To the Graduate Council:

I am submitting herewith a dissertation written by William Joe Phillips entitled "Pressure Broadening Effects on the Lambda Doublets of Nitric Oxide." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Physics.

A. A. Mason, Major Professor

We have read this dissertation
and recommend its acceptance:

Horace W. Crater

Accepted for the Council:

Vice Provost
and Dean of The Graduate School

PRESSURE BROADENING EFFECTS ON THE LAMBDA DOUBLETS OF NITRIC OXIDE

A Dissertation

Presented for

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

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ABSTRACT

In recent years several high resolution pressure broadening measurements have been performed on the fundamental band of NO. These works have assumed that the collision halfwidth of each component of the lambda doublet of NO was equal and neglected any spectral line coupling effects. This work examines the validity of these assumptions by examining, analytically, the effects of collision broadening on the lambda doublets of NO.

The Anderson-Tsao-Curnutte (ATC) pressure broadening theory is extended to a coupled spectral line theory which includes non-$\sum$ state diatomics. From this theory expressions for the coupled line absorption coefficient are obtained which include the dipole-dipole, dipole-quadrupole, quadrupole-dipole, and quadrupole-quadrupole intermolecular potentials. The resolved line approximation was added to the ATC theory in order to obtain expressions for the collision halfwidths of each lambda doublet component in the absence of line coupling effects. The expressions for the halfwidths given by the ATC theory were obtained when it was assumed the rotational eigenstates of NO are equivalent to those of a symmetric top molecule. The effects of collision broadening of NO by CO were calculated utilizing the three different cases above; coupled line formulation, resolved line approximation, and the ATC theory assuming symmetric top eigenstates.

The results confirmed that the equal halfwidth and no coupling assumptions are indeed valid approximations. The percent difference between the halfwidths of the doublet components was found to be no

more than 2.8 percent. The difference between the halfwidths calculated by the ATC theory and that of the modified ATC, which incorporated non-Σ state eigenstates, was no more than 3.2 percent. The line coupling effects were found to be more pronounced in the lines of the 3/2 subband than those of the 1/2 subband due to the small doublet separation in the 3/2 subband. The coupled line effects were never found to exceed 1.42 percent of the absorption coefficient over a frequency range where the absorption was non-negligible at pressures as high as 600 Torr.

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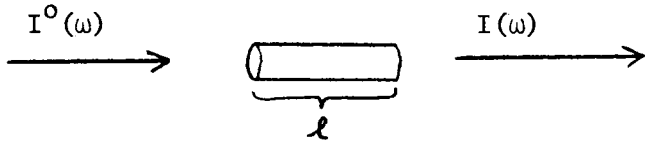
INTRODUCTION

High resolution spectroscopy of gaseous nitric oxide (NO) is of interest because of the basic information to be learned regarding molecular radiation and because of its usefulness to the gas diagnostic community. Nitric oxide is a well known pollutant derived from high temperature combustion and is prevalent in automobile and turbine engine exhaust. Its rate of production is temperature dependent which makes it an ideal gas to use as a temperature diagnostic gas utilizing infrared (IR) absorption techniques. Unlike the IR active free radicals produced in combustion, NO is chemically stable, therefore its spectral line parameters can easily be measured in a laboratory environment under known conditions.

The trend in infrared absorption gas diagnostics has been toward higher resolution measurements. The use of tunable diode lasers has been one of the reasons for this trend. The increasing power, mode separation, lifetime, and decreasing cost of these lasers make them an excellent narrow linewidth (10^{-5} cm^{-1}) infrared source for gas diagnostics on infrared active species. In the past, IR diagnostics have relied on statistical band models which average the radiation over a broad spectral range encompasing many spectral lines of the molecule of interest. High resolution measurements allow one to examine individual spectral lines and are less dependent on approximations than band models. High resolution spectroscopy requires more accurate values for the spectral line parameters of frequency, width, strength, and shape, used to model the radiation. A knowledge of the

temperature and pressure dependence of these spectral line parameters is also needed for accurate radiation modeling under varying conditions. Finally, more emphasis must be placed on the radiation models themselves in order to account for fine structures which appear at higher resolution.

The use of IR spectroscopy for the detection of gases such as NO or as a temperature diagnostic tool requires a physical model. These models can best be examined by considering the hypothetical experiment shown schematically below;



where $I^o(\omega)$ is the spectral intensity of the light incident upon a slab of gas of length ℓ, temperature T, and pressure P. The transmitted spectral intensity is given by $I(\omega)$ and is related to the incident intensity of Beer's law;

$$I(\omega) = I^o(\omega)e^{-k(\omega)\ell}$$

where $k(\omega)$ is the absorption coefficient which is temperature and pressure dependent. The form of $k(\omega)$ depends on the mechanism responsible for the broadening of the spectral line

