASSIGN-MENT	OBSERVED FREQUENCY	FRINGE NUMBER	DELTA NU	WEIGHT	INT	LINE NO
RQ 4,15	4088.3560	439.7930	.0140	.50	10	638
RQ 4,16	4087.9690	438.5920	.0100	1.00	8	636
RR 4, 4	4099.3470	473.9740	.0140	.50	18	685
RR 4, 5	4100.9090	478.8340	.0100	1.00	21	691
RR 4, 6	4102.4710	483.6890	.9999	.00	3	697
RR 4, 7	4103.9910	488.4160	.0140	.50	20	703
RR 4, 8	4105.5020	493.1160	.0100	1.00	14	711
RR 4, 9	4106.9950	497.7590	.0100	1.00	16	716
RR 4,10	4108.4590	502.3110	.0100	1.00	13	723
RR 4,11	4109.9120	506.8320	.0140	.50	16	729
RR 4,12	4111.2920	511.1240	.0100	1.00	14	734
RR 4,13	4112.6440	515.3260	.0200	.25	12	740
RR 4,14	4113.8760	519.1580	.0200	.25	15	744
RR 4,15	4115.1990	523.2740	.0140	.50	9	748
RR 5, 6	4109.4260	505.3200	.9999	.00	21	728
RR 5, 7	4110.9730	510.1300	.0200	.25	10	733
RR 5, 8	4112.4850	514.8330	.9999	.00	8	739
RR 5, 9	4113.9420	519.3640	.0140	.50	14	744A
RR 5,10	4115.4130	523.9390	.9999	.00	14	749
RR 5,11	4116.8490	528.4040	.0140	.50	10	753
RR 5,12	4118.2710	532.8270	.0100	1.00	13	758
RR 5,13	4119.6610	537.1500	.0200	.25	10	762
RR 5,14	4121.0440	541.4490	.9999	.00	11	766
RR 5,15	4122.3890	545.6330	.0200	.25	10	769
RR 5,16	4123.7350	549.8200	.9999	.00	11	773
RR 5,17	4125.0390	553.8730	.9999	.00	11	780
RR 5,18	4126.3030	557.8060	.0200	.25	10	785
RR 5,19	4127.6060	561.8560	.0200	.25	16	788
RQ 5, 8	4079.3670	467.8180	.0200	.25	9	677
RQ 5, 9	4097.1410	467.1140	.9999	.00	8	676
RQ 5,10	4096.9250	466.4440	.0140	.50	10	675
RQ 5,11	4096.6380	465.7050	.0140	.50	9	674
RQ 5,12	4096.4300	464.9030	.0200	.25	12	672A
RQ 5,13	4096.1480	464.0270	.0140	.50	12	671
RQ 5,14	4095.8480	463.0950	.0200	.25	9	670
RQ 5,15	4095.5290	462.1030	.0140	.50	9	669
RQ 5,16	4095.1800	461.0170	.0200	.25	11	667
RQ 5,17	4094.8040	459.8480	.0200	.25	9	665
RQ 5,18	4094.4170	458.6430	.0140	.50	7	664
RQ 5,19	4094.0060	457.3640	.0200	.25	6	662
RQ 5,20	4093.5730	456.0180	.0200	.25	10	661A
RP 5,15	4070.3470	383.7870	.9999	.00	7	560
RP 5,17	4066.2560	371.0670	.9999	.00	11	539
RP 5,19	4062.1060	358.1600	.9999	.00	7	519
RP 6, 8	4091.7300	450.2860	.0200	.25	8	655A
RP 6,10	4087.9690	438.5920	.0200	.25	8	636
RP 6,14	4080.0870	414.0790	.9999	.00	15	601A
RP 6,16	4076.0200	401.4300	.9999	.00	7	584
RP 6,19	4069.7930	383.0650	.9999	.00	5	558A
RP 6,20	4067.6600	375.4310	.9999	.00	13	546A

ASSIGN-MENT	OBSERVED FREQUENCY	FRINGE NUMBER	DELTA NU	WEIGHT	INT	LINE NO
RP 6,21	4065.5300	368.8080	.9999	.00	6	534
RP 6,22	4063.3910	362.1550	.9999	.00	5	524
RP 6,25	4056.7530	341.5110	.9999	.00	4	491
RP 6,26	4054.5010	334.5100	.9999	.00	3	481
RQ 6, 7	4105.2760	492.4150	.9999	.00	19	710
RQ 6, 8	4105.1660	492.0700	.0140	.50	8	709
RQ 6, 9	4104.9610	491.4340	.0100	1.00	11	708
RQ 6,10	4104.7340	490.7280	.0200	.25	15	707
RQ 6,11	4104.4760	489.9250	.0140	.50	15	706
RQ 6,12	4104.1990	489.0650	.0140	.50	13	704
RQ 6,13	4103.8990	488.1300	.9999	.00	26	702
RQ 6,14	4103.5810	487.1430	.0100	1.00	12	701
RQ 6,15	4103.2450	486.0960	.0100	1.00	15	700
RQ 6,16	4102.8930	485.0030	.0140	.50	12	698
RQ 6,17	4102.4710	483.6890	.9999	.00	30	697
RQ 6,18	4102.0890	482.5010	.0100	1.00	14	696
RQ 6,19	4101.6620	481.1760	.0200	.25	11	694
RQ 6,20	4101.2170	479.7910	.0140	.50	11	693
RQ 6,21	4100.7460	478.3260	.0200	.25	10	690
RQ 6,22	4100.2510	476.7870	.9999	.00	10	688
RQ 6,23	4099.7380	475.1910	.0140	.50	13	687B
RQ 6,24	4099.2040	473.6290	.0140	.50	7	684
RQ 6,25	4098.6500	471.9090	.0140	.50	7	682
RQ 6,26	4089.0350	469.9940	.9999	.00	23	679
RQ 6,27	4097.4120	467.9560	.9999	.00	9	677A
RR 6, 6	4117.2650	529.6990	.0070	2.00	23	755
RR 6, 7	4118.7770	534.3990	.0140	.50	22	760
RR 6, 8	4120.2740	539.0570	.0100	1.00	22	764
RR 6, 9	4121.7540	543.6590	.0070	2.00	18	768
RR 6,10	4123.1930	548.1340	.0100	1.00	20	771
RR 6,11	4124.6180	552.5650	.0100	1.00	17	778
RR 6,12	4126.0240	556.9380	.0140	.50	19	783
RR 6,13	4127.3960	561.2040	.0100	1.00	17	787
RR 6,14	4128.7570	565.4380	.0500	.25	16	789
RR 6,15	4130.0860	569.5710	.0100	1.00	17	792
RR 6,16	4131.4050	573.6730	.0140	.50	15	795
RR 6,17	4132.6840	577.6500	.0140	.50	14	798
RR 6,18	4133.9530	581.5970	.0100	1.00	14	800
RR 6,19	4135.1940	585.4550	.0100	1.00	12	803
RR 6,20	4136.4190	589.2640	.0140	.50	14	806A
RR 6,21	4137.6220	593.0060	.9999	.00	9	808
RR 6,22	4138.7920	596.6460	.0200	.25	12	811A
RR 6,23	4139.9490	600.2430	.0140	.50	9	814
RP 7,10	4095.2740	461.3070	.0200	.25		625
RP 7,15	4085.4150	430.6490	.9999	.00	7	625
RP 7,20	4075.0540	398.4250	.9999	.00	11	577
RR 7, 7	4126.1120	557.2100	.0100	1.00	13	784
RR 7, 8	4127.6060	561.8560	.0100	1.00	16	788
RR 7, 9	4129.0850	566.4580	.0140	.50	11	790
RR 7,10	4130.5300	570.9500	.0200	.25	13	793

ASSIGN-MENT	OBSERVED FREQUENCY	FRINGE NUMBER	DELTA NU	WEIGHT	INT	LINE NO
RR 7,11	4131.9590	575.3940	.0140	.50	12	797
RR 7,12	4133.3620	579.7590	.0140	.50	13	799
RR 7,13	4134.7430	584.0540	.0200	.25	11	801
RR 7,14	4136.1040	588.2850	.9999	.00	13	805
RR 7,15	4137.4260	592.3960	.0140	.50	10	807
RR 7,16	4138.7380	596.4780	.0200	.25	10	811
RR 7,17	4140.0220	600.4710	.0200	.25	8	814A
RR 7,18	4141.2980	604.4390	.0200	.25	6	817
RR 7,19	4142.5430	608.3090	.9999	.00	10	821
RQ 7, 8	4112.4850	514.8330	.9999	.00	8	739
RQ 7, 9	4112.3010	514.2610	.9999	.00	7	738
RQ 7,10	4112.0620	513.5160	.0200	.25	5	737A
RQ 7,11	4111.8150	512.7500	.0140	.50	5	736B
RQ 7,12	4111.5550	511.9400	.0200	.25	10	735
RQ 7,15	4110.6010	508.9740	.0140	.50	11	731A
RQ 7,16	4110.2260	507.8070	.0200	.25	8	730A
RQ 7,19	4109.0090	504.0240	.9999	.00	5	725A
RQ 7,20	4108.4910	502.4110	.9999	.00	10	723A
RQ 7,22	4107.5890	499.6060	.0140	.50	7	709
RQ 7,23	4106.9950	497.7590	.9999	.00	16	716
RP 8,15	4092.6760	453.2300	.9999	.00	4	658D
RP 8,17	4088.6500	440.7090	.0140	.50	5	640
RQ 8,11	4119.0940	535.3870	.9999	.00	5	761A
RQ 8,15	4117.8610	531.5520	.0200	.25	4	757B
RQ 8,16	4117.5040	530.2740	.9999	.00	5	756
RQ 8,17	4117.1250	529.2640	.9999	.00	7	754
RQ 8,18	4116.7110	527.9740	.0200	.25	8	752
RQ 8,19	4116.2940	526.6780	.9999	.00	7	751
RQ 8,20	4115.8260	525.2230	.0200	.25	5	750B
RR 8, 8	4134.8760	584.4680	.0100	1.00	14	802
RR 8, 9	4136.3510	589.0540	.0100	1.00	15	806
RR 8,10	4137.7980	593.5530	.0100	1.00	10	809
RR 8,11	4139.2270	597.9980	.0140	.50	11	812
RR 8,12	4140.6270	602.3510	.0200	.25	7	815
RR 8,13	4142.0020	606.6290	.0200	.25	8	820
RR 8,14	4143.3600	610.8520	.0100	1.00	7	823
RR 8,15	4144.7080	615.0430	.9999	.00	7	825
RR 8,16	4145.9970	619.0520	.0200	.25	5	828
RR 8,17	4147.3220	623.1710	.0200	.25	4	833
RR 8,21	4152.1250	638.1080	.0200	.25	9	838
RP 9,14	4101.9630	484.6260	.9999	.00	3	695B
RP 9,18	4093.7350	456.5210	.9999	.00	4	661B
RP 9,20	4089.5160	443.4030	.9999	.00	8	644B
RQ 9,10	4126.5370	558.5330	.0140	.50	8	786
RQ 9,11	4126.3030	557.8060	.0200	.25	10	785
RQ 9,12	4126.0240	556.9380	.9999	.00	10	783
RQ 9,13	4125.7300	556.0230	.0200	.25	4	782B
RQ 9,14	4125.4200	555.0600	.9999	.00	5	782
RQ 9,15	4125.0660	553.9590	.9999	.00	12	780A
RQ 9,16	4124.6860	552.7760	.9999	.00	11	779

ASSIGN-MENT	OBSERVED FREQUENCY	FRINGE NUMBER	DELTA NU	WEIGHT	INT	LINE NO
RQ 9,17	4124.3190	551.6350	.0200	.25	11	776
RQ 9,18	4123.9040	550.3440	.9999	.00	5	774
RQ 9,19	4123.4710	548.9990	.0200	.25	6	772
RQ 9,22	4122.0370	544.5380	.9999	.00	6	768A
RQ 9,23	4121.4950	542.8520	.9999	.00	6	767B
RQ 9,24	4120.9660	541.2080	.9999	.00	6	765A
RQ 9,26	4119.7980	537.5760	.9999	.00	10	763
RQ 9,27	4119.2080	535.7400	.9999	.00	3	761B
RQ 9,29	4117.9110	531.7080	.0200	.25	4	757C
RR 9, 9	4143.5510	611.4450	.0140	.50	13	824
RR 9,10	4145.0040	615.9630	.0100	1.00	16	826
RR 9,11	4146.4200	620.3670	.0100	1.00	11	829
RR 9,12	4147.8210	624.7250	.0100	1.00	13	832
RR 9,13	4149.1990	629.0090	.0140	.50	13	834
RR 9,14	4150.5460	633.1970	.0200	.25	11	835
RR 9,15	4151.8880	637.3710	.0140	.50	10	837
RR 9,16	4153.1890	641.4180	.0200	.25	9	840

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APPENDIX VI

LIST OF OBSERVED GROUND STATE COMBINATION DIFFERENCES FOR $\nu_3+\nu_4$ OF CH_3F

The following pages contain a list of the observed ground state combination differences for $\nu_3+\nu_4$ of CH_3F. The columns of the list, left to right, are: the assignment (cf. Chapter 4); the calculated combination difference (in cm^{-1}) from Appendix II; the observed combination difference (in cm^{-1}); the $\Delta\nu$ (weight = $(NORM)^2/(\Delta\nu)^2$); and the observed minus the calculated difference.

ASSIGN-MENT	CALCULATED GSCD	OBSERVED GSCD	DELTA NU	OBS-CALC
RQ 9,12	20.401	20.4100	.9999	.009
RQ 9,16	27.187	27.2350	.9999	.048
RQ 9,17	28.881	28.8510	.9999	-.030
RQ 9,20	33.960	33.9280	.9999	-.032
RP 9,10	35.706	35.7050	.0245	-.001
RP 9,11	39.103	39.1010	.9999	-.002
RP 9,12	42.499	42.5100	.9999	.011
RP 9,16	56.068	56.1040	.9999	.036
RP 9,17	59.456	59.4650	.9999	.009
RP 9,20	69.612	69.5930	.9999	-.019
QP 9, 9	17.039	16.8940	.9999	-.055
QP 9,12	22.098	22.0800	.0245	-.018
QP 9,13	23.795	23.8240	.0283	.029
QP 9,15	27.187	27.2160	.9999	.029
QP 9,16	28.881	28.8690	.9999	-.012
QP 9,17	30.575	30.6140	.9999	.039
QP 9,18	32.268	32.2490	.9999	-.019
QP 9,19	33.960	33.9810	.0283	.021
QP 9,20	35.652	35.6650	.0283	.013
RP 8,13	45.906	45.9030	.9999	-.003
RP 8,14	49.300	49.2240	.9999	-.076
RP 8,15	52.693	52.6670	.9999	-.026
RQ 8,13	22.105	22.1210	.9999	.016
RQ 8,14	23.802	23.7340	.9999	-.068
QP 8, 8	15.309	15.3060	.9999	-.003
QP 8, 9	17.009	16.9940	.9999	-.015
QP 8,10	18.708	18.7150	.9999	.007
QP 8,12	22.104	22.0940	.0283	-.010
QP 8,13	23.802	23.8240	.9999	.022
QP 8,14	25.499	25.4900	.9999	-.009
RP 7, 9	32.327	32.3150	.9999	-.012
RP 7,11	39.125	39.1380	.0245	.013
RQ 7,11	18.713	18.7280	.9999	.015
QP 7, 7	13.613	13.6210	.9999	.008
QP 7, 8	15.313	15.3180	.9999	.005
QP 7,10	18.713	18.7170	.9999	.004
QP 7,11	20.412	20.4100	.9999	-.002
QP 7,12	22.110	22.0960	.9999	-.014
QP 7,13	23.808	23.8050	.9999	-.003
QP 7,14	25.505	25.5040	.9999	-.001
QP 7,15	27.202	27.2150	.9999	.013
RQ 6, 8	13.616	13.6080	.9999	-.008
RQ 6, 9	15.317	15.3410	.9999	.024
RQ 6,12	20.416	20.4160	.9999	.000
RQ 6,16	27.208	27.2040	.9999	-.004
RQ 6,17	28.904	28.9060	.0283	.002
RP 6, 8	28.933	28.9270	.9999	-.006
RP 6, 9	32.334	32.3610	.9999	.027
RP 6,12	42.532	42.5260	.9999	-.006
RP 6,16	56.112	56.1140	.9999	.002

ASSIGN-MENT	CALCULATED GSCD	OBSERVED GSCD	DELTA NU	OBS-CALC
RP 6,17	59.503	59.5060	.0283	.003
QP 6, 6	11.915	11.9220	.0173	.007
QP 6, 8	15.317	15.3190	.0173	.002
QP 6, 9	17.017	17.0200	.0224	.003
QP 6,10	18.717	18.7130	.0224	-.004
QP 6,12	22.115	22.1100	.0173	-.005
QP 6,13	23.813	23.8090	.0141	-.004
QP 6,14	25.511	25.5080	.0173	-.003
QP 6,15	27.208	27.2010	.0245	-.007
QP 6,16	28.904	28.9100	.0200	.006
QP 6,17	30.599	30.6000	.0283	.001
QP 6,18	32.294	32.3050	.0245	.011
QP 6,19	33.987	33.9760	.9999	-.011
QP 6,20	35.680	35.6830	.0245	.003
QP 5, 5	10.215	10.2120	.9999	-.003
QP 5, 6	11.917	11.9060	.9999	-.011
QP 5, 8	15.320	15.3370	.9999	.017
QP 5, 9	17.020	17.0140	.9999	-.006
QP 5,10	18.721	18.7210	.9999	.000
QP 5,12	22.120	22.1300	.9999	.010
QP 5,13	23.818	23.8410	.9999	.023
RP 5, 7	25.536	25.6350	.9999	.099
RP 5, 8	28.938	28.9310	.9999	-.007
RP 5, 9	32.340	32.3610	.9999	.021
RP 5,10	35.741	35.7530	.9999	.012
RP 5,13	45.938	45.9310	.9999	-.007
RQ 5, 8	13.619	13.5940	.9999	-.025
RQ 5, 9	15.320	15.3470	.9999	.027
RQ 5,10	17.021	17.0320	.9999	.011
RQ 5,13	22.120	22.0900	.9999	-.030
RQ 4, 7	11.919	11.9570	.9999	.038
RQ 4, 8	13.621	13.6550	.9999	.034
RQ 4,11	18.724	18.8250	.9999	.101
RQ 4,13	22.123	22.1770	.0283	.054
RP 4, 7	25.540	25.5660	.0245	.026
RP 4, 8	28.943	28.9480	.9999	.005
RP 4,11	39.147	39.1920	.9999	.045
RP 4,13	45.945	45.9700	.0283	.025
QP 4, 6	11.919	11.8870	.9999	-.032
QP 4, 7	13.621	13.6090	.9999	-.012
QP 4, 8	15.322	15.2930	.9999	-.029
QP 4,13	23.822	23.7930	.0283	-.029
QP 3, 3	6.813	6.8100	.0283	-.003
QP 3, 4	8.516	8.5170	.0173	.001
QP 3, 5	10.218	10.2160	.0200	-.002
QP 3, 6	11.921	11.9260	.0245	.005
QP 3, 7	13.623	13.6230	.0173	.000
QP 3, 8	15.324	15.3330	.0245	.009
QP 3, 9	17.025	17.0420	.0173	.017
QP 3,10	18.726	18.7350	.0200	.009

ASSIGN-MENT	CALCULATED GSCD	OBSERVED GSCD	DELTA NU	OBS-CALC
QP 3,11	20.426	20.4240	.9999	-.002
QP 3,12	22.126	22.1300	.9999	.004
QP 3,13	23.825	23.8260	.9999	.001
QP 3,14	25.523	25.7720	.9999	.249
QP 3,15	27.221	27.2170	.9999	-.004
QP 3,16	28.918	28.9070	.0245	-.011
QP 3,17	30.614	30.5950	.0283	-.019
QP 3,18	32.309	32.3280	.9999	.019
QP 3,19	34.003	34.0570	.9999	.054
QP 3,20	35.697	35.7030	.9999	.006
RQ 3, 4	6.813	6.7930	.9999	-.020
RQ 3, 5	8.517	8.5090	.0245	-.008
RQ 3, 6	10.218	10.2110	.0245	-.007
RQ 3, 7	11.920	11.9230	.0200	.003
RQ 3, 8	13.622	13.6260	.0173	.004
RQ 3, 9	15.324	15.3430	.9999	.019
RQ 3,10	17.025	17.0150	.0245	-.010
RQ 3,11	18.726	18.7270	.9999	.001
RQ 3,12	20.426	20.4180	.9999	-.008
RQ 3,13	22.126	22.1270	.9999	.001
RQ 3,17	28.918	28.9150	.0283	-.003
RQ 3,18	30.614	30.6330	.9999	.019
RQ 3,19	32.309	32.2980	.9999	-.011
RQ 3,20	34.003	33.9860	.9999	-.017
RP 3, 4	15.328	15.3100	.9999	-.018
RP 3, 5	18.734	18.7250	.0245	-.009
RP 3, 6	22.139	22.1370	.0200	-.002
RP 3, 7	25.543	25.5460	.0173	.003
RP 3, 8	28.947	28.9590	.0245	.012
RP 3, 9	32.349	32.3850	.9999	.036
RP 3,10	35.751	35.7500	.0245	-.001
RP 3,11	39.152	39.1510	.9999	-.001
RP 3,12	42.552	42.5480	.9999	-.004
RP 3,13	45.951	45.9530	.0283	.002
RP 3,17	59.531	59.5100	.0283	-.021
RP 3,18	62.923	62.9610	.9999	.038
RP 3,19	66.312	66.3550	.9999	.043
RP 3,20	69.700	69.6890	.9999	-.011
QP 2, 2	5.110	5.1060	.9999	-.005
QP 2, 3	6.813	6.7890	.9999	-.024
QP 2, 4	8.516	8.5210	.9999	.005
QP 2, 5	10.219	10.2160	.9999	-.003
QP 2, 6	11.922	11.9330	.9999	.012
QP 2, 7	13.945	13.9300	.9999	-.015
QP 2, 8	15.325	15.3350	.9999	.010
QP 2, 9	17.027	17.0280	.0283	.001
QP 2,10	18.728	18.7310	.0173	.003
QP 2,11	20.428	20.4460	.0173	.018
QP 2,12	22.128	22.1330	.9999	.005
QP 2,13	23.827	23.8310	.0245	.004