Three main spectral line broadening mechanisms in infrared spectroscopy are natural, Doppler, and pressure (or collision) broadening. Natural line broadening arises from the uncertainty principle such that for a finite transition time the energy level responsible for the transition are uncertain and therefore gives rise to a spread in the transition frequency. Natural broadening halfwidths

at half maximum (HWHM) in the IR are typically 10^{-5} cm^{-1} and can be ignored in comparison to other broadening mechanisms. Doppler broadening results from the shifted frequencies of the light as seen by the moving molecule. When these frequency shifts are averaged over all molecules in the path weighted by Maxwell velocity distribution there results the Doppler profile for the absorption coefficient. The Doppler profile HWHM is proportional to the square root of temperature and for NO at 300K it takes on the value of 2.65×10^{-3} cm^{-1} which is approximately two orders of magnitude larger than the natural broadening HWHM. The third broadening process is collison broadening. Collision broadening is due to perturbations of the molecular energy levels by means of molecular collisions. This results in a smearing of the upper and lower state energy levels thereby producing a spreading of the allowable transition frequency. Doppler broadening is predominant for low number densities, but as the number density, pressure, increases the collision rate increases and collision broadening becomes dominant. For NO at a temperature of 300K Doppler broadening is predominant at pressures of approximately one Torr or less. At pressures of about 50 Torr or more pressure broadening tends to dominate. The typical pressure broadened absorption coefficient profile has a HWHM of 0.07 cm^{-1} at one atmosphere and at a temperature of 300K and is directly proportional to pressure. At pressures intermediate to the Doppler and collision broadening regime the convolution of the Doppler and collision profiles, called the Voigt profile, is used. This simultaneously takes into account Doppler and collision broadening.

Most gas diagnostic situations deal with pressures greater than 50 Torr and less than one atmosphere hence only the collision broadening profile usually need be considered. For the case of pure collision broadening the absorption coefficient function is given by the Lorentz profile;

$$k(\omega) = \frac{S\gamma_L}{\pi[(\omega-\omega_o-\Delta_L)^2 + \gamma_L^2]} \tag{2}$$

where S is the integrated absorptance, γ_L is the collision HWHM, and Δ_L is the line shift. The integrated absorptance is expressed in terms of the pressure independent line strength as;

$$S = S^o P_A \tag{3}$$

where P_A is the pressure of the absorbing gas species in atmospheres and S^o is the line strength in units of cm^{-1} atm^{-1}. The halfwidth and line shift are likewise expressed in terms of pressure independent quantities $\gamma^o_{i_L}$ and $\Delta^o_{i_L}$ by;

$$\gamma_L = \sum_i \gamma^o_{i_L} P_i \tag{4}$$

$$\gamma_L = \sum_i \Delta^o_{i_L} P_i \tag{5}$$

where the sum runs over all species, the pressures are in units of atmospheres, and $\gamma^o_{i_L}$ and $\Delta^o_{i_L}$ have units of cm^{-1} atm^{-1}. The parameter $\gamma^o_{i_L}$ is sometimes denoted as a standard halfwidth or broadening parameter when evaluated at a reference temperature, usually 300K.

The usual approach in modeling the absorption due to several spectral lines is to sum their individual absorption coefficients. Thus for a several line model one usually has;

$$k(\omega) = \sum_i k_i(\omega) \tag{6}$$

where the sum runs over all spectral lines that have a non-negligible contribution in the spectral region of interest. The approach in the past when considering the closely spaced, 10^{-2} cm^{-1}, lambda doublets of NO has been to assume each doublet component has equal line strength and collision halfwidth or ignore the doublets altogether and treat them as a single line with a line strength weighted by a factor of two.[1-5] Calculations of the halfwidths of NO collision broadened by N_2 and O_2 have been performed by Tejwani et al. [2] utilizing the Anderson-Tsao-Curnutte theory [6-8] in which they also treated the lambda doublets as one spectral line.

A theory developed by Gersten and Foley [9] indicates that as spectral lines become blended there is the possibility of interference terms contributing to the absorption coefficient. Thus two closely spaced spectral lines may become coupled in which case the total absorption coefficient may be given by:

$$k(\omega) = k_1(\omega) + k_2(\omega) + k_I(\omega) \tag{7}$$

where $k_1(\omega)$ and $k_2(\omega)$ are the absorption coefficients for the individual spectral lines and $k_I(\omega)$ is the interference term. It is the purpose of this work to examine this coupling effect, and the halfwidths in general, for non-Σ state diatomic molecules such as NO and apply the results to the specific case of NO collision broadened by CO.

The calculation of the effects of collision broadening necessitates knowing the rotational energies of the molecule. These are somewhat more complicated to calculate for NO than other chemically

stable diatomic molecules due to its $^2\pi$ electronic ground state. Thus it is necessary to include in the molecular Hamiltonian terms such as the spin-orbit, spin-spin, and other angular momentum coupling interactions. Although the rotational Hamiltonian matrix elements for a non-Σ state diatomic can be found in the literature their derivation is spread throughout the literature over a period of fifty years. The first three chapters of this work are devoted to the derivation of the molecular Hamiltonian matrix elements and the solution of the Hamiltonian energy eigenvalue equation utilizing these matrix elements.

Presented in Chapter I is a novel approach in deriving the eigenstates of total angular momentum for the Hund's case A coupling scheme. Previously, a derivation of the eigenstates relied solely on the coordinate representation of the total angular momentum operator from which a differential equation was found and solved for the eigenstates. The derivation given in Chapter I makes use of Clebsch-Gordon technology and the properties of spin and orbital angular momentum eigenstates under a rotation of the coordinates frame to arrive at the same result.

Chapter II discusses the total molecular Hamiltonian. The Born-Oppenheimer approximation is applied to separate, initially, the electronic and nuclear energy terms. The electronic Hamiltonian is investigated to determine what quantities commute with the Hamiltonian for the case of a non-Σ state diatomic. The electronic eigenstates are then defined in terms of the eigenstates of these conserved quantities. For the sake of completeness a brief review is made of the vibrational

Hamiltonian and its eigenstates. Finally, the rotational Hamiltonian is given along with the additive angular momentum coupling terms.

The molecular Hamiltonian of Chapter II and the total angular momentum eigenstates of Chapter I are utilized in Chapter III for a perturbative calculation of the molecular rotational energies and eigenstates. With the use of perturbative techniques such as the Van Vleck transformation and degenerate perturbation theory the matrix elements of the Hamiltonian of Chapter II are derived utilizing the eigenstates of Chapter I as the basis set of eigenstates. Terms which are responsible for the lambda doubling are identified. Matrix elements involving interaction of the various angular momentum coupling terms with each other and with the vibrational-rotational coupling terms are also derived. These particular matrix elements could not be found in the literature.

Utilizing published molecular constants and the matrix elements derived in Chapter III, the energy eigenstates and eigenvalues were calculated and are tabulated in Appendix C. These tables include the energies and eigenstates of the rotational Hamiltonian for the cases where lambda doubling was included and ignored and for both the v=0 and v=1 vibrational states. From these values, spectral line positions were calculated for both the cases of lambda doubling present and absent. These are also tabulated in Appendix C.

Presented in Chapter IV is a review of the Anderson-Tsao-Curnutte (ATC) collision broadening theory [6-8] and a development of the coupled line theory for the case of non-Σ state diatomic molecules. The first section of the chapter is an indepth derivation of the

dipole transition absorption coefficient incorporating collision broadening. This review parallels the derivation of Tsao and Curnutte with the exception that the molecular rotational eigenstates are kept in the most general form so as to allow for non-Σ state diatomics. Whereas Tsao and Curnutte consider incident light of only one polarization direction, the derivation presented here makes no such assumption. The derivation here also deviates from that of the ATC theory by not applying the resolved line approximation as is done in the ATC theory. By applying a criterion arrived at by Tsao and Curnutte it is shown that the resolved line approximation does not necessarily hold for the fundamental band spectrum of NO.

Since the resolved line approximation is not necessarily valid a coupled line spectral theory must be employed. A brief examination of a coupled line theory by Gersten and Foley[9] is made. It is demonstrated that the Gersten-Foley (GF) theory contains some unstated premature assumptions early in the derivation of the coupled line spectrum. To avoid any constraints on the theory developed here these assumptions are not made. The ATC theory is then used as a starting point from which a coupled line theory is developed. Unlike other molecular collision broadening theories the molecular eigenstates were assumed to be those of a general non-Σ state diatomic.

The general coupled line theory is used to obtain a coupled line absorption coefficient. This absorption coefficient is expressed in terms of the dipole moment operator matrix elements and a matrix which couples the spectral lines. To obtain expressions for the coupling matrix elements, four intermolecular interaction usually considered in

pressure broadening calculations are examined. For each of the interactions the formulas necessary for a calculation of the matrix elements are derived. Various constraints are then imposed on the expressions for the coupling matrix elements in an effort to obtain the formulas needed for the calculations of the broadening effects on NO due to CO presented in Chapter V. The first of these constraints is that the perturber be in a $^1\Sigma$ electronic state. This simplifies the formulas and allows for easier computer coding for the specific case presented here. Next, the resolved line approximation, as assumed in the ATC theory, is applied thereby reducing further the complexity of the formulas. The last step of the chapter is to show that the results presented here for the coupled line spectra reduce to that of the ATC theory when the appropriate conditions are imposed.

The formula obtained for the coupling matrix elements are employed in Chapter V to calculate the pressure broadening effects of CO perturbing NO. Calculations are made of the absorption coefficient and/or collision half width for selected spectral lines of NO. These calculations include the coupled line absorption coefficient for the lambda doublets and collision half width for each doublet component using the resolved line approximation. Utilizing the ATC theory, half width calculations were also performed where the effects of lambda doubling are ignored. The resulting calculations of pressure broadening effects at elevated temperatures are also presented. The spectral lines chosen for this computational study include spectral lines from both the P and R branch, the 1/2 and 3/2 subband, and those lines which possess both low (J~4.5) and high (J=20.5) J values.

CHAPTER I

TOTAL ANGULAR MOMENTUM IN HUND'S CASE A COUPLING

1. SPACE FIXED COORDINATE SYSTEM AND RELATIVE COORDINATES

The total angular momentum in a diatomic molecule, neglecting nuclear spin, is given by

$$\bar{J} = \bar{K} + \bar{L} + \bar{S} \tag{1-1}$$

where $\bar{K}$ is the rotational angular momentum of the nuclei, and $\bar{L}$ and $\bar{S}$ are the total orbital and spin angular momenta of the electrons, respectively. The angular momenta on the right hand side of equation (1-1) are the sums of the angular momenta of their respective particles and type, that is

$$\bar{K} = \sum_{N} \bar{k}_N = \sum_{N} \bar{R}_N \times \bar{P}_N \tag{1-2}$$

$$\bar{L} = \sum_{t=1}^{n} \bar{l}_t = \sum_{t=1}^{n} \bar{r}_t \times \bar{p}_t \tag{1-3}$$

and

$$\bar{S} = \sum_{t-1}^{n} \bar{s}_t \tag{1-4}$$

where the sum over N runs over the nuclei denoted A and B, and the sum over t runs over the electrons 1, 2,---n. Applying the correspondence principle to equations (1-2) and (1-3), the angular momentum operators are written

$$K = \frac{\hbar}{i} \sum_{N} \bar{R}_N \times \bar{\nabla}_N \tag{1-5}$$

and

$$\bar{L} = \frac{\hbar}{i} \sum_{t=1}^{n} \bar{r}_t \times \bar{\nabla}_t \tag{1-6}$$