ASSIGN-MENT	CALCULATED GSCD	OBSERVED GSCD	DELTA NU	OBS-CALC
QP 2,14	25.525	25.5150	.9999	-.010
QP 2,15	27.223	27.2160	.9999	-.007
QP 2,16	28.920	28.8900	.9999	-.030
QP 2,17	30.616	30.6210	.9999	.005
RQ 2, 3	5.110	5.1450	.9999	.035
RQ 2, 4	6.813	6.8010	.9999	-.013
RQ 2, 5	8.516	8.6360	.9999	.120
RQ 2, 6	10.219	10.2130	.9999	-.006
RQ 2, 7	11.922	11.9300	.0245	.008
RQ 2,10	17.027	17.0320	.0245	.004
RQ 2,11	18.728	18.7360	.0224	.009
RQ 2,13	22.128	22.1280	.0200	.000
RQ 2,14	23.827	23.8500	.9999	.023
RQ 2,15	25.525	25.5360	.0245	.011
RQ 2,16	27.223	27.2480	.9999	.024
RQ 2,17	28.920	28.9290	.9999	.009
RQ 2,18	30.616	30.6220	.9999	.005
RP 2, 3	11.924	11.9340	.9999	.010
RP 2, 4	15.330	15.3210	.9999	-.008
RP 2, 5	18.735	18.8520	.9999	.117
RP 2, 6	22.141	22.1460	.0283	.005
RP 2, 7	25.545	25.5380	.9999	-.007
RP 2,10	35.754	35.7620	.0224	.008
RP 2,11	39.156	39.1670	.0245	.011
RP 2,12	42.556	42.5410	.9999	-.015
RP 2,13	45.955	45.9590	.0245	.004
RP 2,14	49.352	49.3640	.0224	.012
RP 2,15	52.748	52.7520	.9999	.004
RP 2,16	56.143	56.1370	.9999	-.006
RP 2,17	59.536	59.5500	.0283	.014
RQ 1, 5	8.517	8.5220	.0224	.005
RQ 1, 6	10.220	10.2230	.0173	.003
RQ 1, 7	11.922	11.9250	.0245	.003
RQ 1, 8	13.624	13.6290	.0245	.005
RQ 1, 9	15.326	15.3300	.9999	.004
RQ 1,10	17.028	17.0300	.9999	.002
RQ 1,13	22.129	22.1400	.9999	.011
RQ 1,14	23.828	23.8250	.9999	-.003
RQ 1,15	25.527	25.5330	.0173	.006
RQ 1,16	27.224	27.2420	.9999	.018
RQ 1,17	28.922	28.9180	.0173	-.004
RQ 1,18	30.618	30.6260	.9999	.008
RQ 1,19	32.313	32.3090	.9999	-.004
RQ 1,20	34.008	34.0020	.9999	.012
QP 1, 1	3.407	3.4150	.9999	.008
QP 1, 2	5.110	5.1160	.0200	.006
QP 1, 3	6.814	6.8140	.9999	.000
QP 1, 4	8.517	8.5230	.9999	.006
QP 1, 5	10.219	10.2270	.9999	.008
QP 1, 6	11.922	11.9240	.9999	.002

ASSIGN-MENT	CALCULATED GSCD	OBSERVED GSCD	DELTA NU	OBS-CALC
QP 1, 7	13.624	13.6110	.9999	-.013
QP 1, 8	15.005	15.0210	.9999	.016
QP 1, 9	17.028	16.9890	.0283	-.039
QP 1,10	18.729	18.7210	.9999	-.008
QP 1,11	20.429	20.4380	.9999	.009
QP 1,12	22.129	22.1300	.9999	.001
QP 1,13	23.828	23.8310	.0224	.003
QP 1,14	25.527	25.5300	.0245	.003
QP 1,15	27.224	27.2160	.9999	-.008
QP 1,16	28.922	28.9320	.9999	.010
QP 1,17	30.618	30.6140	.9999	.004
QP 1,18	32.313	32.3160	.9999	.003
QP 1,19	34.008	34.0130	.9999	.005
QP 1,20	35.702	35.7240	.9999	.022
RP 1, 5	18.736	18.7490	.9999	.013
RP 1, 6	22.142	22.1470	.9999	.005
RP 1, 7	25.547	25.5370	.9999	-.010
RP 1, 8	28.629	28.6500	.9999	.021
RP 1, 9	32.354	32.3190	.9999	-.035
RP 1,10	35.756	35.7530	.9999	-.003
RP 1,13	45.957	45.9700	.9999	-.013
RP 1,14	49.354	49.3520	.9999	-.002
RP 1,15	52.751	52.7430	.9999	-.008
RP 1,16	56.146	56.1580	.0141	.012
RP 1,17	59.540	59.5320	.9999	-.008
RP 1,18	62.960	62.9410	.9999	-.019
RP 1,19	66.322	66.3220	.9999	.000
RP 1,20	69.709	69.7460	.9999	.037
RP 0, 2	8.518	8.4910	.0224	-.027
RP 0, 3	11.924	11.8690	.0173	-.055
RP 0, 4	15.331	15.3380	.0245	.007
RP 0, 5	18.737	18.7430	.0283	.006
RP 0, 6	22.142	22.1330	.9999	-.009
RP 0, 7	25.547	25.5600	.9999	.013
RP 0, 8	28.951	28.9680	.0224	.017
RP 0, 9	32.354	32.3640	.0283	.010
RP 0,10	35.757	35.7510	.0245	-.006
RP 0,11	39.158	39.1630	.9999	.005
RP 0,12	42.559	42.5610	.0245	.002
RP 0,13	45.958	45.9630	.9999	.005
RP 0,14	49.356	49.3570	.9999	.001
RP 0,15	52.752	52.7650	.0224	.013
RP 0,16	56.147	56.1360	.0245	-.011
RP 0,17	59.541	59.5740	.0173	.033
RP 0,18	62.932	62.8990	.9999	-.033
RP 0,19	66.323	66.3230	.0245	.000
RP 0,20	69.711	69.7060	.0173	-.005
RP 0,21	73.097	73.0970	.0173	.000
QP 1, 2	5.110	5.1250	.9999	.015
QP 1, 3	6.814	6.5970	.9999	-.217

ASSIGN-MENT	CALCULATED GSCD	OBSERVED GSCD	DELTA NU	OBS-CALC
QP 1, 4	8.517	8.4950	.9999	-.022
QP 1, 5	10.220	10.2310	.0245	.011
QP 1, 6	11.922	11.9160	.9999	-.006
QP 1, 7	13.624	13.6190	.9999	-.005
QP 1, 8	15.326	15.3300	.9999	.004
QP 1, 9	17.028	17.0440	.9999	.016
QP 1,10	18.729	18.7470	.0283	.018
QP 1,11	20.429	20.4150	.0283	-.014
QP 1,12	22.129	22.1090	.9999	-.020
QP 1,10	18.729	18.7440	.9999	.015
QP 1,11	20.429	20.4270	.9999	-.002
QP 1,12	22.129	22.1440	.0283	.015
QP 1,13	23.828	23.8460	.9999	.018
QP 1,14	25.527	25.5330	.0245	.006
QP 1,16	28.922	28.9350	.9999	.013
QP 1,17	30.618	30.6090	.9999	-.009
QP 1,18	32.313	32.3160	.9999	.003
QP 1,19	34.008	34.4700	.9999	.462
QP 1,20	35.701	35.6760	.9999	-.025
RP 1, 2	8.518	8.5340	.9999	.016
RP 1, 3	11.924	11.7150	.9999	-.209
RP 1, 4	15.330	15.3140	.9999	-.016
RP 1, 5	18.736	18.7440	.0200	.008
RP 1, 6	22.142	22.1460	.9999	.004
RP 1, 7	25.546	25.5450	.9999	-.001
RP 1, 8	28.951	28.9640	.9999	.013
RP 1, 9	32.354	32.3580	.9999	.004
RP 1,10	35.756	35.7550	.0245	-.001
RP 1,12	42.558	42.5490	.0283	-.009
RP 1,10	35.756	35.7960	.9999	.040
RP 1,12	42.558	42.5800	.0245	.022
RP 1,13	45.957	46.0090	.0245	.052
RP 1,14	49.355	49.3590	.0245	.004
RP 1,16	56.146	56.1690	.9999	.023
RP 1,17	59.540	59.5400	.9999	.000
RP 1,18	62.931	62.9390	.9999	.008
RP 1,19	66.321	66.7820	.9999	.461
RP 1,20	69.710	69.6820	.9999	-.028
RQ 1, 2	3.407	3.4090	.9999	.002
RQ 1, 3	5.110	5.1180	.0224	.008
RQ 1, 4	6.814	6.8190	.0283	.005
RQ 1, 5	8.517	8.5130	.0245	-.004
RQ 1, 6	10.220	10.2300	.9999	.010
RQ 1, 7	11.922	11.9260	.0245	.004
RQ 1, 8	13.624	13.6340	.0245	.010
RQ 1, 9	15.326	15.3140	.0245	-.012
RQ 1,10	17.028	17.0080	.0245	-.020
RQ 1,12	20.429	20.4400	.9999	.011
RQ 1,10	17.028	17.0520	.9999	.024
RQ 1,11	18.729	18.7390	.0283	.010
RQ 1,12	20.429	20.4360	.0245	.007

ASSIGN-MENT	CALCULATED GSCD	OBSERVED GSCD	DELTA NU	OBS-CALC
RQ 1,13	22.129	22.1630	.9999	.034
RQ 1,14	23.828	23.8260	.0200	-.002
RQ 1,15	25.527	25.5240	.0173	-.003
RQ 1,16	27.225	27.2340	.0245	.009
RQ 1,17	28.922	28.9310	.0245	.009
RQ 1,18	30.618	30.6230	.0200	.005
RQ 1,19	32.313	32.3120	.0283	-.001
RQ 1,20	34.008	34.0060	.9999	-.002
RP 2, 3	11.924	11.9410	.9999	.017
RP 2, 4	15.330	15.3290	.9999	-.001
RP 2, 6	22.141	22.1500	.0245	.009
RP 2, 7	25.545	25.5560	.0200	.011
RP 2,10	35.754	35.7630	.9999	.009
RP 2,11	39.156	39.1510	.0245	-.005
RP 2,12	42.556	42.5690	.0283	.013
RP 2,14	49.352	49.3650	.0200	.013
RP 2,15	52.748	52.7430	.0245	-.005
RP 2,16	56.143	56.1190	.9999	-.024
RP 2,17	59.536	59.5340	.0245	-.002
RP 2,19	66.318	66.2840	.9999	-.034
RP 2,21	73.092	73.0610	.9999	-.031
QP 2, 3	6.813	6.8100	.9999	-.003
QP 2, 4	8.516	8.5170	.9999	.001
QP 2, 6	11.922	11.9340	.0224	.012
QP 2, 7	13.624	13.6290	.0200	.005
QP 2, 9	17.027	17.0230	.9999	-.004
QP 2,10	18.406	18.4270	.9999	-.021
QP 2,11	20.428	20.4270	.0245	-.001
QP 2,12	22.128	22.1450	.0283	.017
QP 2,14	25.525	25.5200	.9999	-.005
QP 2,15	27.223	27.2100	.9999	-.013
QP 2,16	28.920	28.9040	.9999	-.016
QP 2,17	30.616	30.6140	.0245	-.002
QP 2,19	34.006	33.9760	.9999	-.030
QP 2,20	35.700	35.6830	.9999	-.017
QP 2,21	37.392	37.3720	.9999	-.020
QP 2,23	40.783	40.7830	.0283	.000
RQ 2, 3	5.110	5.1310	.9999	.021
RQ 2, 4	6.813	6.8120	.0245	-.001
RQ 2, 5	8.516	8.5150	.9999	-.001
RQ 2, 6	10.219	10.2160	.0173	-.003
RQ 2, 7	11.922	11.9280	.0200	.006
RQ 2, 8	13.624	13.6050	.9999	-.019
RQ 2,10	17.027	17.0140	.9999	-.013
RQ 2,11	18.728	18.7240	.0200	-.004
RQ 2,12	20.428	20.4240	.0283	-.004
RQ 2,13	22.128	22.1310	.0200	.003
RQ 2,14	23.827	23.8440	.9999	.017
RQ 2,15	25.525	25.5330	.9999	.008
RQ 2,16	27.223	27.2150	.0224	-.008

ASSIGN-MENT	CALCULATED GSCD	OBSERVED GSCD	DELTA NU	OBS-CALC
RQ 2,17	28.920	28.9200	.0200	.000
RQ 2,18	30.616	30.6420	.9999	.026
RQ 2,19	32.312	32.3080	.9999	-.004
RQ 2,21	35.700	35.6900	.0283	-.010
RQ 2,22	37.392	37.3900	.9999	-.002
RP 3, 4	15.328	15.3060	.9999	-.022
RP 3, 6	22.139	22.2480	.0224	.009
RP 3, 7	25.543	25.5470	.0224	.004
RP 3, 8	28.947	28.9830	.9999	.036
RP 3, 9	32.349	32.3460	.9999	-.003
RP 3,10	35.751	35.7510	.0245	.000
RP 3,11	39.152	39.1630	.0173	.011
RP 3,12	42.552	42.6020	.9999	.050
RP 3,14	49.348	49.3520	.0173	.004
RP 3,15	52.744	52.7550	.9999	.011
RP 3,16	56.138	56.1490	.0200	.011
RP 3,17	59.531	59.5410	.9999	.010
RP 3,18	62.923	62.9300	.9999	.007
RP 3,19	66.312	66.3080	.9999	-.004
RP 3,21	73.085	73.0910	.9999	.006
RQ 3, 4	6.813	6.8160	.0173	.003
RQ 3, 5	8.516	8.5280	.0245	.012
RQ 3, 6	10.218	10.2210	.0173	.003
RQ 3, 7	11.921	11.9180	.0141	-.003
RQ 3, 8	13.623	13.6440	.0224	.021
RQ 3, 9	15.324	15.3330	.9999	.009
RQ 3,10	17.025	17.0240	.0200	-.001
RQ 3,11	18.726	18.7270	.0173	.001
RQ 3,12	20.426	20.4580	.9999	.032
RQ 3,14	23.825	23.8140	.9999	-.011
RQ 3,15	25.523	25.5210	.0245	-.002
RQ 3,16	27.221	27.2230	.0173	.002
RQ 3,17	28.918	28.9260	.9999	.008
RQ 3,18	30.614	30.6070	.9999	-.007
RQ 3,19	32.309	32.3030	.0173	-.006
RQ 3,21	35.697	35.6940	.9999	-.003
QP 3, 4	8.516	8.4890	.9999	-.027
QP 3, 6	11.921	11.9270	.0245	.006
QP 3, 7	13.623	13.6290	.0224	.006
QP 3, 8	15.324	15.3380	.9999	.014
QP 3, 9	17.025	17.0130	.9999	-.012
QP 3,10	18.726	18.7270	.0245	.001
QP 3,11	20.426	20.4360	.0200	.010
QP 3,12	22.126	22.1440	.9999	.018
QP 3,13	23.825	23.8310	.9999	.006
QP 3,14	25.523	25.5380	.9999	.015
QP 3,15	27.221	27.2340	.9999	.013
QP 3,16	28.918	28.9260	.0173	.008
QP 3,17	30.614	30.6160	.9999	.002
QP 3,18	32.309	32.3230	.9999	.014

ASSIGN-MENT	CALCULATED GSCD	OBSERVED GSCD	DELTA NU	OBS-CALC
QP 3,19	34.003	34.0050	.9999	.002
QP 3,20	35.697	35.6930	.9999	-.004
QP 3,22	37.389	37.3970	.9999	.008
QP 4, 8	15.322	15.3200	.9999	-.002
QP 4,10	18.724	18.7190	.9999	-.005
QP 4,12	22.123	22.1220	.9999	-.001
QP 4,13	23.822	23.8190	.9999	-.003
QP 4,15	27.217	27.2140	.9999	-.003
QP 4,16	28.914	28.8770	.0173	-.037
RQ 4, 6	10.217	10.2190	.0173	.002
RQ 4, 7	11.919	12.2320	.9999	.113
RQ 4, 8	13.621	13.6170	.0200	-.004
RQ 4, 9	15.322	15.3180	.0173	-.004
RQ 4,10	17.023	17.0230	.0224	.000
RQ 4,11	18.724	18.7340	.0224	.010
RQ 4,12	20.424	20.4500	.9999	.026
RQ 4,13	22.123	22.1290	.0173	.006
RQ 4,14	23.822	23.8300	.0224	.008
RQ 4,15	25.520	25.5200	.0245	.000
RQ 4,16	27.217	27.2300	.0173	.013
RP 4, 8	28.943	28.9370	.9999	-.006
RP 4,10	35.747	35.7420	.9999	-.005
RP 4,12	42.547	42.5720	.0245	.025
RP 4,13	45.945	45.9480	.9999	.003
RP 4,15	52.737	52.7340	.9999	-.003
RP 4,16	56.131	56.1070	.0200	-.024
RQ 5, 8	13.619	13.6060	.0283	-.013
RQ 5, 9	15.320	15.3440	.9999	.024
RQ 5,10	17.020	17.0170	.0200	-.003
RQ 5,11	18.721	18.7250	.9999	.004
RQ 5,12	20.420	20.4190	.0245	-.001
RQ 5,13	22.120	22.1230	.0173	.003
RQ 5,14	23.818	23.8130	.0283	-.005
RQ 5,15	25.516	25.5150	.9999	-.001
RQ 5,16	27.213	27.2090	.0283	-.004
RQ 5,17	28.910	28.9310	.9999	.021
RQ 5,18	30.605	30.6220	.9999	.017
RQ 5,19	32.300	32.2970	.0283	-.003
RQ 5,20	33.994	34.0330	.0283	.039
RP 5,14	49.334	49.3140	.9999	-.020
RP 5,16	56.123	56.1330	.9999	.010
RP 5,18	62.905	62.9330	.9999	.028
QP 5,14	25.516	25.5010	.9999	-.015
QP 5,16	28.910	28.9240	.9999	.014
QP 5,18	32.300	31.9000	.9999	-.400
RQ 6, 7	11.915	11.9890	.9999	.074
RQ 6, 8	13.616	13.6110	.0200	-.005
RQ 6, 9	15.317	15.3130	.0141	-.004
RQ 6,10	17.017	17.0200	.0212	.003
RQ 6,11	18.717	18.7170	.0173	.000

ASSIGN-MENT	CALCULATED GSCD	OBSERVED GSCD	DELTA NU	OBS-CALC
RQ 6,12	20.417	20.4190	.0173	.002
RQ 6,13	22.115	22.1250	.9999	.010
RQ 6,14	23.814	23.8150	.0141	.001
RQ 6,15	25.511	25.5120	.0224	.001
RQ 6,16	27.208	27.1930	.0173	-.015
RQ 6,17	28.904	28.9340	.9999	.030
RQ 6,18	30.599	30.5950	.0173	-.004
RQ 6,19	32.294	32.2910	.0224	-.003
RQ 6,20	33.987	33.9770	.0173	-.010
RQ 6,21	35.680	35.6730	.0245	-.007
RQ 6,22	37.371	37.3710	.9999	.000
RQ 6,23	39.062	39.0540	.0245	-.008
RQ 6,24	40.751	40.7450	.0200	-.006
QP 6, 7	13.616	13.5460	.9999	-.070
QP 6, 9	17.017	16.9920	.0224	-.025
QP 6,13	23.814	23.8120	.9999	-.002
QP 6,15	27.208	27.2250	.9999	.017
QP 6,18	32.294	32.2960	.9999	.002
QP 6,19	33.987	34.0020	.9999	.015
QP 6,20	35.680	35.6870	.9999	.007
QP 6,21	37.371	37.3550	.9999	-.016
QP 6,24	42.440	42.4510	.9999	.011
QP 6,25	44.127	44.1490	.9999	.022
RP 6, 7	25.531	25.5350	.0212	.004
RP 6, 9	32.334	32.3050	.0224	-.029
RP 6,13	45.929	45.9370	.9999	.008
RP 6,15	52.719	52.7370	.9999	.018
RP 6,18	62.893	62.8910	.9999	-.002
RP 6,19	66.281	66.2930	.9999	.012
RP 6,20	69.667	69.6640	.9999	-.003
RP 6,21	73.051	73.0280	.9999	-.023
RP 6,24	83.191	83.1960	.9999	.005
RQ 7, 8	13.613	13.6270	.9999	.014
RQ 7, 9	15.313	15.3050	.9999	-.008
RQ 7,10	17.013	17.0230	.0245	.010
RQ 7,11	18.713	18.7150	.0245	.002
RQ 7,12	20.412	20.4040	.0245	-.008
RQ 7,15	25.505	25.5030	.9999	-.002
RQ 7,16	27.202	27.2000	.0245	-.002
RQ 7,19	32.286	32.2890	.9999	.003
RQ 7,20	33.979	34.0520	.9999	.073
QP 7, 9	17.013	17.0270	.9999	.014
QP 7,19	33.979	33.9550	.9999	-.024
RP 7, 9	32.327	32.3320	.0224	.005
RP 7,14	49.313	49.3280	.9999	.015
RP 7,19	66.266	66.2440	.9999	-.022
RQ 8,11	18.708	18.8900	.9999	.182
RQ 8,15	25.499	25.4990	.0224	.000
RQ 8,16	27.195	27.2040	.9999	.009
RQ 8,17	28.890	28.8720	.9999	-.018

ASSIGN-MENT	CALCULATED GSCD	OBSERVED GSCD	DELTA NU	OBS-CALC
RQ 8,18	30.584	30.6110	.9999	.027
RQ 8,19	32.278	32.2550	.9999	-.023
RP 8,14	49.301	49.3260	.9999	.025
RP 8,16	56.084	56.0580	.9999	-.026
QP 8,16	28.890	28.8540	.9999	-.036
QP 9,13	23.795	23.7670	.9999	-.028
QP 9,17	30.575	30.5840	.9999	.009
QP 9,19	33.960	33.9550	.9999	-.005
RP 9,13	45.893	45.8580	.9999	-.035
RP 9,17	59.456	59.4540	.9999	-.002
RQ 9,10	17.004	17.0140	.0200	.010
RQ 9,11	18.702	18.7010	.0224	-.001
RQ 9,12	20.400	20.3960	.9999	-.004
RQ 9,13	22.098	22.0910	.0224	-.007
RQ 9,14	23.795	23.7790	.9999	-.016
RQ 9,15	25.491	25.4800	.9999	-.011
RQ 9,16	27.187	27.2020	.9999	.015
RQ 9,17	28.881	28.8700	.0283	-.011

APPENDIX VII

LIST OF ASSIGNMENTS AND FREQUENCIES OF OBSERVED TRANSITIONS FOR $\nu_1+\nu_3$ OF CH_3F

The following pages contain a list of the observed transitions of $\nu_1+\nu_3$ of CH_3F. The columns of the list, left to right, are: the assignment ($\Delta K,\Delta J,K,J$); the observed frequency (in cm^{-1}); the observed fringe number (from which the frequency may be calculated - cf. Chapter 7); the $\Delta\nu$ (weight = $(NORM)^2/(\Delta\nu)^2$); the weight; the observed line height; and the line number.

ASSIGN-MENT	OBSERVED FREQUENCY	FRINGE NUMBER	DELTA NU	WEIGHT	INT	LINE NO
QP 0, 1	4009.2680	193.8380	.9999	.00	5	244
QP 0, 2	4007.5650	188.5440	.0200	.25	10	235A
QP 0, 4	4004.0010	177.4590	.0200	.25	9	220A
QP 0, 5	4002.2030	171.8670	.0200	.25	9	212A
QP 0, 6	4000.3890	166.2260	.0200	.25	10	206
QP 0, 7	3998.5380	160.4710	.9999	.00	14	198A
QP 0, 8	3996.6720	154.6660	.9999	.00	16	190
QP 0, 9	3994.7840	148.7940	.0140	.50	15	181A
QP 0,10	3992.8760	142.8620	.0200	.25	12	173A
QP 0,11	3990.9460	136.8580	.9999	.00	13	167
QP 0,12	3988.9940	130.7900	.9999	.00	12	158A
QP 0,13	3987.0340	124.6940	.9999	.00	11	148
QP 0,14	3985.0230	118.4410	.0200	.25	9	138
QP 0,15	3983.0270	112.2330	.0200	.25	6	128
QP 0,16	3981.0120	105.9670	.9999	.00	7	116
QP 0,17	3978.9620	99.5900	.0200	.25	6	106
QP 0,18	3976.8330	92.9700	.9999	.00	5	94A
QP 0,20	3972.5540	79.6520	.0200	.25	6	77
QP 0,21	3970.4390	73.0860	.9999	.00	5	70
QR 0, 0	4012.6790	204.4480	.0140	.50	11	259
QR 0, 1	4014.2960	209.4730	.0100	1.00	16	277
QR 0, 2	4015.9220	214.5310	.9999	.00	10	286A
QR 0, 3	4017.5410	219.5670	.0200	.25	9	293
QR 0, 4	4019.1240	224.4890	.0200	.25	13	300A
QR 0, 5	4020.6770	229.3210	.9999	.00	17	308
QR 0, 6	4022.2300	234.1490	.9999	.00	22	316
QR 0, 7	4023.7410	238.8480	.0200	.25	16	322A
QR 0, 8	4025.2410	243.5120	.0140	.50	13	330A
QR 0, 9	4026.7060	248.0690	.0140	.50	13	338A
QR 0,10	4028.1500	252.5610	.0140	.50	15	348
QR 0,11	4029.5890	257.0360	.9999	.00	21	355
QR 0,12	4030.9940	261.4030	.0140	.50	14	362
QR 0,13	4032.3770	265.7050	.0140	.50	11	370
QR 0,14	4033.7560	269.9950	.0200	.25	14	376
QR 0,15	4035.0740	274.0920	.0140	.50	6	383
QR 0,17	4037.6290	282.0380	.0200	.25	19	395
QR 0,19	4040.0850	289.6800	.9999	.00	9	407C
QP 1, 2	4007.5400	188.4650	.9999	.00	9	135
QP 1, 4	4003.9570	177.3220	.9999	.00	5	220
QP 1, 5	4002.1670	171.7550	.0200	.25	8	212
QP 1, 6	4000.3480	166.0980	.0200	.25	8	205A
QP 1, 7	3998.4980	160.3460	.9999	.00	14	198
QP 1, 8	3996.6720	154.6660	.9999	.00	16	190
QP 1, 9	3994.7480	148.6820	.0140	.50	15	181
QP 1,10	3992.8380	142.7420	.0200	.25	14	173
QP 1,11	3990.9020	136.7210	.9999	.00	12	166A
QP 1,12	3988.9380	130.6150	.0200	.25	10	158
QP 1,13	3986.9620	124.4690	.0200	.25	9	147
QP 1,14	3984.9590	118.2390	.9999	.00	6	137A
QP 1,15	3982.9280	111.9250	.9999	.00	8	127

ASSIGN-MENT	OBSERVED FREQUENCY	FRINGE NUMBER	DELTA NU	WEIGHT	INT	LINE NO
QP 1,16	3980.8700	105.5230	.9999	.00	6	115
QP 1,17	3978.8030	99.0970	.9999	.00	6	105
QP 1,18	3976.7030	92.5650	.9999	.00	10	93A
QP 1,19	3974.6080	86.0490	.9999	.00	11	86
QP 1,20	3972.4560	79.3560	.0200	.25	7	76C
QP 1,21	3970.3050	72.6670	.9999	.00	6	69
QP 1,22	3968.1290	65.9020	.9999	.00	6	61
QQ 1, 3	4010.7750	198.5260	.0200	.25	5	252A
QQ 1, 4	4010.7150	198.3390	.0200	.25	7	252
QQ 1, 6	4010.4360	197.4720	.9999	.00	20	251
QQ 1, 8	4010.0960	196.4130	.0200	.25	7	249A
QQ 1,10	4009.6240	194.9460	.9999	.00	14	246A
QQ 1,16	4007.7140	189.0060	.0200	.25	6	236
QR 1, 1	4014.2570	209.3540	.9999	.00	14	276A
QR 1, 2	4015.8760	214.3850	.9999	.00	12	286
QR 1, 3	4017.5020	219.4450	.9999	.00	6	292B
QR 1, 4	4019.0920	224.3900	.0200	.25	11	300
QR 1, 5	4020.6440	229.2170	.9999	.00	15	307C
QR 1, 6	4022.2300	234.1490	.9999	.00	22	316
QR 1, 7	4023.6970	238.7110	.0100	1.00	18	322
QR 1, 8	4025.1940	243.3680	.0100	1.00	13	330
QR 1, 9	4026.6530	247.9050	.0140	.50	13	338
QR 1,10	4028.0990	252.4020	.0200	.25	11	347
QR 1,11	4029.5130	256.7980	.0200	.25	17	254B
QR 1,12	4030.9130	261.1520	.0200	.25	11	361
QR 1,13	4032.2990	265.4640	.0200	.25	18	369
QR 1,14	4033.6240	269.5830	.0140	.50	11	375B
QR 1,15	4034.9350	273.6600	.0200	.25	11	382A
QR 1,17	4037.5290	281.7280	.0140	.50	24	394A
QR 1,18	4038.7750	285.6070	.9999	.00	15	401
QR 1,19	4039.9930	289.3950	.9999	.00	12	407B
QR 1,20	4041.2040	293.1590	.9999	.00	16	412A
QR 1,21	4042.3770	296.8070	.9999	.00	9	418A
QR 2, 2	4015.7550	214.0140	.0200	.25	4	285
QR 2, 3	4017.3660	219.0230	.9999	.00	11	292A
QR 2, 4	4018.9660	223.9980	.0200	.25	6	299
QR 2, 5	4020.5220	228.8380	.0200	.25	11	307A
QR 2, 6	4022.0630	233.6290	.0200	.25	11	314A
QR 2, 7	4023.5780	238.3430	.0200	.25	15	321
QR 2, 8	4025.0830	243.0210	.0140	.50	11	329
QR 2, 9	4026.5710	247.6490	.9999	.00	17	337
QR 2,10	4027.9860	252.0500	.9999	.00	15	346
QR 2,11	4029.4020	256.4550	.0100	1.00	22	354A
QR 2,12	4030.8140	260.8460	.0100	1.00	11	360
QR 2,14	4033.5220	269.2650	.0200	.25	19	375A
QR 2,15	4034.8540	273.4080	.9999	.00	21	382
QR 2,16	4036.1900	277.5630	.9999	.00	30	388
QR 2,17	4037.4650	281.5300	.9999	.00	23	394
QR 2,18	4038.6920	285.3480	.0200	.25	13	400
QR 2,19	4039.9200	289.1670	.9999	.00	11	407A

ASSIGN-MENT	OBSERVED FREQUENCY	FRINGE NUMBER	DELTA NU	WEIGHT	INT	LINE NO
QP 2, 3	4005.5980	182.4250	.9999	.00	8	226A
QP 2, 4	4003.8190	176.8930	.9999	.00	7	219A
QP 2, 5	4002.0530	171.4020	.9999	.00	5	211
QP 2, 7	3998.3820	159.9860	.9999	.00	7	197
QP 2, 8	3996.5180	154.1870	.9999	.00	11	189
QP 2, 9	3994.6230	148.2940	.0140	.50	8	180
QP 2,10	3992.7250	142.3920	.0140	.50	8	172
QP 2,11	3990.7860	136.3620	.9999	.00	11	165A
QP 2,12	3988.8300	130.2800	.9999	.00	11	157
QP 2,13	3986.8580	124.1450	.0200	.25	11	146
QP 2,14	3984.8540	117.9140	.0140	.50	5	137
QP 2,15	3892.8330	111.6290	.0200	.25	11	126A
QP 2,16	3980.7860	105.2620	.0200	.25	10	114A
QP 2,17	3978.7240	98.8260	.0200	.25	11	104
QP 2,18	3976.6310	92.3400	.9999	.00	8	92A
QP 2,20	3972.4030	79.1940	.9999	.00	7	76B
QQ 2, 2	4010.7150	198.3390	.0200	.25	7	252
QQ 2, 5	4010.4360	197.4720	.9999	.00	20	251
QQ 2, 8	4009.9480	195.9550	.9999	.00	6	248A
QQ 2, 9	4009.7670	195.3900	.9999	.00	12	247
QQ 2,11	4009.2680	193.8380	.9999	.00	5	244
QQ 2,12	4008.9980	192.9990	.9999	.00	12	243
QQ 2,14	4008.3400	190.9540	.0200	.25	7	238B
QP 3, 4	4003.6290	176.3020	.0200	.25	8	218
QP 3, 5	4001.8540	170.7810	.9999	.00	12	210
QP 3, 6	4000.0240	165.0910	.0200	.25	7	203
QP 3, 7	3998.1930	159.3980	.0140	.50	10	196
QP 3, 8	3996.3410	153.6370	.9999	.00	10	188
QP 3, 9	3994.4620	147.7950	.0140	.50	11	179
QP 3,10	3992.5640	141.8920	.0100	1.00	11	171
QP 3,11	3990.6410	135.9110	.9999	.00	11	165
QP 3,12	3988.7030	129.8830	.0140	.50	10	156
QP 3,13	3986.7400	123.7800	.9999	.00	10	145
QP 3,14	3984.7610	117.6260	.0140	.50	10	136
QP 3,15	3982.7770	111.4550	.9999	.00	10	126
QP 3,16	3980.7500	105.1490	.0200	.25	9	114
QP 3,17	3978.7240	98.8260	.0200	.25	11	104
QP 3,18	3976.6310	92.3400	.9999	.00	8	92A
QP 3,20	3972.4560	79.3560	.0200	.25	7	76C
QP 3,21	3970.3050	72.6670	.9999	.00	6	69
QP 3,22	3968.1290	65.9020	.9999	.00	6	61
QQ 3, 3	4010.4360	197.4720	.9999	.00	20	251
QQ 3, 4	4010.3610	197.2370	.0200	.25	8	250A
QQ 3, 5	4010.2360	196.8480	.0200	.25	7	250
QQ 3, 6	4010.0960	196.4130	.0200	.25	7	249A
QQ 3, 7	4009.9480	195.9550	.9999	.00	6	248A
QQ 3, 8	4009.7670	195.3900	.9999	.00	12	247
QQ 3, 9	4009.5800	194.8080	.9999	.00	17	246
QQ 3,12	4008.8410	192.5110	.9999	.00	11	242
QQ 3,13	4008.5470	191.5960	.9999	.00	9	240A

ASSIGN-MENT	OBSERVED FREQUENCY	FRINGE NUMBER	DELTA NU	WEIGHT	INT	LINE NO
QQ 3,14	4008.2800	190.7650	.0200	.25	2	238A
QQ 3,15	4007.9720	189.8070	.9999	.00	4	237A
QQ 3,16	4007.6070	188.6740	.9999	.00	9	235B
QQ 3,17	4007.2160	187.4580	.9999	.00	11	233C
QQ 3,18	4006.8530	186.3280	.9999	.00	11	232
QQ 3,19	4006.4840	185.1810	.9999	.00	16	230
QQ 3,20	4006.0280	183.7630	.0140	.50	9	228
QQ 3,21	4005.5610	182.3120	.9999	.00	8	226
QR 3, 3	4017.1720	218.4180	.0140	.50	6	291
QR 3, 4	4018.7590	223.3560	.0200	.25	10	298
QR 3, 5	4020.3270	228.2320	.0200	.25	13	306A
QR 3, 6	4021.8820	233.0660	.9999	.00	13	313A
QR 3, 7	4023.4070	237.8110	.0100	1.00	11	320
QR 3, 8	4024.9160	242.5010	.9999	.00	19	328
QR 3, 9	4026.3990	247.1160	.9999	.00	17	336
QR 3,10	4027.8550	251.6420	.9999	.00	18	345
QR 3,11	4029.2950	256.1220	.0200	.25	16	353A
QR 3,12	4030.7170	260.5430	.0140	.50	19	359
QR 3,13	4032.1120	264.8800	.0140	.50	15	367
QR 3,14	4033.4830	269.1600	.0200	.25	23	375
QR 3,15	4034.8540	273.4080	.9999	.00	21	382
QR 3,16	4036.1900	277.5630	.9999	.00	30	388
QR 3,17	4037.4650	281.5300	.9999	.00	23	394
QR 3,18	4038.7750	285.6070	.9999	.00	15	401
QR 3,19	4039.9930	289.3950	.9999	.00	12	407B

APPENDIX VIII

LIST OF OBSERVED COMBINATION DIFFERENCES FOR $\nu_1+\nu_3$ OF CH_3F

The following pages contain a list of the observed ground state combination differences for $\nu_1+\nu_3$ of CH_3F. The columns of the list, left to right, are: the assignment (cf. Chapter 4); the calculated combination difference (in cm^{-1}) from Appendix II; the observed combination difference (in cm^{-1}); the $\Delta\nu$ (weight = $(NORM)^2/(\Delta\nu)^2$); and the observed minus the calculated combination difference.

ASSIGN-MENT	CALCULATED GSCD	OBSERVED GSCD	DELTA NU	OBS-CALC
RP 0, 1	5.111	5.1140	.0245	.003
RP 0, 3	11.924	11.9210	.9999	-.003
RP 0, 4	15.331	15.3380	.0283	.007
RP 0, 5	18.737	18.7350	.0283	-.002
RP 0, 6	22.142	22.1390	.9999	-.003
RP 0, 7	25.547	25.5580	.9999	.011
RP 0, 8	28.951	28.9570	.0245	.006
RP 0, 9	32.354	32.3650	.0245	.011
RP 0,10	35.757	35.7600	.9999	.003
RP 0,11	39.158	39.1560	.9999	-.002
RP 0,12	42.559	42.5550	.9999	-.004
RP 0,13	45.958	45.9710	.0245	.013
RP 0,14	49.356	49.3500	.0245	-.006
RP 0,15	52.752	52.7440	.9999	-.008
RP 0,16	56.147	56.1120	.0245	-.035
RP 0,20	69.711	69.6460	.9999	-.065
RP 1, 3	11.924	11.9190	.9999	-.005
RP 1, 4	15.331	15.3350	.9999	.004
RP 1, 5	18.736	18.7440	.0283	.008
RP 1, 6	22.142	22.1460	.9999	.004
RP 1, 7	25.547	25.5580	.9999	.011
RP 1, 8	28.951	28.9490	.0173	-.002
RP 1, 9	32.354	32.3660	.0224	.012
RP 1,10	35.756	35.7510	.9999	-.005
RP 1,12	42.558	42.5510	.0283	-.007
RP 1,13	45.957	45.9540	.0283	-.003
RP 1,14	49.355	49.3710	.9999	.016
RP 1,15	52.751	52.7540	.9999	.003
RP 1,16	56.146	56.1320	.9999	-.014
RP 1,18	62.931	62.9210	.9999	-.010
RP 1,19	66.321	66.3190	.9999	-.002
RP 1,20	69.710	69.6880	.9999	-.022
RP 1,21	73.096	73.0750	.9999	-.021
RQ 1, 3	5.110	5.1010	.9999	-.009
RQ 1, 4	6.814	6.7870	.9999	.073
RQ 1, 6	10.220	10.2080	.9999	-.012
RQ 1, 8	13.624	13.6010	.0224	-.023
RQ 1,10	17.028	17.0290	.9999	.001
RQ 1,16	27.224	27.2210	.9999	-.003
QP 1, 3	6.814	6.8180	.9999	.004
QP 1, 4	8.517	8.5480	.0283	.031
QP 1, 6	11.922	11.9380	.9999	.016
QP 1, 8	15.326	15.3480	.0245	.022
QP 1,10	18.729	18.7220	.9999	-.007
QP 1,16	28.922	28.9110	.9999	-.011
RP 2, 3	11.924	11.9360	.9999	.012
RP 2, 4	15.330	15.3130	.9999	-.017
RP 2, 6	22.141	22.1400	.9999	-.001
RP 2, 7	25.545	25.5450	.9999	.000
RP 2, 8	28.949	28.9550	.0245	.006

ASSIGN-MENT	CALCULATED GSCD	OBSERVED GSCD	DELTA NU	OBS-CALC
RP 2, 9	32.352	32.3580	.0200	.006
RP 2,10	35.754	35.7850	.9999	.031
RP 2,11	39.156	39.1560	.9999	.000
RP 2,12	42.556	42.5440	.0224	-.012
RP 2,13	45.955	45.9600	.0173	.005
RP 2,15	52.748	52.7360	.0283	-.012
RP 2,16	56.143	56.1300	.9999	-.013
RP 2,19	66.318	66.2890	.9999	-.029
RQ 2, 5	8.516	8.5300	.9999	.014
RQ 2, 8	13.624	13.6300	.9999	.006
RQ 2, 9	15.325	15.3160	.9999	-.009
RQ 2,11	18.728	18.7180	.9999	-.010
RQ 2,12	20.428	20.4040	.9999	-.024
RQ 2,14	23.827	23.9590	.0283	.132
QP 2, 2	5.110	5.1170	.9999	.007
QP 2, 8	15.325	15.3250	.9999	.000
QP 2, 9	17.027	17.0420	.9999	.015
QP 2,11	20.428	20.4380	.9999	.010
QP 2,12	22.128	22.1400	.9999	.012
QP 2,14	25.525	25.5070	.0283	-.018
RP 3, 4	15.328	15.3180	.9999	-.010
RP 3, 5	18.734	18.7350	.0283	.001
RP 3, 6	22.139	22.1340	.0245	-.005
RP 3, 7	25.543	25.5410	.9999	-.002
RP 3, 8	28.946	28.9450	.0173	-.001
RP 3, 9	32.349	32.3520	.9999	.003
RP 3,10	35.751	35.7580	.9999	.007
RP 3,11	39.152	39.1520	.9999	.000
RP 3,12	42.552	42.5550	.9999	.003
RP 3,13	45.951	45.9560	.0200	.005
RP 3,14	49.348	49.3350	.9999	-.013
RP 3,15	52.744	52.7380	.0283	-.006
RP 3,16	56.138	56.1300	.0283	-.008
RP 3,17	59.531	59.5590	.9999	.028
RP 3,19	66.312	66.3190	.9999	.007
RP 3,20	69.700	69.6880	.9999	-.012
RQ 3, 4	6.813	6.8110	.0245	-.002
RQ 3, 5	8.516	8.5230	.0283	.007
RQ 3, 6	10.218	10.2310	.0283	.013
RQ 3, 7	11.921	11.9340	.9999	.013
RQ 3, 8	13.623	13.6400	.9999	.017
RQ 3, 9	15.324	15.3360	.9999	.012
RQ 3,12	20.426	20.4540	.9999	.028
RQ 3,13	22.156	22.1700	.9999	.014
RQ 3,14	23.825	23.8320	.0245	.007
RQ 3,15	25.523	25.5160	.9999	-.007
RQ 3,16	27.221	27.2470	.9999	.026
RQ 3,17	28.918	28.9740	.9999	.056
RQ 3,18	30.614	30.6120	.9999	-.002
RQ 3,19	32.309	32.2910	.9999	-.018

ASSIGN-MENT	CALCULATED GSCD	OBSERVED GSCD	DELTA NU	OBS-CALC
RQ 3,20	34.003	33.9650	.9999	-.038
QP 3, 3	6.813	6.8070	.9999	-.006
QP 3, 4	8.516	8.5070	.9999	-.009
QP 3, 5	10.218	10.2120	.0283	-.006
QP 3, 6	11.920	11.9030	.0245	-.017
QP 3, 7	13.622	13.6070	.9999	-.015
QP 3, 8	15.324	15.3050	.9999	-.019
QP 3, 9	17.025	17.0160	.9999	-.009
QP 3,12	22.126	22.1010	.9999	-.025
QP 3,13	23.825	23.7860	.9999	-.039
QP 3,14	25.523	25.5030	.9999	-.020
QP 3,15	27.221	27.2220	.9999	.001
QP 3,16	28.918	28.8830	.9999	-.035
QP 3,17	30.614	30.5850	.9999	-.029
QP 3,19	34.003	34.0280	.9999	.025
QP 3,20	35.697	35.7230	.9999	.026
QP 3,21	37.389	37.4320	.9999	.043

APPENDIX IX

COMPARISON OF THE OBSERVED AND CALCULATED FREQUENCIES OF $\nu_3+\nu_4$ OF CH_3F

The following pages contain a comparison of the observed and calculated transition frequencies of $\nu_3+\nu_4$ of CH_3F. The analysis of 156 "unperturbed" transitions resulted in the following constants (in cm^{-1}):

$$\nu_0 - A_e\zeta_4^z - \tfrac{1}{4}\eta_4^K = 4057.2074$$

$$A_0 - A_e\zeta_4^z - \tfrac{1}{2}\eta_4^K = 4.6684$$

$$\alpha_3^A + \alpha_4^A - \alpha_3^B - \alpha_4^B - (3/2)\,\eta_4^K = 1.390 \times 10^{-2}$$

$$\alpha_3^B + \alpha_4^B = 1.0816 \times 10^{-2}$$

$$D_0^K - (\tfrac{1}{4})\eta_4^K = 1.46 \times 10^{-4}$$

$$\eta_4^J = 4.7 \times 10^{-5}$$

$$S\ (\text{std. dev.}) = 0.011$$

In the following list, the columns, from left to right, are: the assignment ($\Delta K, \Delta J, K, J$); the calculated frequency (in cm^{-1}); the observed frequency (in cm^{-1}); the $\Delta\nu$ (weight = $(\text{NORM})^2/(\Delta\nu)^2$); the observed minus the calculated frequency; the observed line height; and the line number.