It is advantageous to separate out the angular momentum of the center of mass of the molecule and express the angular momentum in terms of coordinates and operators referenced to the center of mass of the nuclei. Figure 1-1 illustrates the various coordinates used in the derivation. The coordinates of the center of mass of the molecule and nuclei, and the relative nuclear coordinates, using the notation of Judd [10] are given by

$$R_o = \frac{M_A\bar{R}_A + M_B\bar{R}_B + m \sum_{t=1} \bar{r}_t}{M_A + M_B + nm} \tag{1-7}$$

$$\bar{R}_c = \frac{M_A\bar{R}_A + M_B\bar{R}_B}{M_A + M_B} \tag{1-8}$$

and

$$\bar{R}_{BA} = \bar{R}_B - \bar{R}_A \tag{1-9}$$

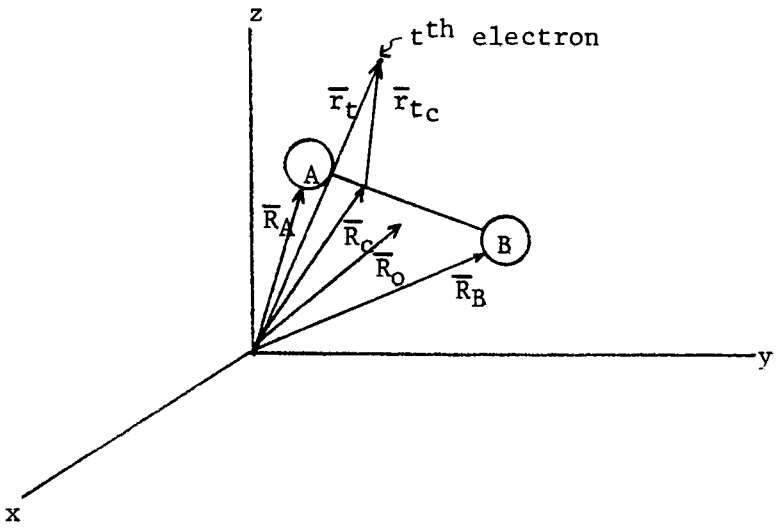


Figure 1-1. Molecular coordinate system.

Equations (1-7) - (1-9) are used to express the various coordinates in terms of the center of mass of the molecule, the relative nuclear coordinates, and the electron coordinates relative to the center of mass of the nuclei;

$$\bar{R}_A = \bar{R}_o - \frac{m}{M_A + M_B + nm} \sum_{t=1}^{n} \bar{r}_{tc} - \frac{M_B}{M_A + M_B} \bar{R}_{BA} \tag{1-10}$$

$$\bar{R}_B = \bar{R}_o - \frac{m}{M_A + M_B + nm} \sum_{t=1}^{n} \bar{r}_{tc} + \frac{M_A}{M_A + M_B} \bar{R}_{BA}, \tag{1-11}$$

and

$$\bar{r}_t = \bar{r}_{tc} + \bar{R}_o - \frac{m}{M_A + M_B + nm} \sum_{t=1}^{n} \bar{r}_{tc} \tag{1-12}$$

where

$$\bar{r}_{tc} = \bar{r}_t - \bar{R}_c \tag{1-13}$$

The gradient operators are likewise transformed using equations (1-7) through equation (1-13), yielding:

$$\bar{\nabla}_A = \frac{M_A}{M_A + M_B + nm} \bar{\nabla}_o - \frac{M_A}{M_A + M_B} \sum_{t=1}^{n} \bar{\nabla}_{tc} - \bar{\nabla}_{BA}, \tag{1-14}$$

$$\bar{\nabla}_B = \frac{M_B}{M_A + M_B + nm} \bar{\nabla}_o - \frac{M_B}{M_A + M_B} \sum_{t=1}^{n} \bar{\nabla}_{tc} + \bar{\nabla}_{BA} \tag{1-15}$$

and

$$\bar{\nabla}_t = \bar{\nabla}_{tc} + \frac{m}{M_A + M_B + nm} \bar{\nabla}_o \tag{1-16}$$

The total angular momentum operator becomes, upon using equation (1-10) - (1-16);

$$\bar{J} = \frac{\hbar}{i} (\bar{R}_o \times \bar{\nabla}_o + \bar{R}_{BA} \times \bar{\nabla}_{BA} + \sum_{t=1}^{n} \bar{r}_{tc} \times \bar{\nabla}_{tc}) + \bar{S}. \qquad (1\text{-}17)$$

The angular momentum of the center of mass of the molecule is now neglected and the orgin of the coordinate system is moved to the center of mass of the nuclei. This new coordinate system is denoted as the space fixed coordinate system (SFS) and is shown in Figure 1-2.