The first part of the list contains the transitions included in the least squares fit, the second contains the comparison of transitions not included in the analysis due to perturbations, the third contains a comparison of transitions not included in the analysis since they were assigned a zero weight (i.e., $\Delta\nu \approx 0.9999$).

ASSIGN-MENT	CALCULATED FREQUENCY	OBSERVED FREQUENCY	DELTA NU	OBS-CALC	INT	LINE NO
PR 3, 4	4046.2743	4046.2735	.0200	-.0008	5	438A
PR 3, 5	4047.8491	4047.8404	.0140	-.0086	7	445
PQ 3, 3	4037.9503	4037.9491	.0200	-.0012	9	397
PQ 3, 4	4037.8651	4037.8684	.0140	.0033	16	396B
PQ 3, 5	4037.7587	4037.7629	.0140	.0043	18	396
PQ 3, 6	4037.6309	4037.6288	.0200	-.0020	19	395
PP 3, 4	4031.1375	4031.1383	.0200	.0007	23	363
PP 3, 5	4029.3495	4029.3504	.0100	.0009	25	354
PP 3, 6	4027.5404	4027.5468	.0140	.0064	17	343
PP 3, 7	4025.7104	4025.7034	.0140	-.0070	18	333
PR 2, 5	4055.5144	4055.5198	.0200	.0054	4	485
PR 2, 6	4057.0667	4057.0803	.0140	.0136	9	493
PR 2, 9	4061.5928	4061.5952	.0200	.0024	9	516
PR 2,10	4063.0577	4063.0570	.0200	-.0007	7	522A
PQ 2, 4	4045.5313	4045.5449	.0140	.0136	11	435
PQ 2, 5	4045.4240	4045.4281	.0100	.0041	13	434
PQ 2, 7	4045.1452	4045.1506	.0200	.0055	14	432
PQ 2, 8	4044.9736	4044.9738	.0100	.0002	19	431A
PQ 2, 9	4044.7805	4044.7886	.0200	.0080	18	430
PQ 2,10	4044.5661	4044.5635	.0140	-.0026	14	429
PQ 2,11	4044.3301	4044.3207	.0100	-.0094	17	427
PQ 2,12	4044.0727	4044.0670	.0200	-.0057	16	426
PP 2,10	4027.7538	4027.7610	.0200	.0072	13	344
PP 2,11	4025.8385	4025.8329	.0100	-.0055	14	334
PP 2,12	4023.9022	4023.8904	.0140	-.0118	16	323A
PR 1, 4	4061.5836	4061.5952	.0200	.0116	9	516
PR 1, 5	4063.1568	4063.1628	.0140	.0060	5	523
PR 1, 6	4064.7082	4064.7217	.0200	.0135	8	530
PR 1, 7	4066.2376	4066.2549	.0200	.0173	11	539
PR 1,14	4076.3251	4076.3273	.0140	.0021	8	586
PQ 1, 2	4053.3261	4053.3242	.0140	-.0018	15	475
PQ 1, 3	4053.2613	4053.2567	.0140	-.0046	17	474A
PQ 1, 5	4053.0668	4053.0734	.0100	.0066	13	473
PQ 1, 6	4052.9372	4052.9396	.0100	.0024	15	472
PQ 1, 7	4052.7860	4052.7962	.0140	.0102	13	471
PQ 1, 8	4052.6132	4052.6261	.0140	.0130	15	470
PQ 1, 9	4052.4187	4052.4258	.0200	.0071	23	469
PQ 1,10	4052.2027	4052.2084	.0200	.0057	18	468
PQ 1,11	4051.9651	4051.9795	.0100	.0144	12	467
PQ 1,12	4051.7059	4051.7190	.0100	.0132	18	465
PQ 1,13	4051.4250	4051.4332	.0100	.0082	15	464
PQ 1,14	4051.1226	4051.1258	.0140	.0032	14	462
PQ 1,15	4050.7985	4050.7946	.0100	-.0040	15	460
RP 0, 3	4055.8341	4055.8510	.0200	.0169	11	487
RP 0, 5	4052.2754	4052.2625	.0140	-.0130	21	468A
RP 0, 6	4050.4638	4050.4669	.0200	.0031	24	459A
RP 0, 8	4046.7761	4046.7954	.0200	.0193	18	441
RQ 0, 1	4060.9882	4060.9782	.0140	-.0100	16	514A
RQ 0, 2	4060.9447	4060.9322	.0100	-.0125	18	514
RQ 0, 3	4060.8794	4060.8640	.0100	-.0154	20	513

ASSIGN-MENT	CALCULATED FREQUENCY	OBSERVED FREQUENCY	DELTA NU	OBS-CALC	INT	LINE NO
RQ 0, 4	4060.7924	4060.7830	.0100	-.0094	21	512
RQ 0, 5	4060.6836	4060.6734	.0100	-.0102	21	511
RQ 0, 6	4060.5531	4060.5438	.0100	-.0093	21	510
RQ 0, 7	4060.4008	4060.3888	.0070	-.0120	20	509
RQ 0, 8	4060.2267	4060.2167	.0070	-.0100	22	508
RR 0, 0	4062.6918	4062.6882	.0200	-.0035	5	521
RR 0, 1	4064.3518	4064.3423	.0100	-.0095	8	528
RR 0, 2	4065.9899	4065.9861	.0140	-.0039	14	538
RR 0, 3	4067.6062	4067.6003	.0200	-.0059	18	546
RR 0, 4	4069.2005	4069.2100	.0200	.0094	16	555
RQ 1, 3	4068.4680	4068.4546	.0200	-.0133	16	552
RQ 1, 4	4068.3803	4068.3627	.0200	-.0177	20	551
RQ 1, 5	4068.2708	4068.2569	.0200	-.0139	19	550
RR 1, 2	4073.5784	4073.5728	.0100	-.0056	21	571
RR 1, 3	4075.1941	4075.1819	.0200	-.0122	17	578
RQ 2, 6	4075.6926	4075.6980	.0100	.0054	11	581
RQ 2, 7	4075.5381	4075.5459	.0140	.0078	11	580
RQ 2, 9	4075.1630	4075.1819	.0200	.0189	17	578
RR 2, 5	4085.9117	4085.9141	.0140	.0024	16	627
RR 2, 6	4087.4597	4087.4736	.0140	.0139	14	633
RR 2, 7	4088.9853	4088.9971	.0140	.0119	18	642A
RR 2, 9	4091.9692	4091.9641	.0140	-.0050	11	656A
RP 3, 7	4071.2887	4071.2843	.0200	-.0044	7	563B
RP 3,11	4063.7279	4063.7641	.0200	.0362	9	526
RR 3, 5	4093.4275	4093.4323	.0100	.0049	20	661
RR 3, 6	4094.9743	4094.9793	.0100	.0051	24	666
RQ 3, 5	4083.3426	4083.3371	.0140	-.0054	14	616
RQ 3, 6	4083.2093	4083.2117	.0140	.0025	17	615
RQ 3, 7	4083.0537	4083.0616	.0100	.0078	17	614
RQ 3, 8	4082.8760	4082.8883	.0100	.0123	21	613
RQ 3, 9	4082.6760	4082.7014	.0140	.0254	25	612
RR 4, 4	4099.3347	4099.3467	.0140	.0120	18	685
RR 4, 5	4100.9029	4100.9094	.0100	.0066	21	691
RR 4, 7	4103.9712	4103.9906	.0140	.0194	20	703
RR 4, 8	4105.4712	4105.5019	.0100	.0307	14	711
RQ 4, 6	4090.6859	4090.6901	.0140	.0042	7	651
RQ 4, 8	4090.3503	4090.3740	.0140	.0237	14	649A
RQ 6, 8	4105.1649	4105.1655	.0140	.0007	8	709
RQ 6, 9	4104.9608	4104.9610	.0100	.0002	11	708
RQ 6,10	4104.7340	4104.7340	.0200	.0000	15	707
RQ 6,11	4104.4845	4104.4758	.0140	-.0087	15	706
RQ 6,12	4104.2124	4104.1993	.0140	-.0131	13	704
RQ 6,14	4103.6001	4103.5812	.0100	-.0188	12	701
RQ 6,15	4103.2599	4103.2446	.0100	-.0153	15	700
RQ 6,16	4102.8970	4102.8931	.0140	-.0039	12	698
RQ 6,18	4102.1033	4102.0886	.0100	-.0147	14	696
RQ 6,19	4101.6724	4101.6625	.0200	-.0099	11	694

ASSIGN-MENT	CALCULATED FREQUENCY	OBSERVED FREQUENCY	DELTA NU	OBS-CALC	INT	LINE NO
RQ 6,20	4101.2188	4101.2172	.0140	-.0017	11	693
RQ 6,21	4100.7426	4100.7461	.0200	.0035	10	690
RQ 6,23	4099.7221	4099.7380	.0140	.0160	13	687B
RR 6, 6	4117.2612	4117.2653	.0070	.0041	23	755
RR 6, 7	4118.7810	4118.7766	.0140	-.0044	22	760
RR 6, 8	4120.2777	4120.2744	.0100	-.0033	22	764
RR 6, 9	4121.7513	4121.7542	.0070	.0029	18	768
RR 6,10	4123.2017	4123.1932	.0100	-.0086	20	771
RR 6,11	4124.6290	4124.6180	.0100	-.0110	17	778
RR 6,12	4126.0329	4126.0241	.0140	-.0088	19	783
RR 6,13	4127.4136	4127.3959	.0100	-.0178	17	787
RR 6,14	4128.7710	4128.7573	.0500	-.0136	16	789
RR 6,15	4130.1049	4130.0863	.0100	-.0186	17	792
RR 6,16	4131.4154	4131.4053	.0140	-.0101	15	795
RR 6,17	4132.7025	4132.6842	.0140	-.0183	14	798
RR 6,18	4133.9660	4133.9533	.0100	-.0126	14	800
RR 6,19	4135.2059	4135.1939	.0100	-.0120	12	803
RR 6,20	4136.4222	4136.4187	.0140	-.0035	14	806A
RR 6,22	4138.7837	4138.7924	.0200	.0087	12	811A
RR 6,23	4139.9288	4139.9490	.0140	.0202	9	814
RP 6, 8	4091.7302	4091.7297	.0200	-.0005	8	655A
RR 7, 7	4126.1111	4126.1116	.0100	.0004	13	784
RR 7, 8	4127.6061	4127.6055	.0100	-.0005	16	788
RR 7, 9	4129.0777	4129.0853	.0140	.0076	11	790
RR 7,10	4130.5261	4130.5297	.0200	.0036	13	793
RR 7,11	4131.9511	4131.9587	.0140	.0076	12	797
RR 7,12	4133.3527	4133.3623	.0140	.0096	13	799
RR 7,13	4134.7309	4134.7434	.0200	.0125	11	801
RR 7,15	4137.4166	4137.4258	.0140	.0092	10	807
RR 7,16	4138.7242	4138.7384	.0200	.0142	10	811
RR 7,17	4140.0080	4140.0224	.0200	.0143	8	814A
RR 7,18	4141.2682	4141.2983	.0200	.0300	6	817
RQ 7,10	4112.0643	4112.0616	.0200	-.0027	5	737A
RQ 7,11	4111.8132	4111.8153	.0140	.0021	5	736B
RQ 7,15	4110.5802	4110.6011	.0140	.0209	11	731A
RQ 7,16	4110.2149	4110.2258	.0200	.0109	8	730A
RP 7,10	4095.2792	4095.2736	.0200	-.0056		625
RP 7,15	4085.4174	4085.4154	.9999	-.0020	7	625
RQ 8,15	4117.8465	4117.8611	.0200	.0146	4	757B
RR 8, 8	4134.8799	4134.8765	.0100	-.0034	14	802
RR 8, 9	4136.3496	4136.3512	.0100	.0016	15	806
RR 8,10	4137.7958	4137.7978	.0100	.0020	10	809
RR 8,11	4139.2185	4139.2271	.0140	.0086	11	812
RR 8,12	4140.6177	4140.6269	.0200	.0092	7	815
RR 8,13	4141.9932	4142.0025	.0200	.0092	8	820
RR 8,14	4143.3452	4143.3604	.0100	.0153	7	823
RR 8,16	4145.9778	4145.9972	.0200	.0193	5	828
RQ 9,10	4126.5593	4126.5370	.0140	-.0223	8	786
RQ 9,11	4126.3048	4126.3032	.0200	-.0016	10	785
RQ 9,13	4125.7263	4125.7299	.0200	.0036	4	782B
RQ 9,19	4123.4355	4123.4713	.0200	.0358	6	772
RR 9, 9	4143.5633	4143.5511	.0140	-.0122	13	824
RR 9,10	4145.0073	4145.0039	.0100	-.0035	16	826

ASSIGN-MENT	CALCULATED FREQUENCY	OBSERVED FREQUENCY	DELTA NU	OBS-CALC	INT	LINE NO
RR 9,11	4146.4277	4146.4200	.0100	-.0077	11	829
RR 9,12	4147.8244	4147.8213	.0100	-.0030	13	832
RR 9,13	4149.1973	4149.1989	.0140	.0016	13	834
RR 9,14	4150.5464	4150.5455	.0200	-.0008	11	835
RR 9,15	4151.8716	4151.8877	.0140	.0161	10	837
RR 9,16	4153.1730	4153.1890	.0200	.0161	9	840

EXCUDED FROM LEAST SQUARES ANALYSIS DUE TO PERTURBATIONS

PP 9, 9	3975.7558	3975.7650	.0140	.0092	14	90
PP 9,10	3973.8734	3973.9177	.0200	.0443	14	83
PP 9,11	3971.9711	3972.0456	.0140	.0745	14	75
PP 9,12	3970.0489	3970.1677	.0140	.1188	13	68
PP 9,13	3968.1069	3968.2654	.0140	.1584	8	62
PP 9,14	3966.1452	3966.3605	.0200	.2153	9	54
PP 9,15	3964.1638	3964.4373	.0140	.2735	10	46
PP 9,16	3962.1627	3962.5086	.0140	.3459	7	39
PP 9,17	3960.1420	3960.5593	.0140	.4173	8	32
PP 9,18	3958.1018	3958.5744	.0140	.4726	9	26
PP 9,19	3956.0420	3956.6219	.0200	.5799	5	19
PP 9,20	3953.9627	3954.6283	.0200	.6655	7	15
PP 9,21	3951.8641	3952.6372	.0200	.7731	4	8
PQ 9,12	3990.2050	3990.3655	.0200	.1605	4	164
PQ 9,13	3989.9401	3990.1845	.0200	.2443	4	163A
PQ 9,19	3987.9231	3988.6095	.0200	.6863	4	155
PQ 9,20	3987.5157	3988.3021	.0200	.7864	3	154
PR 9, 9	4007.6776	4007.7513	.0200	.0737	6	236A
PP 8, 8	3985.3395	3985.3714	.0200	.0320	7	139
PP 8, 8	3985.3395	3985.4284	.0200	.0889	5	139A
PP 8, 9	3983.4753	3983.5318	.0200	.0565	8	130
PP 8,10	3981.5910	3981.6626	.0100	.0716	9	119
PP 8,11	3979.6867	3979.7828	.0140	.0962	10	109
PP 8,12	3977.7623	3977.8696	.0140	.1073	9	100
PP 8,13	3975.8180	3975.9653	.0200	.1473	6	91
PP 8,14	3973.8538	3974.0373	.0140	.1835	7	84
PP 8,15	3971.8697	3972.0925	.0200	.2228	12	75A
PP 8,16	3969.8658	3970.1677	.0200	.3019	13	68
PQ 8,12	3997.9226	3998.0587	.0200	.1361	4	195C
PP 7, 7	3994.9052	3994.9824	.0140	.0772	12	182
PP 7, 8	3993.0596	3993.1479	.0140	.0883	9	174
PP 7, 9	3991.1938	3991.2954	.0200	.1017	8	168
PP 7,10	3989.3077	3989.4282	.0200	.1205	12	160
PP 7,11	3987.4013	3987.5265	.0140	.1252	8	150

ASSIGN-MENT	CALCULATED FREQUENCY	OBSERVED FREQUENCY	DELTA NU	OBS-CALC	INT	LINE NO
PP 7,12	3985.4749	3985.6181	.0140	.1432	6	140
PP 7,13	3983.5283	3983.7055	.0200	.1772	6	131
PP 7,14	3981.5616	3981.7925	.0140	.2309	9	120
PP 7,15	3979.5749	3979.7828	.0200	.2079	10	109
PP 7,16	3977.5683	3977.8696	.0200	.3013	9	100
PR 7,10	4024.5997	4024.7557	.0200	.1560	3	327
PP 6, 7	4002.6222	4003.0222	.0100	.4000	14	216
PP 6, 8	4000.7752	4001.1707	.0140	.3955	15	208
PP 6, 9	3998.9077	3999.3012	.0140	.3934	14	201
PP 6,10	3997.0198	3997.4220	.0200	.4022	15	193
PP 6,11	3995.1116	3995.5438	.0100	.4322	15	184
PP 6,12	3993.1830	3993.6511	.0140	.4681	14	176
PP 6,13	3991.2342	3991.7527	.0140	.5185	12	169
PP 6,14	3989.2652	3989.8436	.0100	.5784	14	162
PP 6,15	3987.2760	3987.9339	.0100	.6579	13	151
PP 6,16	3985.2666	3986.0300	.0200	.7633	10	142
PP 6,17	3983.2372	3984.1216	.0140	.8843	9	134
PP 6,18	3981.1878	3982.2340	.0200	1.0462	8	123
PP 6,19	3979.1184	3980.3738	.0200	1.2554	7	112
PQ 6, 6	4014.5372	4014.9438	.0140	.4067	5	281
PQ 6, 8	4014.2246	4014.6203	.0100	.3957	7	279
PQ 6, 9	4014.0371	4014.4422	.0100	.4051	10	278
PQ 6,10	4013.8288	4014.2570	.0200	.4282	14	276A
PQ 6,12	4013.3496	4013.8628	.0100	.5132	11	275
PQ 6,13	4013.0787	4013.6534	.0100	.5747	11	273
PQ 6,14	4012.7870	4013.4418	.0140	.6548	12	272
PQ 6,15	4012.4745	4013.2312	.0140	.7567	10	271
PQ 6,16	4012.1412	4013.0319	.0140	.8907	12	270
PQ 6,17	4011.7870	4012.8344	.0200	1.0474	9	260
PQ 6,18	4011.4120	4012.6794	.0140	1.2675	11	259
PQ 6,19	4011.0161	4012.5399	.0140	1.5238	9	258
PQ 6,20	4010.5994	4012.4479	.0140	1.8485	13	257
PR 6,16	4040.6909	4041.7415	.0200	1.0506	6	414A
PP 5, 6	4012.1589	4012.2113	.0200	.0524	11	256
PP 5, 9	4006.6136	4006.7689	.0200	.1553	8	231
PP 5,11	4002.8139	4003.0222	.0100	.2083	14	216
PP 5,12	4000.8834	4001.1707	.0140	.2873	15	208
PP 5,14	3996.9610	3997.3130	.0200	.3520	5	192
PQ 5, 6	4022.2483	4022.3425	.0200	.0942	7	316A
PP 4, 6	4019.8573	4019.8559	.0140	-.0014	10	303
PP 4, 7	4018.0283	4018.0391	.0200	.0108	15	295A
PP 4, 8	4016.1785	4016.1744	.0140	-.0041	14	288
PP 4, 9	4014.3080	4014.2953	.0100	-.0128	16	277
PP 4,10	4012.4168	4012.3881	.0140	-.0286	12	256A
PP 4,12	4008.5723	4008.5468	.0200	-.0255	9	240A
PP 4,13	4006.6192	4006.6130	.0200	-.0062	3	230A
PP 4,14	4004.6456	4004.6075	.0200	-.0381	6	222
PQ 4, 9	4029.4400	4029.4025	.0100	-.0374	22	354A
PQ 4,11	4028.9960	4028.9138	.0200	-.0822	8	351
PQ 4,13	4028.4674	4028.3999	.0200	-.0675	5	349

ASSIGN-MENT	CALCULATED FREQUENCY	OBSERVED FREQUENCY	DELTA NU	OBS-CALC	INT	LINE NO
PR 4, 6	4041.7184	4041.7415	.0200	.0231	6	414A
PR 4,12	4050.5905	4050.5772	.0200	-.0133	5	459B
PR 3, 6	4049.4023	4049.3884	.0140	-.0139	6	453
PR 3, 7	4050.9339	4050.9090	.0140	-.0249	8	461
PR 3, 9	4053.9321	4053.8394	.0200	-.0927	9	477
PR 3,12	4058.2659	4058.0266	.0200	-.2393	8	497
PR 3,16	4063.7374	4063.5107	.0200	-.2266	9	525A
PR 3,17	4065.0501	4064.8153	.0200	-.2348	13	531
PQ 3, 7	4037.4818	4037.4655	.0140	-.0163	23	394
PQ 3, 8	4037.3114	4037.2835	.0140	-.0280	26	393
PQ 3, 9	4037.1198	4037.0761	.0100	-.0437	26	392
PQ 3,10	4036.9068	4036.8240	.0140	-.0828	23	391
PQ 3,15	4035.5226	4035.4304	.0140	-.0922	11	385
PQ 3,16	4035.1819	4034.9349	.0200	-.2470	11	382A
PQ 3,17	4034.8199	4034.5959	.0200	-.2239	11	381
PQ 3,19	4034.0319	4033.7564	.0140	-.2756	14	376
PP 3, 8	4023.8593	4023.8425	.0100	-.0168	18	323
PP 3, 9	4021.9873	4021.9499	.0200	-.0375	25	314
PP 3,10	4020.0945	4020.0344	.0140	-.0602	21	305
PP 3,11	4018.1809	4018.0886	.0140	-.0922	21	296
PP 3,17	4006.2644	4006.0281	.0140	-.2363	9	228
PP 3,18	4004.2063	4004.0010	.0200	-.2053	9	220A

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PR 2,12	4065.9216	4065.8993	.0140	-.0223	15	537
PR 2,13	4067.3204	4067.2864	.0200	-.0340	10	544
PR 2,14	4068.6971	4068.6264	.0200	-.0708	8	553
PR 2,16	4071.3841	4071.2158	.0200	-.1682	6	563
PQ 2,13	4043.7939	4043.7712	.0140	-.0227	15	425
PQ 2,15	4043.1719	4043.0904	.0140	-.0814	16	422A
PQ 2,18	4042.0779	4041.8062	.0100	-.2718	14	415
PP 2, 3	4040.5712	4040.5949	.0200	.0236	13	410
PP 2, 4	4038.8037	4038.8617	.0100	.0580	18	402
PP 2, 7	4033.3738	4033.4078	.0200	.0340	20	374A
PP 2,14	4019.9671	4019.9405	.0200	-.0266	13	304
PP 2,15	4017.9683	4017.9221	.0100	-.0462	12	295
PP 2,17	4013.9086	4013.7988	.0140	-.1099	9	274
PP 2,18	4011.8478	4011.6659	.0200	-.1819	8	253
PR 1,15	4077.6773	4077.6611	.0100	-.0163	5	592
PR 1,16	4079.0072	4078.9608	.0140	-.0464	9	596
PQ 1,17	4050.0856	4050.0428	.0100	-.0429	15	457
PQ 1,18	4049.6968	4049.6170	.0140	-.0798	12	455

ASSIGN-MENT	CALCULATED FREQUENCY	OBSERVED FREQUENCY	DELTA NU	OBS-CALC	INT	LINE NO
PQ 1,19	4049.2863	4049.1533	.0140	-.1330	15	452
RP 0, 4	4054.0656	4054.1172	.0200	.0516	16	479
RP 0, 9	4044.9002	4044.9246	.0100	.0244	17	431
RP 0,10	4043.0030	4043.0293	.0140	.0264	15	422
RP 0,11	4041.0844	4041.1338	.0200	.0494	23	412
RP 0,12	4039.1447	4039.1848	.0140	.0402	19	403
RP 0,13	4037.1837	4037.2295	.0200	.0458	17	392A
RP 0,16	4031.1742	4031.1990	.0200	.0248	20	363A
RP 0,17	4029.1290	4029.1568	.0200	.0278	19	353
RP 0,18	4027.0628	4027.0118	.0140	-.0511	17	340
RP 0,20	4022.8678	4022.6287	.0140	-.2392	11	317
RP 0,21	4020.7391	4020.2659	.0140	-.4732	16	306
RP 0,22	4018.5896	4017.7507	.0140	-.8390	19	
RP 0,22	4018.5896	4017.7507	.0140	-.8390	10	294
RQ 0,10	4059.8133	4059.7997	.0140	-.0136	23	505
RQ 0,11	4059.5740	4059.5518	.0140	-.0222	20	504
RQ 0,12	4059.3129	4059.2884	.0100	-.0245	25	503
RQ 0,13	4059.0301	4058.9865	.0100	-.0436	21	501
RQ 0,14	4058.7255	4058.6652	.0140	-.0603	24	500
RQ 0,15	4058.3992	4058.3038	.0140	-.0953	21	499
RQ 0,16	4058.0511	4057.9016	.0200	-.1495	29	496
RQ 0,17	4057.6812	4057.4658	.0100	-.2153	19	495
RQ 0,18	4057.2896	4056.9639	.0140	-.3257	18	492
RQ 0,19	4056.8762	4056.3902	.0100	-.4860	19	489
RQ 0,20	4056.4411	4055.7243	.0100	-.7168	19	486
RQ 0,21	4055.9842	4054.9587	.0100	-1.0255	14	483
RR 0, 7	4073.8513	4073.8918	.0200	.0405	24	572
RR 0, 8	4075.3574	4075.3925	.0200	.0351	21	579
RR 0, 9	4076.8413	4076.8842	.0140	.0429	58	9
RR 0, 9	4076.8413	4076.8842	.0140	.0429	18	589
RR 0,11	4079.7423	4079.7898	.0140	.0475	19	599
RR 0,12	4081.1593	4081.2072	.0200	.0479	23	600A
RR 0,13	4082.5540	4082.6069	.0140	.0529	18	611
RR 0,14	4083.9262	4083.9642	.0100	.0380	16	619
RR 0,15	4085.2760	4085.2932	.0140	.0172	15	624
RR 0,16	4086.6032	4086.5865	.0100	-.0168	14	630
RR 0,17	4087.9079	4087.8148	.0140	-.0931	16	635
RR 0,18	4089.1900	4088.9524	.0200	-.2376	19	642
RR 0,19	4090.4494	4089.9721	.0100	-.4773	16	646
RR 0,20	4091.6861	4090.8483	.0100	-.8378	8	552
RP 1, 6	4058.0512	4058.0266	.0140	-.0245	8	497
RP 1,11	4048.6658	4048.3713	.0200	-.2945	12	449
RP 1,12	4046.7244	4045.9484	.0200	-.7760	2	437A
RP 1,13	4044.7616	4042.9428	.0200	-1.8188	7	421B
RP 1,11	4048.6658	4049.6190	.0140	.9531	12	455
RP 1,13	4044.7616	4044.9738	.0200	.2122	19	431A
RP 1,14	4042.7776	4042.9428	.0200	.1653	7	421B
RP 1,15	4040.7723	4040.9634	.0200	.1911	9	410E
RP 1,21	4028.2970	4026.8503	.0200	-1.4466	10	339
RQ 1, 6	4068.1393	4068.1167	.0200	-.0226	19	549

ASSIGN-MENT	CALCULATED FREQUENCY	OBSERVED FREQUENCY	DELTA NU	OBS-CALC	INT	LINE NO
RQ 1, 7	4067.9860	4067.9463	.0140	-.0397	18	548
RQ 1, 8	4067.8107	4067.7495	.0140	-.0612	21	547
RQ 1, 9	4067.6135	4067.5115	.0200	-.1020	22	545
RQ 1,10	4067.3944	4067.1176	.0200	-.2768	24	543
RQ 1,11	4067.1534	4066.3626	.0200	-.7908	12	540
RQ 1,11	4067.1534	4067.5115	.0200	.3582	22	545
RQ 1,12	4066.8905	4067.1176	.0200	.2272	24	543
RQ 1,14	4066.2989	4066.4964	.0140	.1975	13	541
RQ 1,15	4065.9702	4066.1404	.0140	.1702	14	538C
RQ 1,16	4065.6197	4065.7591	.0140	.1394	15	536
RQ 1,17	4065.2472	4065.3436	.0140	.0964	14	533
RQ 1,18	4064.8528	4064.8153	.0140	-.0375	13	531
RQ 1,19	4064.4365	4063.9677	.0200	-.4688	10	527
RR 1, 1	4071.9408	4071.9249	.0100	-.0159	11	566
RR 1, 4	4076.7876	4076.7704	.0140	-.0172	15	588
RR 1, 6	4079.9081	4079.8721	.0200	-.0361	13	600
RR 1, 7	4081.4351	4081.3834	.0200	-.0517	13	605B
RR 1, 8	4082.9397	4082.8249	.0140	-.1148	14	612B
RR 1, 9	4084.4220	4084.1259	.0140	-.2961	9	620
RR 1,11	4087.3194	4085.4919	.0200	-1.8276	5	626
RR 1,10	4085.8820	4086.2501	.0200	.3682	10	628
RR 1,11	4087.3194	4087.5537	.0140	.2342	16	634
RR 1,12	4088.7345	4088.9524	.0140	.2180	19	642
RR 1,13	4090.1269	4090.3219	.0140	.1950	13	647
RR 1,14	4091.4968	4091.6641	.0100	.1673	12	655
RR 1,15	4092.8441	4092.9934	.0200	.1493	10	659
RR 1,16	4094.1687	4094.2751	.0200	.1064	7	663
RR 1,17	4095.4706	4095.4379	.0140	-.0328	7	668
RR 1,18	4096.7498	4096.2810	.0200	-.4688	11	671B
RP 2,12	4054.2718	4054.3275	.0200	.0557	11	480
RP 2,13	4052.3072	4052.3454	.0200	.0382	12	468B
RP 2,15	4048.3139	4048.3713	.0140	.0574	12	449
RP 2,16	4046.2852	4046.3629	.0200	.0777	4	439
RP 2,18	4042.1639	4033.5300	.0200	-8.6339	16	417A
RP 2,24	4029.2926	4029.0099	.0200	-.2827	6	352
RQ 2, 4	4075.9353	4075.9253	.0140	-.0099	9	583
RQ 2,11	4074.6997	4074.7545	.0140	.0548	13	575
RQ 2,12	4074.4349	4074.4905	.0200	.0556	13	574
RQ 2,13	4074.1481	4074.2063	.0140	.0582	11	573
RQ 2,16	4073.1552	4073.2246	.0100	.0694	14	570
RQ 2,17	4072.7801	4072.8255	.0140	.0454	12	569
RQ 2,19	4071.9638	4071.9249	.0100	-.0389	11	566
RQ 2,20	4071.5225	4071.4213	.0200	-.1012	7	564
RQ 2,21	4071.0592	4070.8933	.0200	-.1659	9	562
RQ 2,22	4070.5738	4070.3306	.0200	-.2432	7	560
RQ 2,23	4070.0663	4069.7930	.0200	-.2733	5	558A
RR 2, 3	4082.7486	4082.7387	.0200	-.0099	25	612A
RR 2, 4	4084.3413	4084.3343	.0100	-.0070	13	621
RR 2,10	4093.4273	4093.4790	.0140	.0517	21	661A
RR 2,11	4094.8629	4094.9147	.0200	.0519	16	665B

ASSIGN-MENT	CALCULATED FREQUENCY	OBSERVED FREQUENCY	DELTA NU	OBS-CALC	INT	LINE NO
RR 2,12	4096.2758	4096.3369	.0140	.0612	16	672
RR 2,13	4097.6660	4097.7360	.0140	.0700	11	678
RR 2,14	4099.0335	4099.1058	.0140	.0723	11	683
RR 2,15	4100.3783	4100.4397	.0200	.0614	9	689
RR 2,16	4101.7002	4101.7458	.0140	.0456	11	695
RR 2,17	4102.9992	4102.9976	.0200	-.0016	8	699
RR 2,20	4106.7586	4106.5830	.0200	-.1757	7	714
RP 3, 8	4069.4312	4069.3682	.0200	-.0630	6	556
RP 3,12	4061.7833	4061.8274	.0140	.0441	9	517
RP 3,15	4055.8199	4055.9243	.0140	.1044	11	487A
RP 3,17	4051.7367	4051.8962	.0140	.1595	11	466
RP 3,19	4047.5679	4047.7392	.0140	.1713	7	444
RR 3, 3	4090.2664	4090.2560	.0100	-.0104	20	648
RR 3, 4	4091.8582	4091.8654	.0200	.0072	21	656
RR 3, 7	4096.4985	4096.5324	.0200	.0340	24	673
RR 3, 9	4099.4791	4099.5149	.0140	.0357	21	686
RR 3,10	4100.9354	4100.9908	.0100	.0554	22	692
RR 3,13	4105.1677	4105.2765	.0100	.1087	19	710
RR 3,14	4106.5328	4106.6720	.0140	.1392	16	715
RR 3,15	4107.8749	4108.0438	.0140	.1689	16	721
RR 3,18	4111.7633	4111.9590	.0100	.1958	14	737
RR 3,20	4114.2400	4114.2247	.0100	-.0153	12	745
RQ 3, 4	4083.4536	4083.4397	.0140	-.0139	10	617
RQ 3,11	4082.2095	4082.2635	.0140	.0540	18	609
RQ 3,10	4082.4539	4082.4908	.0140	.0370	19	610
RQ 3,12	4081.9429	4082.0123	.0140	.0695	19	608
RQ 3,13	4081.6540	4081.7329	.0140	.0789	19	607
RQ 3,15	4081.0097	4081.1512	.0200	.1415	25	605
RQ 3,16	4080.6542	4080.8203	.0100	.1661	8	604
RQ 3,19	4079.4545	4079.6560	.0140	.2015	16	598
RQ 3,20	4079.0102	4079.1698	.0140	.1596	13	597
RR 4, 9	4106.9485	4106.9949	.0100	.0464	16	716
RR 4,10	4108.4029	4108.4586	.0100	.0557	13	723
RR 4,11	4109.8344	4109.9123	.0140	.0779	16	729
RR 4,12	4111.2430	4111.2924	.0100	.0495	14	734
RR 4,13	4112.6286	4112.6436	.0200	.0150	12	740
RR 4,14	4113.9911	4113.8758	.0200	-.1153	15	744
RR 4,15	4115.3306	4115.1993	.0140	-.1313	9	748
RQ 4, 9	4090.1490	4090.1843	.0140	.0353	13	647
RQ 4,10	4089.9253	4089.9721	.0200	.0468	16	646
RQ 4,11	4089.6792	4089.7255	.0200	.0463	9	645
RQ 4,13	4089.1199	4089.1627	.0140	.0428	13	643
RQ 4,14	4088.8067	4088.8145	.0100	.0078	10	641
RQ 4,15	4088.4712	4088.3556	.0140	-.1155	10	638
RQ 4,16	4088.1132	4087.9695	.0100	-.1438	8	636
RP 4,13	4067.2877	4067.3398	.0200	.0521	8	544A
RP 4,17	4059.1992	4059.0923	.0140	-.1069	7	502
RR 5, 7	4111.3998	4110.9728	.0200	-.4270	10	733
RR 5, 9	4114.3737	4113.9420	.0140	-.4317	14	744A
RR 5,11	4117.2556	4116.8489	.0140	-.4067	10	753

ASSIGN-MENT	CALCULATED FREQUENCY	OBSERVED FREQUENCY	DELTA NU	OBS-CALC	INT	LINE NO
RR 5,12	4118.6619	4118.2711	.0100	-.3907	13	758
RR 5,13	4120.0450	4119.6612	.0200	-.3838	10	762
RR 5,15	4122.7417	4122.3890	.0200	-.3528	10	769
RR 5,18	4126.6121	4126.3032	.0200	-.3088	10	785
RR 5,19	4127.8554	4127.6055	.0200	-.2498	16	788
RQ 5,10	4097.3532	4096.9254	.0140	-.4278	10	675
RQ 5,11	4097.1054	4096.6878	.0140	-.4176	9	674
RQ 5,12	4096.8351	4096.4299	.0200	-.4052	12	672A
RQ 5,13	4096.5423	4096.1482	.0140	-.3941	12	671
RQ 5,14	4096.2269	4095.8485	.0200	-.3784	9	670
RQ 5,15	4095.8890	4095.5295	.0140	-.3595	9	669
RQ 5,16	4095.5287	4095.1803	.0200	-.3483	11	667
RQ 5,17	4095.1457	4094.8044	.0200	-.3413	9	665
RQ 5,18	4094.7403	4094.4169	.0140	-.3233	7	664
RQ 5,19	4094.3123	4094.0057	.0200	-.3066	6	662
RQ 5,20	4093.8618	4093.5729	.0200	-.2890	10	661A
RQ 6,24	4099.1778	4099.2358	.0140	.0580	7	684
RQ 6,25	4098.6103	4098.6505	.0140	.0397	7	682
RP 6,10	4087.9435	4087.9695	.0200	.0260	8	636
RQ 7,12	4111.5392	4111.5548	.0200	.0157	10	735
RQ 7,22	4107.5436	4107.5888	.0140	.0452	7	709
RP 7,20	4075.0026	4075.0536	.9999	.0510	11	577
RP 8,17	4088.5889	4088.6502	.0140	.0613	5	640
RQ 8,18	4116.6742	4116.7106	.0200	.0364	8	752
RQ 8,20	4115.7778	4115.8260	.0200	.0482	5	750B
RR 8,15	4144.6734	4144.7080	.9999	.0347	7	825
RR 8,17	4147.2585	4147.3216	.0200	.0631	4	833
RR 8,21	4152.1423	4152.1247	.0200	-.0176	9	838
RQ 9,17	4124.2917	4124.3189	.0200	.0273	11	776
RQ 9,29	4117.7664	4117.9113	.0200	.1449	4	757C

EXCUDED FROM LEAST SQUARES ANALYSIS DUE TO ZERO WEIGHT

PQ 9, 9	3990.8773	3990.9015	.9999	.0242	12	166A
PQ 9,15	3989.3493	3989.7246	.9999	.3753	4	161
PQ 9,16	3989.0233	3989.4282	.9999	.4048	12	160
PQ 9,17	3988.6770	3989.1876	.9999	.5107	4	159
PQ 9,18	3988.3102	3988.8706	.9999	.5604	10	157A
PR 9,10	4009.1520	4009.2677	.9999	.1157	5	244
PR 9,11	4010.6056	4010.7752	.9999	.1696	5	252A
PR 9,15	4016.2099	4016.6632	.9999	.4533	4	289
PR 9,16	4017.5583	4018.0391	.9999	.4808	15	295A
PR 9,19	4021.4761	4022.2299	.9999	.7538	22	316

ASSIGN-MENT	CALCULATED FREQUENCY	OBSERVED FREQUENCY	DELTA NU	OBS-CALC	INT	LINE NO
PP 8,17	3967.8422	3968.1294	.9999	.2872	6	61
PQ 8, 8	3998.7847	3998.8378	.9999	.0531	6	200
PQ 8, 9	3998.6000	3998.6574	.9999	.0574	10	199
PQ 8,10	3998.3947	3998.4983	.9999	.1035	14	198
PQ 8,13	3997.6557	3997.8609	.9999	.2052	7	195A
PQ 8,13	3997.6557	3997.8191	.9999	.1634	7	195
PQ 8,14	3997.3684	3997.5966	.9999	.2283	6	194
PR 8, 8	4013.9094	4013.8628	.9999	-.0467	11	275A
PR 8,12	4019.7603	4019.9405	.9999	.1801	13	304
PR 8,13	4021.1703	4021.3315	.9999	.1612	5	311A
PR 8,14	4022.5591	4022.8338	.9999	.2747	5	318
PQ 7, 7	4006.6727	4006.7689	.9999	.0963	8	231
PQ 7, 8	4006.5072	4006.6130	.9999	.1058	3	230A
PQ 7,10	4006.1143	4006.2432	.9999	.1289	6	229A
PQ 7,11	4005.8868	4006.0281	.9999	.1413	9	228
PQ 7,12	4005.6386	4005.8014	.9999	.1628	9	227
PQ 7,13	4005.3698	4005.5978	.9999	.2281	8	226A
PQ 7,14	4005.0802	4005.2872	.9999	.2070	8	225
PQ 7,15	4004.7700	4005.0850	.9999	.3149	8	224
PR 7, 8	4021.6345	4021.7428	.9999	.1082	11	313
PP 6,20	3977.0291	3978.5645	.9999	1.5354	4	103
PP 6,21	3974.9198	3976.7647	.9999	1.8449	6	94
PR 6, 7	4027.8407	4028.2285	.9999	.3878	13	348A
PR 6, 8	4029.3540	4029.7829	.9999	.4289	14	356
PR 6,11	4033.7661	4034.2792	.9999	.5131	8	379A
PR 6,15	4039.3491	4040.2370	.9999	.8879	11	408A
PP 5, 7	4010.3311	4010.4363	.9999	.1052	20	251
PP 5, 8	4008.4827	4008.6246	.9999	.1420	15	241
PP 5,10	4004.7240	4004.8933	.9999	.1693	12	223A
PP 5,13	3998.9324	3999.3012	.9999	.3688	14	201
PQ 5, 5	4022.3742	4022.4229	.9999	.0486	5	316B
PQ 5, 7	4022.1014	4022.2299	.9999	.1285	22	316
PQ 5, 8	4021.9335	4022.1058	.9999	.1723	14	315
PQ 5, 9	4021.7446	4021.9499	.9999	.2053	25	314
PQ 5,10	4021.5347	4021.7428	.9999	.2081	11	313
PQ 5,12	4021.0520	4021.3315	.9999	.2795	5	311A
PQ 5,13	4020.7791	4021.1543	.9999	.3752	3	310
PR 5, 6	4034.0186	4034.1818	.9999	.1632	4	378B
PR 5, 7	4035.5522	4035.6998	.9999	.1477	17	385A
PR 5, 8	4037.0644	4037.2295	.9999	.1651	17	392A
PR 5, 9	4038.5552	4038.7765	.9999	.2212	15	401
PR 5,12	4042.8987	4043.2454	.9999	.3467	8	423
PQ 4, 6	4029.9474	4029.9260	.9999	-.0214	10	356A
PQ 4, 7	4029.7994	4029.7829	.9999	-.0165	14	356
PQ 4, 8	4029.6302	4029.5893	.9999	-.0409	21	355
PQ 4,10	4029.2285	4029.1568	.9999	-.0717	19	353
PQ 4,12	4028.7423	4028.6739	.9999	-.0684	9	350A
PR 4, 7	4043.2511	4043.2454	.9999	-.0057	8	423
PR 4,10	4047.7197	4047.7392	.9999	.0195	7	444
PR 3, 3	4044.6779	4044.6609	.9999	-.0170	15	429B