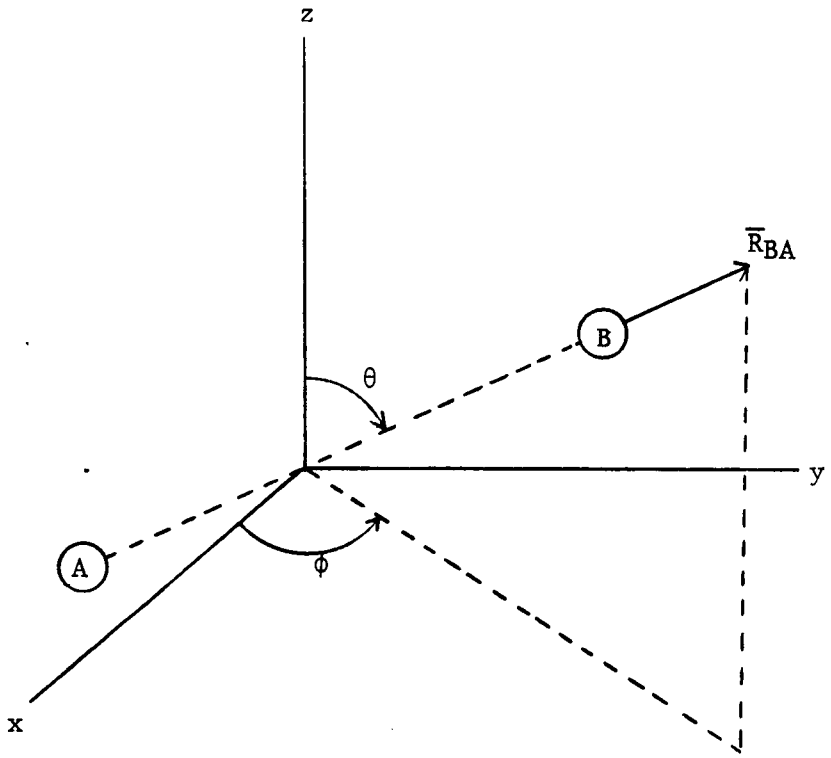


Figure 1-2. Space fixed coordinate system.

The rotational angular momentum of the nuclei is expressed in spherical polar coordinates in the SFS, as shown in Figure 2, which yields the familiar results

$$K_x = \frac{\hbar}{i}\left(-\sin\phi\ \frac{\partial}{\partial\theta} - \cot\theta\ \cos\phi\ \frac{\partial}{\partial\phi}\right), \tag{1-18}$$

$$K_y = \frac{\hbar}{i}\left(\cos\phi\ \frac{\partial}{\partial\theta} - \cot\theta\ \sin\phi\ \frac{\partial}{\partial\phi}\right), \tag{1-19}$$

and

$$K_z = \frac{\hbar}{i}\ \frac{\partial}{\partial\phi} \tag{1-20}$$

This is the usual orbital angular momentum of a particle in a central field and has the commutation relations

$$[K_i, K_j] = i\hbar\varepsilon_{ijk}K_k \tag{1-21}$$

The eigenstates of K^2 and K_z are the spherical harmonics and obey the following relations [11]

$$K^2 \mid KN\rangle = K(K+1)\hbar^2 \mid KN\rangle \tag{1-22}$$

and

$$K_z \mid KN\rangle = N\hbar \mid KN\rangle \tag{1-23}$$

where

$$\langle\theta\phi \mid KN\rangle = Y_N^K(\theta,\phi) \tag{1-24}$$

The constituent angular momenta all commute with one another;

$$[\bar{K},\bar{L}] = [\bar{K},\bar{S}] = [\bar{L},\bar{S}] = 0 \tag{1-25}$$

and $\bar{L}$ and $\bar{S}$ have the same relations with respect to their eigenstates as does $\bar{K}$ to its eigenstates:

$$L^2 \mid L\Lambda\rangle = L(L+1)\hbar^2 \mid L\Lambda\rangle, \tag{1-26}$$

$$L_z \mid L\Lambda\rangle = \Lambda\hbar \mid L\Lambda\rangle, \tag{1-27}$$

$$S^2 \mid S\Sigma\rangle = S(S+1)\hbar^2 \mid S\Sigma\rangle, \tag{1-28}$$

and

$$S_z \mid S\Sigma\rangle = \Sigma\hbar \mid S\Sigma\rangle \tag{1-29}$$

The angular momenta $\bar{L}$ and $\bar{S}$ are coupled in Hund's case A coupling to form a resultant angular momentum $\bar{P}$ which is in turn coupled to $\bar{K}$ to form $\bar{J}$. The eigenstates of P^2 and P_z are calculated using Clebsch-Gordon coefficients and are given by

$$\mid P\Omega\rangle = \sum_{\Sigma,\Lambda} \langle L S \Lambda \Sigma \mid LSP\Omega\rangle \mid LS\Lambda\Sigma\rangle \tag{1-30}$$

where

$$P^2 \mid P\Omega\rangle = P(P+1)\hbar^2 \mid P\Omega\rangle \tag{1-31}$$

and

$$P_z \mid P\Omega\rangle = \Omega\hbar \mid P\Omega\rangle \tag{1-32}$$

The eigenstates of J^2 and J_z are likewise calculated by coupling the eigenstates of P^2 and P_z to those of K^2 and K_z

$$\mid JM\rangle = \sum_{\Lambda,\Sigma,N} \langle PK\Omega N \mid PKJM\rangle \langle LS\Lambda\Sigma \mid LSP\Omega\rangle \mid KN\rangle \mid L\Lambda\rangle \mid S\Sigma\rangle \tag{1-33}$$

2. TOTAL ANGULAR MOMENTUM OPERATOR AND THE MOLECULAR FIXED COORDINATE SYSTEM

The Born-Oppenheimer approximation applied to the molecular Hamiltonian separates the Hamiltonian into two parts, the electronic Hamiltonian and the nuclear kinetic energy operator [12]. The electronic Hamiltonian is a function of R_{BA}, which is treated only as a parameter, and the Schrodinger equation is solved for various values of R_{BA}. In this approximation, R_{BA} fixed, the only component of $\bar{L}$

that commutes with the electronic spin independent Hamiltonian is that component along the internuclear axis. Therefore, it is advantageous to express the eigenstates of J^2 and J_z, and the operator $\bar{J}$ in terms of the eigenstates of P^2 and $\bar{P}\cdot\hat{R}_{BA}$. This is accomplished by expressing the internal angular momentum operators and their eigenstates in terms of a coordinate system fixed on the molecule.