ASSIGN-MENT	CALCULATED FREQUENCY	OBSERVED FREQUENCY	DELTA NU	OBS-CALC	INT	LINE NO
PR 3, 8	4052.4439	4052.4194	.9999	-.0245	23	469
PR 3,10	4055.3986	4055.2529	.9999	-.1456	13	484
PR 3,11	4056.8432	4056.6076	.9999	-.2356	9	490
PR 3,18	4066.3407	4066.0536	.9999	-.2871	9	538B
PR 3,19	4067.6090	4067.2864	.9999	-.3226	10	544
PQ 3,11	4036.6726	4036.5262	.9999	-.1463	19	389
PQ 3,12	4036.4170	4036.1899	.9999	-.2271	30	388
PQ 3,13	4036.1402	4035.8998	.9999	-.2403	10	387A
PQ 3,14	4035.8421	4099.5544	.9999	63.7124	27	384
PQ 3,15	4035.5226	4033.9863	.9999	-1.5363	7	378
PQ 3,13	4036.1402	4037.7954	.9999	1.6552	17	396A
PQ 3,14	4035.8421	4036.5471	.9999	.7051	18	388A
PQ 3,18	4034.4365	4034.1818	.9999	-.2548	4	378B
PQ 3,20	4033.6060	4033.3004	.9999	-.3056	19	373A
PP 3,12	4016.2464	4016.1021	.9999	-.1444	17	287
PP 3,13	4014.2913	4014.0605	.9999	-.2308	26	276
PP 3,14	4012.3154	4012.0743	.9999	-.2412	4	255A
PP 3,16	4008.3019	4006.7689	.9999	-1.5330	8	231
PP 3,15	4010.3190	4010.7752	.9999	.4562	5	252A
PP 3,19	4002.1278	4001.8537	.9999	-.2741	12	210
PP 3,20	4000.0289	3999.6989	.9999	-.3300	4	202
PP 3,21	3997.9097	3997.5966	.9999	-.3130	6	194
PR 2, 2	4050.7273	4050.7962	.9999	.0689	15	460
PR 2, 3	4052.3446	4052.3454	.9999	.0008	12	468B
PR 2, 4	4053.9404	4054.0644	.9999	.1241	10	478B
PR 2,11	4064.5006	4064.4905	.9999	-.0101	10	529
PR 2,15	4070.0517	4069.9360	.9999	-.1157	5	559
PR 2,17	4072.6942	4072.4278	.9999	-.2664	11	568A
PQ 2, 2	4045.6814	4045.7005	.9999	.0191	10	436A
PQ 2, 3	4045.6171	4045.6510	.9999	.0339	12	436
PQ 2, 6	4045.2953	4045.3069	.9999	.0116	12	433
PQ 2,14	4043.4936	4043.4368	.9999	-.0568	5	423A
PQ 2,16	4042.8287	4042.6885	.9999	-.1402	14	420
PQ 2,17	4042.4640	4042.2866	.9999	-.1775	17	417B
PQ 2,19	4041.6704	4041.2048	.9999	-.4656	16	412A
PP 2, 5	4037.0149	4037.0240	.9999	.0091	15	391A
PP 2, 6	4035.2049	4035.2120	.9999	.0071	24	383B
PP 2, 8	4031.5215	4031.5418	.9999	.0203	13	365
PP 2, 9	4029.6482	4029.6392	.9999	-.0090	22	355B
PP 2,13	4021.9450	4021.9499	.9999	.0048	25	314
PP 2,16	4015.9488	4015.8747	.9999	-.0741	12	286
PR 1, 8	4067.7450	4067.7495	.9999	.0045	21	547
PR 1, 9	4069.2304	4069.2405	.9999	.0102	17	555A
PR 1,12	4073.5538	4073.5728	.9999	.0190	21	571
PR 1,13	4074.9506	4074.9504	.9999	-.0003	14	576
PR 1,17	4080.3146	4080.2428	.9999	-.0718	14	603
PR 1,18	4081.5996	4081.4628	.9999	-.1368	23	606
PR 1,19	4082.8620	4082.7014	.9999	-.1606	25	612
PQ 1, 1	4053.3693	4053.3728	.9999	.0035	11	475A
PQ 1,16	4050.4529	4050.4354	.9999	-.0175	22	459

ASSIGN-MENT	CALCULATED FREQUENCY	OBSERVED FREQUENCY	DELTA NU	OBS-CALC	INT	LINE NO
PQ 1,20	4048.8543	4048.6791	.9999	-.1752	17	450A
RP 0, 7	4048.6307	4048.6533	.9999	.0227	19	450
RP 0,14	4035.2016	4035.2436	.9999	.0419	27	384
RP 0,15	4033.1984	4033.2496	.9999	.0511	22	373
RP 0,19	4024.9758	4024.9155	.9999	-.0602	19	328
RP 0,23	4016.4194	4015.1406	.9999	-1.2788	11	282
RQ 0, 9	4060.0309	4060.0325	.9999	.0016	25	507
RR 0, 5	4070.7729	4070.7856	.9999	.0127	19	561
RR 0, 6	4072.3231	4072.3554	.9999	.0323	20	568
RR 0,10	4078.3029	4078.3469	.9999	.0440	23	594
RP 1, 3	4063.4233	4063.3908	.9999	-.0325	5	524
RP 1, 4	4061.6543	4061.6425	.9999	-.0117	6	516A
RP 1, 5	4059.8636	4059.8682	.9999	.0046	15	506
RP 1, 7	4056.2172	4056.2015	.9999	-.0157	8	488
RP 1, 8	4054.3616	4054.3275	.9999	-.0341	11	480
RP 1, 9	4052.4844	4052.4194	.9999	-.0651	23	469
RP 1,10	4050.5858	4050.4669	.9999	-.1189	24	459A
RP 1,12	4046.7244	4047.0845	.9999	.3601	6	442
RP 1,17	4036.6981	4036.8240	.9999	.1259	23	391
RP 1,18	4034.6294	4034.7355	.9999	.1061	6	381A
RP 1,19	4032.5396	4032.4994	.9999	-.0402	6	370B
RP 1,20	4030.4287	4029.9762	.9999	-.4526	11	357
RQ 1, 2	4068.5337	4068.5164	.9999	-.0173	11	552A
RQ 1,12	4066.8905	4065.0520	.9999	-1.8385	9	532
RQ 1,10	4067.3944	4068.3627	.9999	.9683	20	551
RQ 1,13	4066.6056	4066.7893	.9999	.1837	16	542
RQ 1,20	4063.9983	4062.5265	.9999	-1.4718	4	520A
RR 1, 5	4078.3590	4078.3469	.9999	-.0120	23	594
RR 1, 9	4084.4220	4085.4154	.9999	.9933	7	625
RR 1,19	4098.0061	4096.5324	.9999	-1.4736	24	673
RP 2, 4	4069.2102	4069.2100	.9999	-.0002	16	555
RP 2, 5	4067.4189	4067.4083	.9999	-.0106	6	544B
RP 2, 7	4063.7710	4063.7641	.0200	-.0069	9	526
RP 2, 8	4061.9144	4061.9171	.0140	.0027	6	518
RP 2,10	4058.1363	4058.1591	.9999	.0228	7	498
RP 2,11	4056.2148	4056.2015	.9999	-.0133	8	488
RP 2,17	4044.2352	4044.3207	.9999	.0855	17	427
RP 2,20	4037.9578	4037.9491	.9999	-.0087	9	397
RP 2,21	4035.8230	4035.7384	.9999	-.0846	22	386
RP 2,22	4033.6672	4033.5216	.9999	-.1456	19	375A
RQ 2, 3	4076.0235	4076.0199	.9999	-.0037	7	584
RQ 2, 5	4075.8249	4075.8195	.9999	-.0054	9	582
RQ 2, 8	4075.3616	4075.3925	.9999	.0309	21	579
RQ 2,10	4074.9424	4074.9504	.9999	.0080	14	576
RQ 2,14	4073.8392	4073.8918	.9999	.0526	24	572
RQ 2,15	4073.5082	4057.4951	.9999	-16.0131	21	571
RQ 2,18	4072.3830	4072.3554	.9999	-.0276	11	568A
RR 2, 2	4081.1337	4081.1512	.9999	.0175	25	605
RR 2,18	4104.2753	4104.2327	.9999	-.0426	11	704A
RR 2,21	4107.9657	4107.7364	.9999	-.2294	4	719B

ASSIGN-MENT	CALCULATED FREQUENCY	OBSERVED FREQUENCY	DELTA NU	OBS-CALC	INT	LINE NO
RP 3, 5	4074.9380	4074.9504	.9999	.0123	14	576
RP 3, 9	4067.5519	4067.5498	.9999	-.0021	18	545A
RP 3,10	4065.6508	4065.6883	.9999	.0376	13	535
RP 3,13	4059.8171	4059.8682	.9999	.0511	15	506
RP 3,14	4057.8293	4057.9016	.9999	.0723	29	496
RP 3,16	4053.7891	4053.9175	.9999	.1284	10	478
RP 3,18	4049.6630	4049.8849	.9999	.2219	10	456A
RP 3,20	4045.4515	4045.6510	.9999	.1995	12	436
RP 3,21	4043.3138	4043.4766	.9999	.1628	21	424
RP 3,22	4041.1549	4041.1338	.9999	-.0211	23	412
RR 3, 8	4098.0001	4098.0348	.9999	.0346	23	679
RR 3,11	4102.3690	4102.4706	.9999	.1016	30	697
RR 3,16	4109.1941	4109.4261	.9999	.2321	21	728
RR 3,17	4110.4902	4110.6693	.9999	.1791	15	732
RQ 3,14	4081.3430	4081.4628	.9999	.1198	23	606
RQ 3,17	4080.2765	4080.5001	.9999	.2235	14	603
RQ 3,18	4079.8766	4080.0872	.9999	.2106	15	601A
RQ 3,21	4078.5436	4078.5309	.9999	-.0127	12	595
RQ 3,22	4078.0548	4077.4939	.9999	-.5609	5	591
RR 4, 6	4102.4484	4102.4706	.9999	.0222	3	697
RQ 4, 7	4090.5293	4090.5396	.9999	.0103	15	650A
RQ 4,12	4089.4107	4089.4618	.9999	.0510	12	644
RP 4, 9	4075.0281	4075.0536	.9999	.0255	11	577
RP 4,11	4071.2016	4071.2528	.9999	.0512	6	563A
RP 4,14	4065.2981	4065.3436	.9999	.0455	14	533
RP 4,16	4061.2533	4061.1425	.9999	-.1113	4	515
RR 5, 6	4109.8785	4109.4261	.9999	-.4524	21	728
RR 5, 8	4112.8982	4112.4851	.9999	-.4132	8	739
RR 5,10	4115.8261	4115.4132	.9999	-.4130	14	749
RR 5,14	4121.4050	4121.0436	.9999	-.3614	11	766
RR 5,16	4124.0552	4123.7353	.9999	-.3199	11	773
RR 5,17	4125.3453	4125.0386	.9999	-.3068	11	780
RP 5,15	4070.7110	4070.3467	.9999	-.3643	7	560
RP 5,17	4066.6192	4066.2565	.9999	-.3627	11	539
RP 5,19	4062.4405	4062.1062	.9999	-.3343	7	519
RQ 5, 8	4097.7811	4097.3672	.0200	-.4139	9	677
RQ 5, 9	4097.5784	4097.1408	.9999	-.4376	8	676
RQ 6, 7	4105.3463	4105.2765	.9999	-.0698	19	710
RQ 6,13	4103.9176	4103.8986	.9999	-.0190	26	702
RQ 6,17	4102.5115	4102.4706	.9999	-.0409	30	697
RQ 6,22	4100.2437	4100.2512	.9999	.0076	10	688
RQ 6,26	4098.0212	4098.0348	.9999	.0136	23	679
RQ 6,27	4097.4089	4097.4116	.9999	.0027	9	677A
RR 6,21	4137.6148	4137.6219	.9999	.0072	9	808
RP 6,14	4080.1040	4080.0872	.9999	-.0168	15	601A
RP 6,16	4076.0520	4076.0199	.9999	-.0322	7	584
RP 6,19	4069.8097	4070.1145	.9999	.3048	5	558A
RP 6,20	4067.6854	4067.6598	.9999	-.0256	13	546A
RP 6,21	4065.5393	4065.5301	.9999	-.0092	6	534
RP 6,22	4063.3715	4063.3908	.9999	.0193	5	524

ASSIGN-MENT	CALCULATED FREQUENCY	OBSERVED FREQUENCY	DELTA MU	OBS-CALC	INT	LINE NO
RP 6,25	4056.7385	4056.7526	.9999	.0141	4	491
RP 6,26	4054.4845	4054.5014	.9999	.0169	3	481
RR 7,14	4136.0855	4136.1039	.9999	.0184	13	805
RR 7,19	4142.5047	4142.5427	.9999	.0380	10	821
RQ 7, 8	4112.4981	4112.4851	.9999	-.0130	8	739
RQ 7, 9	4112.2926	4112.3012	.9999	.0085	7	738
RQ 7,19	4108.9820	4109.0094	.9999	.0274	5	725A
RQ 7,20	4108.5253	4108.4907	.9999	-.0346	10	723A
RQ 7,23	4107.0184	4106.9949	.9999	-.0236	16	716
RP 8,15	4092.6927	4092.6764	.9999	-.0163	4	658D
RQ 8,11	4119.0877	4119.0943	.9999	.0066	5	761A
RQ 8,16	4117.4787	4117.4502	.9999	-.0285	5	756
RQ 8,17	4117.0880	4117.1254	.9999	.0374	7	754
RQ 8,19	4116.2375	4116.2939	.9999	.0564	7	751
RP 9,14	4101.9314	4102.7719	.9999	.8405	3	695B
RP 9,18	4093.7165	4093.7346	.9999	.0181	4	661B
RP 9,20	4089.4751	4089.5165	.9999	.0413	8	644B
RQ 9,12	4126.0271	4126.0241	.9999	-.0030	19	783
RQ 9,14	4125.4024	4125.4202	.9999	.0179	5	782
RQ 9,15	4125.0553	4125.0662	.9999	.0109	12	780A
RQ 9,16	4124.6850	4124.6858	.9999	.0008	11	779
RQ 9,18	4123.8752	4123.9038	.9999	.0286	5	774
RQ 9,22	4121.9777	4122.0369	.9999	.0591	6	768A
RQ 9,23	4121.4455	4121.4947	.9999	.0492	6	767B
RQ 9,24	4120.8902	4120.9661	.9999	.0759	6	765A
RQ 9,26	4119.7101	4119.7982	.9999	.0881	10	763
RQ 9,27	4119.0853	4119.2078	.9999	.1225	3	761B

APPENDIX X

COMPARISON OF THE OBSERVED AND CALCULATED FREQUENCIES OF K"=0 SERIES OF $\nu_3+\nu_4$ OF CH_3F

The following page contains a comparison of the observed and calculated $^{R}R_0(J)$, $^{R}Q_0(J)$, and $^{R}P_0(J)$ transitions. The analysis of this subband including a Coriolis resonance constant q, and a J^6 term whose coefficient is ρ resulted in the constants (in cm^{-1}):

$$\nu_{sub} = 4060.987$$
$$a_B^3+a_B^4 = 0.01057$$
$$q = 2.73 \times 10^{-4}$$
$$\rho = 1.06 \times 10^{-8}$$
$$S \text{ (std. dev.)} = 0.015 \text{ cm}^{-1}$$

The columns of the list, left to right, are the assignment ($\Delta K, \Delta J, K, J$); the calculated frequency (in cm^{-1}); the observed frequency (in cm^{-1}); the $\Delta\nu$ (weight = $(NORM)^2/(\Delta\nu)^2$), the observed minus the calculated frequency; the observed line height; and the line number.

ASSIGN-MENT	CALCULATED FREQUENCY	OBSERVED FREQUENCY	DELTA NU	OBS-CALC	INT	LINE NO
RP 0, 6	4050.4655	4050.4669	.0200	.0014	24	459A
RP 0, 8	4046.7980	4046.7954	.0200	-.0026	18	441
RP 0, 9	4044.9333	4044.9246	.0100	-.0088	17	431
RP 0,10	4043.0474	4043.0293	.0140	-.0180	15	422
RP 0,11	4041.1392	4041.1338	.0200	-.0054	23	412
RP 0,12	4039.2075	4039.1848	.0140	-.0227	19	403
RP 0,13	4037.2507	4037.2295	.0200	-.0213	17	392A
RP 0,16	4031.2049	4031.1990	.0200	-.0058	20	363A
RP 0,17	4029.1194	4029.1568	.0200	.0375	19	353
RQ 0, 1	4060.9656	4060.9782	.0140	.0126	16	514A
RQ 0, 2	4060.9233	4060.9322	.0100	.0089	18	514
RQ 0, 3	4060.8597	4060.8640	.0100	.0043	20	513
RQ 0, 4	4060.7750	4060.7830	.0100	.0080	21	512
RQ 0, 5	4060.6689	4060.6734	.0100	.0044	21	511
RQ 0, 6	4060.5414	4060.5438	.0100	.0024	21	510
RQ 0, 7	4060.3921	4060.3888	.0070	-.0033	20	509
RQ 0, 8	4060.2206	4060.2167	.0070	-.0038	22	508
RQ 0,10	4059.8081	4059.7997	.0140	-.0084	23	505
RQ 0,11	4059.5649	4059.5518	.0140	-.0131	20	504
RQ 0,12	4059.2949	4059.2884	.0100	-.0065	25	503
RQ 0,13	4058.9959	4058.9865	.0100	-.0094	21	501
RQ 0,14	4058.6651	4058.6652	.0140	.0002	24	500
RQ 0,15	4058.2989	4058.3038	.0140	.0049	21	499
RQ 0,16	4057.8931	4057.9016	.0200	.0084	29	496
RQ 0,17	4057.4425	4057.4658	.0100	.0234	19	495
RQ 0,18	4056.9406	4056.9639	.0140	.0233	18	492
RQ 0,19	4056.3801	4056.3902	.0100	.0101	19	489
RQ 0,20	4055.7523	4055.7243	.0100	-.0280	19	486
RR 0, 0	4062.6703	4062.6882	.0200	.0179	5	521
RR 0, 1	4064.3337	4064.3423	.0100	.0086	8	528
RR 0, 2	4065.9768	4065.9861	.0140	.0092	14	538
RR 0, 4	4069.2022	4069.2100	.0200	.0078	16	555
RR 0, 7	4073.8845	4073.8918	.0200	.0073	24	572
RR 0, 8	4075.4018	4075.3925	.0200	-.0093	21	579
RR 0, 9	4076.8960	4076.8842	.0140	-.0118	58	9
RR 0, 9	4076.8960	4076.8842	.0140	-.0118	13	589
RR 0,11	4079.8093	4079.7898	.0140	-.0195	19	599
RR 0,12	4081.2243	4081.2072	.0200	-.0172	23	600A
RR 0,13	4082.6080	4082.6069	.0140	-.0011	18	611
RR 0,14	4083.9568	4083.9642	.0100	.0073	16	619
RR 0,15	4085.2664	4085.2932	.0140	.0268	15	624

APPENDIX XI

LIST OF ASSIGNMENTS AND FREQUENCIES OF OBSERVED TRANSITIONS FOR $\nu_1+\nu_2$ OF CHD_3

The following pages contain a list of the observed frequency (in cm^{-1}), together with the assignment ($\Delta K, \Delta J, K, J,$) and weight, of the observed transitions of $\nu_1+\nu_2$ of CHD_3.

ASSIGN-MENT	OBSERVED FREQUENCY	WEIGHT
QP 6,10	5063.6030	.50
QP 7,10	5064.4700	.50.
QP 8,10	5065.2130	.50
QP 9,10	5066.2700	.25
QP 0, 9	5069.2690	.25
QP 1, 9	5069.3980	.50
QP 2, 9	5069.7000	.50
QP 3, 9	5070.2030	.50
QP 4, 9	5070.7540	.50
QP 5, 9	5071.2970	.50
QP 6, 9	5071.8270	.50
QP 7, 9	5072.4500	.25
QP 8, 9	5073.3890	.00
QP 0, 8	5077.9340	.00
QP 2, 8	5078.1150	.50
QP 3, 8	5078.3680	1.00
QP 4, 8	5078.6670	.50
QP 5, 8	5079.0900	.50
QP 6, 8	5079.6190	.25
QP 7, 8	5080.4650	.12
QP 0, 7	5085.6320	.00
QP 2, 7	5085.7610	.50
QP 3, 7	5085.9900	1.00
QP 4, 7	5086.2950	.50
QP 5, 7	5086.7430	.50
QP 6, 7	5087.4660	.25
QP 0, 6	5093.0640	.00
QP 1, 6	5093.0640	.00
QP 2, 6	5093.2160	.50
QP 3, 6	5093.4420	1.00
QP 4, 6	5093.8320	.50
QP 5, 6	5094.3760	.12
QP 0, 5	5100.3970	.00
QP 1, 5	5100.3970	.00
QP 2, 5	5100.5580	1.00
QP 3, 5	5100.8560	1.00
QP 4, 5	5101.3810	.12
QP 0, 4	5107.6150	.00
QP 1, 4	5107.6150	.00
QP 2, 4	5107.8350	1.00
QP 3, 4	5108.2130	.50
QP 0, 3	5114.6830	.25
QP 1, 3	5114.7630	.50
QP 2, 3	5115.0170	.25
QP 0, 2	5121.7680	.00
QP 1, 2	5121.7680	.00
QQ 9,12	5125.8610	.25
QQ16,16	5126.0100	.25
QQ 7,11	5126.6180	.25
QQ10,12	5126.7200	.25

ASSIGN-MENT	OBSERVED FREQUENCY	WEIGHT
QQ15,15	5126.9250	.50
QQ 8,11	5127.1190	.50
QQ 6,10	5127.6580	.00
QQ14,14	5127.8510	.50
QQ 7,10	5128.2540	.25
QP 0, 1	5128.5050	.50
QQ13,13	5128.7600	.25
QQ10,11	5129.0450	.12
QQ 6, 9	5129.2630	.25
QQ12,12	5129.5980	.25
QQ 5, 8	5130.1940	.25
QQ11,11	5130.3500	1.00
QQ 8, 9	5130.6560	.50
QQ 6, 8	5130.7270	.50
QQ10,10	5131.0660	1.00
QQ 7, 8	5131.3700	.50
QQ 2, 7	5130.4790	.12
QQ 5, 7	5131.4580	.25
QQ 9, 9	5131.7170	1.00
QQ 2, 6	5131.6200	.10
QQ 3, 6	5131.8220	.25
QQ 6, 7	5132.0190	1.00
QQ 4, 6	5132.1580	.50
QQ 8, 8	5132.3150	1.00
QQ 5, 6	5132.6080	.50
QQ 7, 7	5132.8540	.50
QQ 3, 5	5132.7680	.50
QQ 4, 5	5133.1570	.50
QQ 3, 4	5133.6340	.50
QQ 6, 6	5133.3310	1.00
QQ 1, 3	5133.8750	.12
QQ 5, 5	5133.7260	.50
QQ 2, 3	5134.0760	.25
QQ 4, 4	5134.1640	.50
QQ 3, 3	5134.4390	1.00
QQ 2, 2	5135.0890	.50
QQ 1, 1	5134.8770	.25
QR 0, 0	5141.4250	.12
QR 0, 1	5147.4800	.25
QR 1, 1	5147.5410	.25
QR 0, 2	5153.5120	.00
QR 1, 2	5153.5120	.00
QR 2, 2	5153.7360	.12
QR 0, 3	5159.3850	.00
QR 1, 3	5159.3850	.00
QR 2, 3	5159.5480	.25
QR 3, 3	5159.8570	.25
QR 0, 4	5165.1490	.00
QR 1, 4	5165.1490	.00
QR 2, 4	5165.2980	.50

ASSIGN-MENT	OBSERVED FREQUENCY	WEIGHT
QR 3, 4	5165.5340	.50
QR 4, 4	5165.9220	.50
QR 0, 5	5170.7840	.00
QR 1, 5	5170.7840	.00
QR 2, 5	5170.9380	.50
QR 3, 5	5171.1460	1.00
QR 4, 5	5171.4700	1.00
QR 5, 5	5171.9090	.25
QR 0, 6	5176.1420	.00
QR 1, 6	5176.1420	.00
QR 2, 6	5176.3290	.50
QR 3, 6	5176.5850	1.00
QR 4, 6	5176.9000	.25
QR 5, 6	5177.3230	.50
QR 6, 6	5177.8770	.50
QR 0, 7	5180.5270	.25
QR 1, 7	5180.6400	.25
QR 2, 7	5180.9590	.12
QR 3, 7	5181.4610	1.00
QR 4, 7	5182.0250	1.00
QR 5, 7	5182.5780	1.00
QR 6, 7	5183.1180	1.00
QR 7, 7	5183.7630	.50
QR 5, 8	5186.6640	.12
QR 6, 8	5187.9060	.25
QR 7, 8	5188.8660	.12
QR 8, 8	5189.6230	.12

APPENDIX XII

COMPARISON OF THE OBSERVED AND CALCULATED GROUND STATE COMBINATION DIFFERENCES OF $\nu_1+\nu_2$ OF CHD_3

The following pages contain a comparison of the observed and calculated ground state combination differences of $\nu_1+\nu_2$ of CH_3D from a simultaneous least squares analysis of these ground state combination differences. The constants determined are (in cm^{-1}):

$$B_o = 3.27944$$
$$D_o^{JK} = -4.8 \times 10^{-5}$$
$$D_o^{J} = 5.22 \times 10^{-5}$$

The columns, left to right, are the assignment (cf. Chapter 4); the calculated combination difference (in cm^{-1}); the observed combination difference (in cm^{-1}); the $\Delta\nu$ (weight = $(NORM)^2/(\Delta\nu)^2$); and the observed minus the calculated combination difference.

ASSIGNMENT	CALCULATED GSCD	OBSERVED GSCD	DELTA NU	OBS-CALC
QP 2, 2	19.6722	19.6702	.0245	-.0020
QP 2, 3	26.2237	26.2412	.0224	.0175
QP 2, 6	45.8433	45.8595	.0316	.0162
QP 2, 7	52.3673	52.3638	.0316	-.0034
RP 2, 3	45.8959	45.9017	.0300	.0059
RP 2, 4	58.9939	58.9896	.0224	-.0044
RP 2, 5	72.0807	72.0814	.0200	.0007
RP 2, 7	98.2105	98.2145	.0200	.0040
RP 2, 8	111.2485	111.2590	.0316	.0105
QP 3, 3	26.2256	26.2255	.0173	-.0001
QP 3, 4	32.7727	32.7777	.0173	.0050
QP 3, 5	39.3134	39.3254	.0173	.0120
QP 3, 6	45.8467	45.8318	.0224	-.0149
RP 3, 4	58.9983	59.0008	.0224	.0025
RP 3, 5	72.0861	72.0923	.0173	.0062
RP 3, 6	85.1601	85.1556	.0140	-.0045
RP 3, 7	98.2178	98.2165	.0140	-.0013
RP 3, 8	111.2567	111.2574	.0173	.0006
RQ 3, 4	26.2256	26.2231	.0245	-.0025
RQ 3, 5	32.7727	32.7668	.0200	-.0058
RQ 3, 6	39.3134	39.3238	.0224	.0104
RP 4, 5	72.0935	72.0907	.0200	-.0029
RP 4, 6	85.1689	85.1745	.0173	.0056
RP 4, 7	98.2280	98.2330	.0245	.0050
RP 4, 8	111.2683	111.2714	.0173	.0032
QP 4, 4	32.7761	32.7833	.0316	.0073
QP 4, 5	39.3175	39.3254	.0200	.0080
QP 4, 6	45.8514	45.8631	.0200	.0117
RQ 4, 5	32.7761	32.7652	.0200	-.0108
RQ 4, 6	39.3175	39.3114	.0173	-.0061
RP 5, 6	85.1802	85.1657	.0245	-.0146
RP 5, 7	98.2410	98.2330	.0200	-.0080
RP 5, 8	111.2831	111.2807	.0173	-.0024
QP 5, 6	45.8575	45.8651	.0200	.0076
QP 5, 7	52.3835	52.3683	.0245	-.0153
QP 5, 8	58.8995	58.8971	.0245	-.0024
RQ 5, 7	45.8575	45.8547	.0245	.0072
RQ 5, 8	52.3835	52.3835	.0224	.0000
RP 6, 7	98.2570	98.2575	.0245	.0005
RP 6, 8	111.3012	111.2915	.0173	-.0097
RP 6, 9	124.3241	124.3030	.0245	-.0211
QP 6, 6	45.8650	45.8651	.0224	.0002
QP 6, 7	52.3921	52.3996	.0224	.0076
QP 6, 8	58.9091	58.9003	.0200	-.0088
RQ 6, 7	45.8650	45.8579	.0173	-.0071
RQ 6, 8	52.3921	52.3912	.0173	-.0009
RP 7, 8	111.3226	111.3124	.0245	-.0102
RP 7, 9	124.3480	124.3958	.0316	.0478
QP 7, 7	52.4021	52.3892	.0316	-.0130
QP 7, 8	58.9205	58.9192	.0245	-.0012

ASSIGN-MENT	CALCULATED GSCD	OBSERVED GSCD	DELTA NU	OBS-CALC
RQ 7, 8	52.4021	52.3932	.0200	-.0090
RP 8, 9	124.3756	124.4107	.0316	.0351
RQ 8, 9	58.9336	58.9675	.0316	.0339
QP 9, 9	65.4585	65.4477	.0224	-.0109

APPENDIX XIII

COMPARISON OF THE OBSERVED AND CALCULATED GROUND STATE COMBINATION DIFFERENCES OF $\nu_2+\nu_3$ OF CH_3D

The following pages contain a comparison of the observed and calculated ground state combination differences of $\nu_2+\nu_3$ of CH_3D from a simultaneous least squares analysis of these ground state combination differences. The constants determined are (in cm^{-1}):

$$B_0 = 3.88107$$
$$D_0^{JK} = 1.192 \times 10^{-4}$$
$$D_0^{J} = 5.28 \times 10^{-5}$$

The columns, left to right, are: the assignment (cf. Chapter 4); the calculated combination differences (in cm^{-1}); the observed combination difference (in cm^{-1}); the $\Delta\nu$ (weight = $(NORM)^2/(\Delta\nu)^2$); and the observed minus the calculated combination difference.

ASSIGN-MENT	CALCULATED GSCD	OBSERVED GSCD	DELTA NU	OBS-CALC
RP 2, 3	54.3091	54.3210	.0122	.0119
RP 2, 4	69.8107	69.8068	.0122	-.0039
RP 2, 5	85.3009	85.3030	.0122	.0020
RP 2, 6	100.7772	100.7837	.0122	.0065
RP 2, 7	116.2370	116.2351	.0100	-.0018
RP 2, 8	131.6777	131.6792	.0100	.0015
RP 2, 9	147.0969	147.0972	.0212	.0003
RP 2,12	193.1995	193.2103	.0292	.0108
RQ 2, 3	23.2779	23.2878	.0122	.0100
RQ 2, 4	31.0312	31.0454	.0300	.0142
RQ 2, 5	38.7795	38.7733	.0212	-.0062
RQ 2, 7	54.2558	54.2605	.0212	.0047
RQ 2, 8	61.9812	61.9508	.0212	-.0304
RQ 2, 9	69.6965	69.7161	.0292	.0196
RQ 2,10	77.4004	77.4039	.0346	.0035
QP 2, 3	31.0312	31.0331	.0100	.0019
QP 2, 4	38.7795	38.7614	.0292	-.0181
QP 2, 5	46.5214	46.5296	.0224	.0082
QP 2, 7	61.9812	61.9746	.0212	-.0066
QP 2, 8	69.6965	69.7283	.0158	.0318
QP 2, 9	77.4004	77.3811	.0346	-.0193
RP 3, 4	69.8000	69.8039	.0141	.0039
RP 3, 5	85.2878	85.2888	.0141	.0010
RP 3, 6	100.7617	100.7641	.0122	.0023
RP 3, 7	116.2191	116.2052	.0122	-.0139
RP 3, 8	131.6574	131.6602	.0122	.0028
RP 3, 9	147.0742	147.0891	.0158	.0149
RP 3,11	177.8329	177.8232	.0212	-.0097
RP 3,12	193.1697	193.1749	.0300	.0052
RQ 3, 4	31.0264	31.0418	.0173	.0154
RQ 3, 7	54.2474	54.2409	.0141	-.0066
RQ 3, 8	61.9717	61.9721	.0173	.0004
RQ 3, 9	69.6858	69.6901	.0100	.0043
RQ 3,10	77.3885	77.3962	.0173	.0077
RQ 3,12	92.7545	92.7434	.0173	-.0111
QP 3, 4	38.7735	38.7621	.0173	-.0115
QP 3, 7	61.9717	61.9643	.0122	-.0073
QP 3, 8	69.6858	69.6881	.0158	.0024
QP 3, 9	77.3885	77.3991	.0158	.0106
QP 3,12	100.4153	100.4315	.0316	.0162
RP 4, 5	85.2695	85.2846	.0122	.0152
RP 4, 6	100.7400	100.7551	.0122	.0150
RP 4, 7	116.1941	116.1817	.0100	-.0123
RP 4, 9	147.0425	147.0399	.0212	-.0026
RP 4,10	162.4319	162.4631	.0292	.0312
RP 4,11	177.7945	177.7418	.0300	-.0527
RP 4,12	193.1280	193.1174	.0245	-.0107
RQ 4, 6	46.5043	46.5100	.0158	.0057
RQ 4, 9	69.6708	69.6576	.0122	-.0132
QP 4, 6	54.2357	54.2451	.0173	.0093

ASSIGN-MENT	CALCULATED GSCD	OBSERVED GSCD	DELTA NU	OBS-CALC
QP 4, 9	77.3718	77.3823	.0224	.0106
RQ 5, 6	46.4914	46.4901	.0158	-.0013
RQ 5, 7	54.2207	54.2270	.0122	.0063
RQ 5, 8	61.9412	61.9306	.0100	-.0106
RQ 5, 9	69.6515	69.6518	.0292	.0003
RQ 5,10	77.3503	77.3399	.0122	-.0104
RQ 5,11	85.0365	85.0296	.0200	-.0069
RQ 5,12	92.7087	92.7039	.0158	-.0049
RQ 5,14	108.0062	108.0296	.0316	.0234
RP 5, 6	100.7121	100.7071	.0122	-.0050
RP 5, 7	116.1619	116.1615	.0122	-.0004
RP 5, 8	131.5926	131.5817	.0212	-.0109
RP 5, 9	147.0018	147.0023	.0122	.0005
RP 5,10	162.3868	162.3872	.0292	.0004
RP 5,11	177.7452	177.7450	.0200	-.0002
QP 5, 6	54.2207	54.2171	.0173	-.0037
QP 5, 7	61.9412	61.9344	.0141	-.0067
QP 5, 8	69.6515	69.6512	.0212	-.0003
QP 5, 9	77.3503	77.3505	.0300	.0002
QP 5,10	85.0365	85.0473	.0300	.0108
QP 5,11	92.7087	92.7154	.0200	.0067
RP 6, 7	116.1226	116.1190	.0158	-.0036
RP 6, 8	131.5481	131.5409	.0173	-.0072
RP 6,10	162.3318	162.3286	.0245	-.0031
RP 6,11	177.6849	177.6881	.0173	.0032
RP 6,12	193.0089	192.9607	.0300	-.0481
RQ 6, 7	54.2024	54.1830	.0212	-.0194
RQ 6, 8	61.9202	61.9158	.0346	-.0044
RQ 6,10	77.3241	77.3122	.0158	-.0119
RQ 6,13	100.3316	100.3530	.0245	.0214
QP 6, 7	61.9202	61.9360	.0245	.0158
QP 6, 8	69.6279	69.6251	.0300	-.0028
QP 6, 9	77.3241	77.3396	.0224	.0155
QP 6,10	85.0077	85.0164	.0212	.0087
RP 7, 8	131.4954	131.4885	.0173	-.0069
RP 7, 9	146.8931	146.8997	.0173	.0066
RP 7,10	162.2667	162.2778	.0173	.0111
RP 7,11	177.6137	177.6299	.0200	.0162
RP 7,12	192.9314	192.8906	.0346	-.0408
RQ 7, 8	61.8954	61.8904	.0224	-.0050
RQ 7, 9	69.6000	69.6039	.0158	.0039
RQ 7,10	77.2931	77.3090	.0224	.0159
RQ 7,11	84.9736	84.9785	.0173	.0049
RQ 7,12	92.6401	92.6479	.0283	.0078
QP 7, 8	69.6000	69.5981	.0245	-.0019
QP 7, 9	77.2931	77.2958	.0122	.0027
QP 7,10	84.9736	84.9688	.0283	-.0048
QP 7,11	92.6401	92.6514	.0173	.0114
QP 7,12	100.2913	100.2427	.0346	-.0486
RP 8,10	162.1916	162.1762	.0212	-.0154

ASSIGN-MENT	CALCULATED GSCD	OBSERVED GSCD	DELTA NU	OBS-CALC
RP 8,11	177.5314	177.5292	.0283	-.0022
RQ 8,11	84.9343	84.9389	.0224	.0046
RQ 8,12	92.5972	92.5964	.0200	-.0007
QP 8,11	92.5972	92.5903	.0224	-.0068
RP 9,10	162.1066	162.1064	.0212	-.0001
RP 9,13	208.0115	208.0710	.0346	.0594
RQ 9,11	84.8897	84.8730	.0141	-.0167
RQ 9,13	100.1922	100.2562	.0346	.0640
QP 9,13	107.8193	107.8147	.0400	-.0046

EXCLUDED FROM LEAST SQUARES ANALYSIS DUE TO ZERO WEIGHT

RP 2,10	162.4919	162.4808	.9999	-.0112
RQ 2,12	92.7688	92.8949	.9999	.1261
QP 2,10	85.0915	85.0769	.9999	-.0147
RP 3,10	162.4669	162.4656	.9999	-.0012
RQ 3, 6	46.5143	46.4901	.9999	-.0242
QP 3, 6	54.2474	54.2746	.9999	.0272
QP 3,10	85.0784	85.0695	.9999	-.0090
RP 4, 8	131.6291	131.6441	.9999	.0150
RQ 4, 5	38.7652	38.7624	.9999	-.0028
RQ 4, 7	54.2357	54.2209	.9999	-.0148
RQ 4,10	77.3718	77.3061	.9999	-.0656
RQ 4,12	92.7344	92.7090	.9999	-.0254
QP 4, 5	46.5043	46.5222	.9999	.0179
QP 4, 7	61.9583	61.9608	.9999	.0025
QP 4,10	85.0601	85.1570	.9999	.0969
QP 4,12	100.3936	100.4084	.9999	.0148
RP 5,12	193.0744	193.1084	.9999	.0339
QP 5,12	100.3657	100.4045	.9999	.0388
RQ 6,11	85.0077	85.0318	.9999	.0242
RQ 6,14	107.9695	107.9598	.9999	-.0097
QP 6,11	92.6773	92.5984	.9999	-.0789
RP 8,12	192.8420	192.8524	.9999	.0103
QP 8,12	100.2449	100.2559	.9999	.0110
RP 9,11	177.4383	177.4353	.9999	-.0029
RP 9,12	192.7408	192.7774	.9999	.0367
RQ 9,12	92.5486	92.5476	.9999	-.0010
RQ 9,15	115.4287	115.3356	.9999	-.0931
QP 9,11	92.5486	92.5624	.9999	.0138
QP 9,12	100.1922	100.2299	.9999	.0377
RQ 7,15	115.5431	115.3562	.0346	-.1870

APPENDIX XIV

COMPARISON OF THE OBSERVED AND CALCULATED UPPER STATE COMBINATION DIFFERENCES OF $\nu_2+\nu_3$ OF CH_3D

The following pages contain a comparison of the observed and calculated upper state combination differences of $\nu_2+\nu_3$ of CHD_3 from a simultaneous least squares analysis of these upper state combination differences. The constants determined are (in cm^{-1}):

$$B_v = 3.74260$$
$$D_v^{JK} = 2.51 \times 10^{-4}$$
$$D_v^{J} = -1.5 \times 10^{-5}$$

The columns, left to right, are: the assignment (cf. Chapter 4); the calculated combination differences (in cm^{-1}); the observed combination difference (in cm^{-1}); the $\Delta\nu$ (weight = $(NORM)^2/(\Delta\nu)^2$); and the observed minus the calculated combination difference.