The molecular fixed coordinate system (MFS), whose axes are ξ, η and ζ, is defined as the x, y, and z frame rotated such that the ζ axis (old z axis) points along the vector $\bar{R}_{BA}$. Figure 1-3 shows the MFS and its relation to the SFS and the molecule.

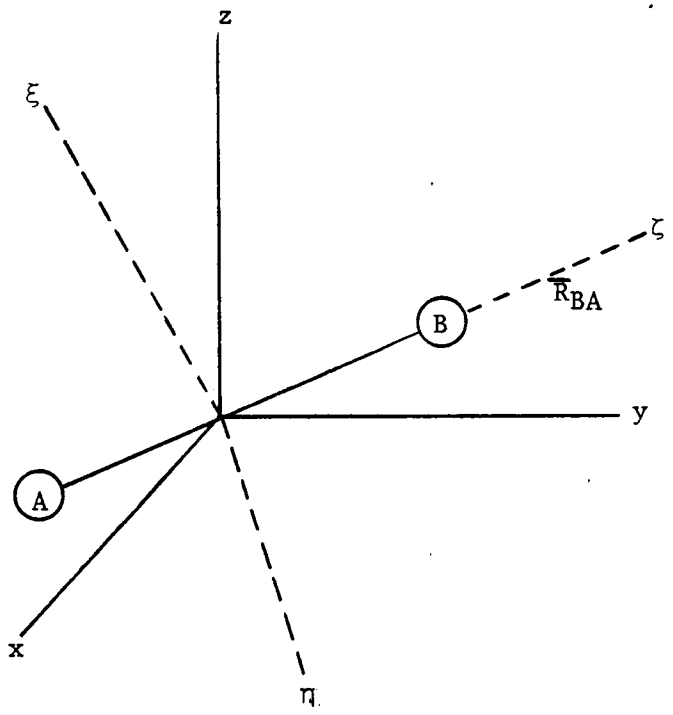


Figure 1-3. The molecular fixed coordinate system; ξ, η and ζ, and the space fixed coordinate system; x, y, and z.

The rotation of the x, y, and z axes necessary to form the ξ, η and ζ axes is performed by rotating the SFS through the Euler angles ϕ, θ, and ψ as given in Baym [11]. Note that the Euler angles ϕ and θ are equal to the ϕ and θ spherical polar angles used in the $\bar{K}$ operators.

The approach taken to express J in terms of the internal angular momentum in the MFS parallels that of Judd [10]. The components of the total angular momentum are expressed in terms of the three components of a spherical tensor of rank one with respect to $\bar{J}$:

$$J^1_{+1} = -\frac{1}{\sqrt{2}} J_+ = K^1_{+1} + P^1_{+1}, \tag{1-34}$$

$$J_0 = J_z = K^1_0 + P^1_0, \tag{1-35}$$

and

$$J^1_{-1} = \frac{1}{\sqrt{2}} J_- = K^1_{-1} + P^1_{-1}. \tag{1-36}$$

These components are operators which act on the eigenstates of J^2 and J_z, $|\, JM\rangle$, which can be represented as functions of the Euler angles, electron coordinates, and spin, that is;

$$|\, JM\rangle \rightarrow \langle \theta, \phi, \psi, \bar{r}, \bar{s}_s \,|\, JM\rangle \tag{1-37}$$

and

$$J^1_q \rightarrow J^1_q(\theta, \phi, \psi, P^1_{sq}), \tag{1-38}$$

where a subscript s or m on the internal angular momentum operators or coordinates denotes that they are expressed in the SFS or MFS, respectively. The total angular momentum operator is written in terms of the electron's angular momenta operators in the MFS by utilizing the rotation operator $R_p(\phi\theta\psi)$ [11,13];

$$R^\dagger_p J^1_q(\theta, \phi, \psi, P^1_{mq}) R_p = J^1_q(\theta, \phi, \psi, P^1_{sq}) \tag{1-39}$$

where

$$R_p(\phi\theta\psi) = e^{-i\phi P_z/\hbar} e^{-i\theta P_y/\hbar} e^{-i\psi P_z/\hbar}$$
$$= e^{-i\phi P_\zeta/\hbar} e^{-i\theta P_\eta/\hbar} e^{-i\psi P_\zeta/\hbar} \qquad (1\text{-}40)$$

The eigenstates $|\, JM\rangle$ expressed in terms of the electron's coordinates and spins in the MFS are given by:

$$R_p^\dagger \langle \phi,\theta,\psi,\bar{\rho},\bar{S}_m \,|\, JM\rangle = \langle \phi,\theta,\psi,\bar{r},\bar{S}_s \,|\, JM\rangle \qquad (1\text{-}41)$$

where $\bar{\rho}$ is the electron coordinate expressed in the MFS.