ASSIGN-MENT	CALCULATED USCD	OBSERVED USCD	DELTA NU	OBS-CALC
RP 2, 3	52.3879	52.3688	.0122	-.0192
RP 2, 4	67.3603	67.3616	.0100	.0013
RP 2, 5	82.3360	82.3458	.0100	.0098
RP 2, 6	97.3157	97.3206	.0122	.0049
RP 2, 7	112.3001	112.2964	.0122	-.0037
RP 2, 8	127.2900	127.2963	.0100	.0063
RP 2, 9	142.2861	142.2881	.0212	.0020
RQ 2, 3	29.9367	29.9348	.0122	-.0019
RQ 2, 4	37.4236	37.4390	.0292	.0154
RQ 2, 5	44.9124	44.9187	.0212	.0063
RQ 2, 7	59.8968	59.9031	.0212	.0064
RQ 2, 8	67.3932	67.3693	.0158	-.0239
RQ 2, 9	74.8929	74.9066	.0346	.0137
QP 2, 3	22.4512	22.4339	.0100	-.0173
QP 2, 4	29.9367	29.9226	.0292	-.0141
QP 2, 5	37.4236	37.4271	.0212	.0035
QP 2, 7	52.4033	52.3932	.0224	-.0101
QP 2, 8	59.3963	59.9269	.0158	.0302
QP 2, 9	67.3932	67.3815	.0292	-.0117
QP 2,10	74.8929	74.8838	.0346	-.0092
RP 3, 4	67.3377	67.3311	.0141	-.0067
RP 3, 5	82.3084	82.3094	.0121	.0010
RP 3, 6	97.2830	97.2788	.0141	-.0043
RP 3, 7	112.2624	112.2719	.0141	.0095
RP 3, 8	127.2473	127.2451	.0100	-.0022
RP 3, 9	142.2384	142.2351	.0121	-.0034
RP 3,10	157.2365	157.2388	.0158	.0023
RQ 3, 4	37.4111	37.4235	.0173	.0125
RQ 3, 7	59.8767	59.8819	.0141	.0052
RQ 3, 8	67.3706	67.3709	.0158	.0003
RQ 3, 9	74.8678	74.8661	.0122	-.0018
RQ 3,10	82.3687	82.3699	.0158	.0012
QP 3, 4	29.9267	29.8995	.0173	-.0272
QP 3, 7	52.3857	52.3900	.0141	.0043
QP 3, 8	59.8767	59.8742	.0158	-.0025
QP 3, 9	67.3706	67.3690	.0100	-.0016
QP 3,10	74.8678	74.8690	.0200	.0011
QP 3,12	89.8735	89.8814	.0245	.0079
RP 4, 5	82.2697	82.2583	.0122	-.0114
RP 4, 6	97.2373	97.2315	.0121	-.0059
RP 4, 7	112.2097	112.2198	.0121	.0101
RP 4, 8	127.1876	127.1885	.0100	.0009
RP 4,10	157.1627	157.1591	.0224	-.0036
RP 4,11	172.1614	172.1702	.0316	.0089
QP 4, 6	44.8762	44.8688	.0173	-.0074
RQ 4, 6	52.3611	52.3627	.0158	.0015
RQ 4, 9	74.8327	74.8294	.0122	-.0033
RP 5, 6	97.1786	97.1678	.0100	-.0108
RP 5, 7	112.1420	112.1301	.0122	-.0119
RP 5, 8	127.1108	127.1146	.0122	.0038

ASSIGN-MENT	CALCULATED USCD	OBSERVED USCD	DELTA NU	OBS-CALC
RP 5, 9	142.0858	142.0871	.0212	.0013
RP 5,10	157.0678	157.0767	.0173	.0089
RP 5,11	172.0575	172.0667	.0292	.0092
RP 5,12	187.0555	187.0605	.0158	.0049
RQ 5, 6	52.3295	52.3302	.0158	.0007
RQ 5, 7	59.8125	59.8073	.0122	-.0052
RQ 5, 8	67.2983	67.3008	.0100	.0025
RQ 5, 9	74.7875	74.7869	.0292	-.0005
RQ 5,10	82.2803	82.2792	.0173	-.0011
RQ 5,11	89.7772	89.7698	.0158	-.0073
RQ 5,12	97.2784	97.2791	.0158	.0007
RQ 5,14	112.2955	112.2153	.0400	-.0801
QP 5, 6	44.8491	44.8376	.0158	-.0115
QP 5, 7	52.3295	52.3202	.0141	-.0093
QP 5, 8	59.8125	59.8137	.0122	.0013
QP 5, 9	67.2983	67.3002	.0346	.0019
QP 5,10	74.7875	74.7976	.0141	.0101
QP 5,11	82.2803	82.2969	.0316	.0166
QP 5,12	89.7772	89.7814	.0200	.0042
RP 6, 7	112.0591	112.0333	.0200	-.0258
RP 6, 9	141.9809	141.9897	.0173	.0088
RP 6,10	156.9518	156.9841	.0224	.0323
RP 6,11	171.9305	171.9660	.0224	.0356
RQ 6, 7	59.7683	59.7478	.0245	-.0205
RQ 6, 9	74.7323	74.7249	.0173	-.0074
RQ 6,10	82.2196	82.2319	.0122	.0123
RQ 6,13	104.7071	104.6793	.0173	-.0277
RQ 6,14	112.2126	112.1815	.0200	-.0311
QP 6, 7	52.2908	52.2855	.0245	-.0054
QP 6, 8	59.7683	59.7681	.0316	-.0002
QP 6, 9	67.2486	67.2648	.0141	.0162
QP 6,10	74.7323	74.7522	.0212	.0199
QP 6,13	97.2066	97.1742	.0346	-.0324

EXCLUDED FROM LEAST SQUARES ANALYSIS DUE TO PERTURBATIONS OR ZERO WEIGHT OR BOTH

RP 2,11	172.2999	172.2400	.9999	-.0599
RP 2,12	187.3191	187.2624	.9999	-.0566
RP 2,13	202.3474	202.1466	.9999	-.2008
RP 3,11	172.2422	172.2249	.9999	-.0173
RP 4,12	187.1685	187.0598	.9999	-.1087
RP 4, 9	142.1717	142.1949	.9999	.0232
RP 3,13	202.2796	202.1321	.0245	-.1475

ASSIGN-MENT	CALCULATED USCD	OBSERVED USCD	DELTA NU	OBS-CALC
RP 3,12	187.2563	187.1666	.0212	-.0897
QP 3, 6	44.8973	44.9225	.9999	.0252
RQ 3, 6	52.3857	52.3562	.9999	-.0295
RQ 3,12	97.3828	97.3141	.0158	-.0687
RP 4,13	202.1847	202.1540	.9999	-.0308
QP 4, 5	37.3935	37.4017	.9999	.0082
QP 4, 7	52.3611	52.3813	.9999	.0202
QP 4, 8	59.8486	59.8134	.9999	-.0352
QP 4, 9	67.3390	67.3655	.9999	.0265
QP 4,10	74.8327	74.9056	.9999	.0729
QP 4,11	82.3300	82.3104	.9999	-.0196
QP 4,12	89.8314	90.0242	.9999	.1928
RQ 4, 5	44.8762	44.8566	.9999	-.0196
RQ 4, 7	59.8486	59.8488	.9999	.0002
RQ 4, 8	67.3390	67.3751	.9999	.0361
RQ 4,10	82.3300	82.2535	.9999	-.0766
RQ 4,11	89.8314	89.8599	.9999	.0285
RQ 4,12	97.3371	97.2672	.9999	-.0699
RP 5,13	202.0627	202.0437	.9999	-.0191
RQ 6,11	89.7109	89.7495	.9999	.0387
RQ 6,12	97.2066	97.2373	.9999	.0307
QP 6,11	82.2196	82.2165	.9999	-.0031
QP 6,12	89.7109	89.7248	.9999	.0139
RP 6,12	186.9175	186.9724	.0200	.0549
RP 6,13	201.9136	201.8536	.0224	-.0601

APPENDIX XV

COMPARISON OF THE OBSERVED AND CALCULATED TRANSITION FREQUENCIES OF $\nu_2+\nu_3$ OF CH_3D

The following pages contain a comparison of the observed and calculated transition frequencies of $\nu_2+\nu_3$ of CH_3D from a simultaneous least squares analysis of these transition frequencies. The constants determined (cf. Chapter 9) are (in cm^{-1}):

$$\nu_0 = 3499.6291$$

$$\alpha_2^A + \alpha_3^A - \alpha_2^B - \alpha_3^B = 0.15718$$

The first set of transitions are those which were included in the least squares analysis. The second set contains those excluded due to perturbations or zero weight, (i.e., $\Delta\nu \approx 0.9999$).

The columns, left to right, are: the assignment ($\Delta K, \Delta J, K, J$); the calculated transition frequency (in cm^{-1}); the observed transition frequency (in cm^{-1}); the $\Delta\nu$ (weight = $(NORM)^2/(\Delta\nu)^2$); and the observed minus the calculated frequency.

ASSIGN-MENT	CALCULATED FREQUENCY	OBSERVED FREQUENCY	DELTA NU	OBS-CALC
QP 2, 3	3476.1485	3476.1674	.0070	.0189
QP 2, 4	3467.5685	3467.5681	.0070	-.0004
QP 2, 5	3458.7257	3458.7293	.0070	.0036
QP 2, 6	3449.6278	3449.6268	.0010	-.0010
QP 2, 7	3440.2844	3440.2937	.0100	.0093
QP 2, 8	3430.7064	3430.7122	.0070	.0058
QP 2, 9	3420.9067	3420.9108	.0070	.0042
QP 2,10	3410.8995	3410.9113	.0100	.0119
QP 2,12	3390.3282	3390.2932	.0200	-.0350
QP 3, 4	3468.3513	3468.3580	.0100	.0067
QP 3, 5	3459.5044	3459.5034	.0100	-.0009
QP 3, 6	3450.4011	3450.4003	.0100	-.0009
QP 3, 7	3441.0510	3441.0482	.0100	-.0028
QP 3, 8	3431.4650	3431.4738	.0070	.0088
QP 3, 9	3421.6559	3421.6599	.0070	.0040
QP 3,10	3411.6380	3411.6298	.0140	-.0082
QP 4, 5	3460.5945	3460.5972	.0100	.0027
QP 4, 6	3451.4837	3451.4767	.0100	-.0071
QP 4, 7	3442.1242	3442.1108	.0100	-.0134
QP 4, 8	3432.5269	3432.5210	.0070	-.0060
QP 4,10	3412.6719	3412.6696	.0200	-.0024
QP 4,11	3402.4445	3402.4182	.0283	-.0262
QP 4,13	3381.4777	3381.4711	.0200	-.0066
QP 5, 6	3452.8757	3452.8789	.0070	.0032
QP 5, 7	3443.5040	3443.4995	.0100	-.0046
QP 5, 8	3433.8923	3433.8852	.0100	-.0071
QP 5, 9	3424.0533	3424.0478	.0200	-.0055
QP 5,10	3414.0013	3413.9975	.0100	-.0038
QP 5,11	3403.7522	3403.7478	.0283	-.0045
QP 5,12	3393.3238	3393.3292	.0140	.0054
QP 6, 7	3445.1905	3445.2053	.0140	.0148
QP 6, 8	3435.5611	3435.5547	.0140	-.0064
QP 6, 9	3425.7015	3425.6977	.0100	-.0038
QP 6,10	3415.6260	3415.6229	.0200	-.0031
QP 6,11	3405.3506	3405.3587	.0200	.0081
QP 6,12	3394.8929	3394.9189	.0140	.0260
QQ 2, 3	3498.5997	3498.6013	.0700	.0016
QQ 2, 4	3497.5052	3497.4908	.0283	-.0144
QQ 2, 5	3496.1492	3496.1564	.0200	.0072
QQ 2, 7	3492.6876	3492.6869	.0200	-.0007
QQ 2, 8	3490.6031	3490.6392	.0140	.0361
QQ 2, 9	3488.2997	3488.2924	.0283	-.0073
QQ 2,10	3485.7922	3485.7951	.0283	.0029
QQ 3, 4	3498.2779	3498.2655	.0140	-.0124
QQ 3, 7	3493.4366	3493.4382	.0100	.0016
QQ 3, 8	3491.3416	3491.3480	.0140	.0064
QQ 3, 9	3489.0263	3489.0289	.0070	.0025
QQ 3,10	3486.5056	3486.4988	.0140	-.0068
QQ 3,12	3480.9147	3480.8979	.0140	-.0168
QQ 4, 6	3496.3599	3496.3455	.0140	-.0144

ASSIGN-MENT	CALCULATED FREQUENCY	OBSERVED FREQUENCY	DELTA NU	OBS-CALC
QQ 4, 9	3490.0436	3490.0519	.0100	.0083
QQ 5, 6	3497.7247	3497.7165	.0140	-.0082
QQ 5, 7	3495.8334	3495.8197	.0100	-.0138
QQ 5, 8	3493.7047	3493.6990	.0700	-.0057
QQ 5, 9	3491.3515	3491.3480	.0283	-.0035
QQ 5,10	3488.7886	3488.7951	.0100	.0065
QQ 5,11	3486.0323	3486.0447	.0140	.0123
QQ 5,12	3483.1007	3483.1106	.0140	.0099
QQ 6, 7	3497.4813	3497.4908	.0200	.0095
QQ 6, 8	3495.3293	3495.3228	.0283	-.0065
QQ 6, 9	3492.9500	3492.9625	.0100	.0125
QQ 6,10	3490.3581	3490.3751	.0070	.0170
QR 2, 2	3521.8775	3521.8891	.0100	.0115
QR 2, 3	3528.5364	3528.5361	.0100	-.0002
QR 2, 4	3534.9287	3534.9297	.0700	.0010
QR 2, 5	3541.0615	3541.0751	.0070	.0136
QR 2, 6	3546.9433	3546.9474	.0070	.0041
QR 2, 7	3552.5842	3552.5900	.0070	.0058
QR 2, 8	3557.9961	3558.0085	.0070	.0124
QR 2, 9	3563.1924	3563.1990	.0200	.0065
QR 3, 3	3529.3043	3529.3074	.0100	.0030
QR 3, 4	3535.6889	3535.6891	.0100	.0002
QR 3, 5	3541.8126	3541.8129	.0070	.0002
QR 3, 6	3547.6840	3547.6790	.0100	-.0050
QR 3, 7	3553.3132	3553.3201	.0100	.0069
QR 3, 8	3558.7120	3558.7189	.0070	.0069
QR 3, 9	3563.8940	3563.8949	.0100	.0010
QR 3,10	3568.8740	3568.8686	.0070	-.0054
QR 3,11	3573.6690	3573.6413	.0100	-.0276
QR 4, 4	3536.7532	3536.7613	.0070	.0081
QR 4, 5	3542.8641	3542.8555	.0070	-.0086
QR 4, 6	3548.7209	3548.7027	.0070	-.0182
QR 4, 7	3554.3337	3554.3306	.0070	-.0031
QR 4, 8	3559.7143	3559.7095	.0070	-.0048
QR 4, 9	3564.8761	3564.8813	.0070	.0053
QR 4,10	3569.8342	3569.8286	.0100	-.0055
QR 4,11	3574.6053	3574.5885	.0140	-.0168
QR 5, 5	3544.2161	3544.2066	.0070	-.0095
QR 5, 6	3550.0541	3550.0467	.0070	-.0074
QR 5, 7	3555.6458	3555.6296	.0070	-.0162
QR 5, 8	3561.0028	3560.9998	.0070	-.0030
QR 5, 9	3566.1388	3566.1350	.0070	-.0038
QR 5,10	3571.0687	3571.0742	.0140	.0056
QR 5,11	3575.8092	3575.8145	.0070	.0053
QR 5,12	3580.3787	3580.3897	.0070	.0110
QR 6, 6	3551.6836	3551.6737	.0070	-.0098
QR 6, 7	3557.2494	3557.2386	.0140	-.0109
QR 6, 9	3567.6821	3567.6874	.0140	.0053
QR 6,10	3572.5775	3572.6070	.0100	.0296

ASSIGN-MENT	CALCULATED FREQUENCY	OBSERVED FREQUENCY	DELTA NU	OBS-CALC

EXCLUDED FROM LEAST SQUARES ANALYSIS DUE TO PERTURBATIONS OR ZERO WEIGHT OR BOTH

QP 2,13	3379.8010	3379.7479	.0283	-.0531
QP 4,12	3392.0400	3392.0868	.0283	.0469
QP 6,13	3384.2721	3384.3640	.0283	.0919
QP 0, 2	3483.8299	3483.9249	.9999	.0950
QP 0, 3	3475.5201	3475.6229	.0200	.1028
QP 0, 4	3466.9423	3467.0381	.0140	.0959
QP 0, 5	3458.1027	3458.1964	.0140	.0937
QP 0, 6	3449.0092	3449.1045	.0140	.0953
QP 0, 7	3439.6711	3439.7588	.0200	.0877
QP 0, 8	3430.0996	3430.1838	.0140	.0842
QP 0, 9	3420.3073	3420.3770	.0140	.0697
QP 0,10	3410.3086	3410.3524	.0140	.0437
QP 0,12	3389.7576	3389.7728	.0200	.0152
QP 2,11	3400.7008	3400.7182	.9999	.0174
QP 3,11	3401.4273	3401.4293	.9999	.0020
QP 4, 9	3422.7047	3422.6865	.9999	-.0183
QP 5,13	3382.7352	3382.7061	.9999	-.0291
QP 7, 8	3437.5334	3437.5838	.0200	.0504
QP 7, 9	3427.6495	3427.6788	.0140	.0294
QP 7,10	3417.5462	3417.5658	.0100	.0196
QP 7,11	3407.2396	3407.2678	.0140	.0282
QP 7,12	3396.7473	3396.8029	.0140	.0556
QP 7,13	3386.0885	3386.2560	.0283	.1675
QP 8,11	3409.4192	3409.4921	.0200	.0728
QP 8,12	3398.8870	3398.9931	.0200	.1061
QP 8,13	3388.1844	3388.3388	.9999	.1544
QP 9,11	3411.8895	3412.0289	.0200	.1394
QQ 3, 6	3495.2983	3495.3228	.9999	.0244
QQ 4, 7	3494.4852	3494.4818	.9999	-.0034
QQ 4, 8	3492.3754	3492.3344	.9999	-.0410
QQ 4,12	3481.8711	3481.8795	.9999	.0084
QQ 5,14	3476.7913	3476.7202	.0283	-.0711
QQ 6,11	3487.5700	3487.5752	.9999	.0052
QQ 6,13	3481.4784	3481.5382	.0200	.0599
QQ 6,14	3478.2158	3478.2578	.0140	.0420
QQ 7, 8	3497.2493	3497.2769	.0200	.0276
QQ 7, 9	3494.8392	3494.8616	.0070	.0224
QQ 7,10	3492.2130	3492.2366	.0200	.0236
QQ 7,11	3489.3872	3489.4544	.0100	.0672
QQ 7,12	3486.3796	3486.4988	.0200	.1192
QQ 7,13	3483.2099	3483.3409	.0283	.1309

ASSIGN-MENT	CALCULATED FREQUENCY	OBSERVED FREQUENCY	DELTA NU	OBS-CALC
QQ 7,15	3476.4709	3476.4298	.0200	-.0411
QQ 8, 9	3497.0190	3497.2769	.0200	.2579
QQ 8,10	3494.3533	3494.4818	.0140	.1285
QQ 8,11	3491.4840	3491.5834	.0100	.0995
QQ 8,12	3488.4289	3488.5947	.0100	.1658
QQ 8,13	3485.2079	3485.4600	.0140	.2521
QQ 8,14	3481.8420	3481.8795	.0283	.0375
QQ 9,11	3493.8603	3493.9916	.0100	.1313
QQ 9,12	3490.7515	3490.7955	.0140	.0439
QQ 9,13	3487.4722	3487.5752	.9999	.1030
QQ 9,13	3487.4722	3488.0380	.0200	.5658
QR 0, 1	3514.3233	3514.4313	.0140	.1079
QR 0, 2	3521.2580	3521.3571	.0140	.0991
QR 0, 3	3527.9220	3528.0174	.0140	.0954
QR 0, 4	3534.3206	3534.4232	.0140	.1026
QR 0, 5	3540.4606	3540.5653	.0140	.1047
QR 0, 6	3546.3508	3546.4434	.0140	.0926
QR 0, 7	3552.0011	3552.0767	.0140	.0756
QR 0, 8	3557.4234	3557.4598	.0140	.0364
QR 0, 9	3562.6312	3562.6345	.0200	.0033
QR 0,10	3567.6396	3567.6874	.0140	.0478
QR 0,11	3572.4651	3572.6070	.0200	.1419
QR 0,12	3577.1263	3577.1636	.0200	.0374
QR 0,13	3581.6430	3581.5423	.0200	-.1006
QR 0,14	3586.0368	3585.7255	.9999	-.3113
QR 2,11	3573.0002	3572.9582	.0070	-.0419
QR 2,12	3577.6467	3577.5557	.0200	-.0910
QR 3,12	3578.2971	3578.2121	.0070	-.0851
QR 3,13	3582.7785	3582.5985	.0200	-.1800
QR 3,14	3587.1346	3586.7939	.0140	-.3407
QR 4,12	3579.2078	3579.1467	.9999	-.0611
QR 4,14	3587.9884	3587.7678	.0140	-.2207
QR 4,15	3592.2114	3591.7860	.0200	-.4255
QR 5,13	3584.7972	3584.7498	.0140	-.0474
QR 5,14	3589.0862	3588.9355	.0283	-.1507
QR 5,15	3593.2691	3592.9354	.0200	-.3337
QR 6,11	3577.2806	3577.3247	.0100	.0442
QR 6,12	3581.8098	3581.8913	.0140	.0815
QR 6,13	3586.1850	3586.2176	.9999	.0326
QR 6,14	3590.4280	3590.4394	.0140	.0114
QR 6,15	3594.5618	3594.4595	.0140	-.1023
QR 7, 7	3559.1447	3559.1673	.0100	.0226
QR 7, 8	3564.4391	3564.4655	.0140	.0264
QR 7, 9	3569.5060	3569.5456	.0100	.0396
QR 7,10	3574.3606	3574.4328	.0140	.0722
QR 7,11	3579.0195	3579.1467	.0200	.1272
QR 7,12	3583.5010	3583.6251	.9999	.1241
QR 7,13	3587.8252	3588.0012	.0140	.1760
QR 7,14	3592.0136	3591.7866	.0283	-.2270
QR 7,15	3596.0896	3596.0740	.0200	-.0156

ASSIGN-MENT	CALCULATED FREQUENCY	OBSERVED FREQUENCY	DELTA NU	OBS-CALC
QR 8, 8	3566.5867	3566.7341	.0200	.1474
QR 8, 9	3571.6105	3571.6683	.0070	.0577
QR 8,10	3576.4180	3576.5223	.0200	.1043
QR 8,11	3581.0259	3581.1911	.0140	.1653
QR 8,14	3593.8433	3594.2604	.0200	.4171
QR 8,15	3597.8524	3598.1625	.0283	.3101
QR 9, 9	3573.9957	3574.1353	.0070	.1397
QR 9,10	3578.7498	3578.8646	.0100	.1148
QR 9,11	3583.2998	3583.3430	.0140	.0432
QR 9,12	3587.6641	3588.2942	.0200	.6301
QR 9,13	3591.8626	3591.7860	.0200	-.0766
QR 9,14	3595.9169	3596.2335	.0140	.3166
QR 9,15	3599.8502	3600.4852	.0140	.6350



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