The spherical tensor components of the newly expressed total angular momentum operator and its eigenstates, using equations (1-32) - (1-35), are given by

$$J^1_q = R_p^\dagger K^1_q R_p + R_p^\dagger P^1_{mq} R_p \qquad (1\text{-}42)$$

and

$$|\, JM\rangle = \sum_{\Lambda,\Sigma,N,\Omega} \langle PK\Omega N \,|\, PKJM\rangle \langle LS\Lambda\Sigma \,|\, LSP\Omega\rangle$$
$$R_p^\dagger \,|\, KN\rangle \,|\, L\Lambda\rangle_m \,|\, S\Sigma\rangle_m . \qquad (1\text{-}43)$$

The second term on the right in equation (1-41) is easily expanded by noting that P^1_{mq} is a tensor operator of rank one with respect to $\bar{P}_m$ therefore the rotated components can be expanded using the following relation [2];

$$R_p^\dagger P^1_{mq} R_p = \sum_{q'=-1}^{1} D^1_{q,q'}(\phi\theta\psi) P^1_{mq'} . \qquad (1\text{-}44)$$

Expanding the sum above and evaluating the d matrix elements [14] the components of equation (1-44) become:

$$R_p^\dagger P^1_{m\pm1} R_p = e^{\pm i\theta} e^{-i\psi} \frac{1\mp\cos\theta}{2} P^1_{m_{-1}}$$

$$\mp e^{\pm i\phi} \frac{\sin\theta}{\sqrt{2}} P^1_{m_0}$$

$$+ e^{i\psi} e^{\pm i\phi} \frac{1\pm\cos\theta}{2} P^1_{m+1} \qquad (1\text{-}45)$$

and

$$R_p^\dagger P^1_{m_0} R_p = e^{-i\psi} \frac{\sin\theta}{\sqrt{2}} P^1_{m_{-1}} + \cos\theta P^1_{m_0}$$

$$+ e^{i\psi} \frac{\sin\theta}{\sqrt{2}} P^1_{m_1}. \qquad (1\text{-}46)$$

The first term in equation (1-42) becomes on expansion;

$$R_p^\dagger K^1_{\pm1} R_p = R_p^\dagger \frac{\hbar}{i\sqrt{2}} e^{\pm i\phi}(-i \frac{\partial}{\partial\theta} \pm \cot\theta \frac{\partial}{\partial\phi}) R_p \qquad (1\text{-}47)$$

and

$$R_p^\dagger K^1_o R_p = R_p^\dagger \frac{\hbar}{i} \frac{\partial}{\partial\phi} R_p. \qquad (1\text{-}48)$$

The two terms involving the partial derivatives are evaluated using the form of the rotation operator in equation (1-40) to yield:

$$R_p^\dagger \frac{\partial}{\partial\phi} R_p = \frac{\partial}{\partial\phi} + \frac{i}{\hbar} P_\xi \sin\theta \cos\psi - \frac{i}{\hbar} P_\eta \cos\theta \sin\psi$$

$$- \frac{1}{\hbar} P_\zeta \cos\theta \qquad (1\text{-}49)$$

and

$$R_p^\dagger \frac{\partial}{\partial\theta} R_p = \frac{\partial}{\partial\theta} - \frac{i}{\hbar} P_\zeta \sin\psi - \frac{i}{\hbar} P_\eta \cos\psi. \tag{1-50}$$

Substitution of equations (1-49) and (1-50) in equations (1-47) and (1-48) yields:

$$\begin{aligned} R_p^\dagger K_{\pm1}^1 R_p = K_{\pm1}^1 &- P_{m_{+1}}^1 e^{\pm i\phi} e^{i\psi} \left(\frac{1 \pm \cos\theta}{2}\right) \\ &- P_{m_{-1}}^1 e^{\pm i\phi} e^{-i\psi} \left(\frac{1 \mp \cos\theta}{2}\right) \\ &\pm P_{m_0}^1 \frac{\sin\theta}{\sqrt{2}} e^{\pm i\phi} \mp P_{m_0}^1 \frac{\csc\theta}{\sqrt{2}} e^{\pm i\phi} \end{aligned} \tag{1-51}$$

and

$$R_p^\dagger K_0^1 R_p = K_0^1 - P_{m_{+1}}^1 \frac{\sin\theta}{\sqrt{2}} e^{i\psi} + P_{m_{-1}}^1 \frac{\sin\theta}{\sqrt{2}} e^{-i\psi} - P_{m_0}^1 \cos\theta \tag{1-52}$$

Thus the form of the operator in equation (1-42) is now written with the aid of equations (1-45), (1-46), (1-51), and (1-52)

$$J_{\pm1}^1 = \mp \frac{\hbar}{\sqrt{2}} e^{\pm i\phi} \left(\pm \frac{\partial}{\partial\theta} + i\cot\theta \frac{\partial}{\partial\phi} + \frac{P_\zeta}{\hbar} \csc\theta\right) \tag{1-53}$$

or

$$J_\pm = \hbar e^{\pm i\phi} \left(\pm \frac{\partial}{\partial\theta} + i\cot\theta \, \partial/\partial\phi + \frac{P_\zeta}{\hbar} \csc\theta\right) \tag{1-54}$$

and

$$J_0 = J_z = \frac{\hbar}{i} \partial/\partial\phi. \tag{1-55}$$

3. TOTAL ANGULAR MOMENTUM EIGENSTATES

The total angular momentum eigenstates, in terms of the eigenstates of the internal angular momentum referred to the MFS, are

investigated by examining equation (1-43). Note that the rotation operator $R_p(\phi\theta\psi)$ can be written as the product $R_L(\phi\theta\psi)\ R_s(\phi\theta\psi)$ since $\bar{L}$ commutes with $\bar{S}$, thus the eigenstates $|\ JM\rangle$ become

$$|\ JM\rangle = \sum_{\Lambda,\Sigma} \sum_{\Lambda',\Sigma'} \sum_{N,\Omega} \langle P K \Omega N\ |\ PKJM\rangle \langle LS\Lambda\Sigma\ |\ LSP\Omega\rangle X$$

$$d^{L*}_{\Lambda,\Lambda'}(\phi\theta\psi)\ d^{S*}_{\Sigma,\Sigma'}(\phi\theta\psi)\ |\ KN\rangle\ |\ L\Lambda'\rangle\ |\ S\Sigma'\rangle \qquad (1\text{-}56)$$

where the subscript m on the kets has been dropped. Coupling the d-matrices and applying the various properties of the d-matrices [11,13] the eigenstates are given by:

$$|\ JM\rangle = \sum_{N,\Omega} \sum_{\Sigma,\Lambda} \sum_{A,\Sigma'} \sum_{\Lambda',G} \sum_{G'} (-1)^{\Sigma+\Lambda-\Sigma'-\Lambda'} \langle KPN\Omega\ |\ KPJM\rangle\ X$$

$$\langle LS\Lambda\Sigma\ |\ LSP\Omega\rangle \langle LS-\Lambda-\Sigma\ |\ LSAG\rangle \langle LS-\Lambda'-\Sigma'\ |\ LSAG\rangle X$$

$$d^{A}_{G,G'}(\phi\theta\psi)\ |\ KN\rangle\ |\ L\Lambda'\rangle\ |\ S\Sigma'\rangle. \qquad (1\text{-}57)$$

The coordinate representation of the eigenstates of K^2 and K_z, $|\ KN\rangle$, are the spherical harmonics. They are also the rotational Hamiltonian eigenstates for a Σ state zero spin diatomic molecule. Using the relation between the spherical harmonics and the d-matrices [11], given by

$$\langle\theta,\phi\ |\ KN\rangle = Y_N^K(\theta,\phi) = \left(\frac{2K+1}{4\pi}\right)^{1/2} d^{K}_{-N,0}(\theta\phi\psi)(-1)^N \qquad (1\text{-}58)$$

the coordinate representation of the eigenstates $|\ JM\rangle$ in equation (1-57) are written

$$\langle\theta,\phi,\psi,\rho\,|\,JM\rangle = \left(\frac{2K+1}{4\pi}\right)^{1/2} \sum_{N,\Omega,\Lambda} \sum_{\Sigma,A,\Sigma'} \sum_{\Lambda',G,G'} (-1)^{\Sigma+\Lambda+N-\Sigma'-\Lambda'} \times$$

$$\langle KPN\Omega\,|\,KPJM\rangle\langle LS\Lambda\Sigma\,|\,LSP\Omega\rangle\langle LS-\Lambda-\Sigma\,|\,LSAG\rangle \times$$

$$\langle LS-\Lambda'-\Sigma'\,|\,LSAG'\rangle\, d^{A}_{G,G'}(\theta\phi\psi)\, d^{K}_{-N,0}(\theta\phi\psi)\,\langle\rho\,|\,L\Lambda\rangle\,|\,S\Sigma'\rangle. \qquad (1\text{-}59)$$

The coordinate representation of the eigenstates $|\,JM\rangle$ is further reduced by using the various properties of the d-matrices and Clebsch-Gordon coefficients. Coupling the d-matrices in equation (1-59) as was done in equation (1-56), and applying the properties of the Clebsch-Gordon coefficients yields the following

$$\langle\phi,\theta,\psi,\rho\,|\,JM\rangle = \left(\frac{2K+1}{4\pi}\right)^{1/2} (-1)^{2L+2S} \sum_{N,\Omega,} \sum_{\Sigma,\Lambda} \sum_{A,F} \sum_{B,G} \times$$

$$\sum_{\Sigma',\ \Lambda'} \sum_{G',B'} (-1)^{2A+\Sigma+\Lambda+N-\Sigma'-\Lambda'} \langle KPN\Omega\,|\,KPJM\rangle \times$$

$$\langle LS\Lambda\Sigma\,|\,LSP\Omega\rangle\langle LS\Lambda\Sigma\,|\,LSA\text{-}G\rangle\langle LS\Lambda'\Sigma'\,|\,LSA\text{-}G'\rangle \times$$

$$\langle KA\text{-}NG\,|\,KAFB\rangle\langle KAOG'\,|\,KAFB'\rangle \times$$

$$d^{F}_{B,B'}(\theta\phi\psi)\langle\rho\,|\,L\Lambda'\rangle\,|\,S\Sigma'\rangle. \qquad (1\text{-}60)$$

Applying the orthogonality condition along with other properties of the Clebsch-Gordon coefficients to equation (1-60) results in

$$\langle\theta,\phi,\psi,\rho\,|\,JM\rangle = \left(\frac{2K+1}{4\pi}\right)^{1/2} (-1)^{2L+2S-P+K-J} \times$$

$$\sum_{\Lambda'\Sigma'} \langle LS\Lambda'\Sigma'\,|\,LSP\Omega\rangle\langle KPO\text{-}\Omega\,|\,KPJ\text{-}\Omega\rangle \times$$

$$d^{J*}_{M,\Omega}(\theta\phi\psi)\langle\rho\,|\,L\Lambda'\rangle\,|\,S\Sigma'\rangle. \qquad (1\text{-}61)$$

Note that the above eigenstate is a simultaneous eigenstate of J^2, J_z, L^2, and S^2 therefore it will be represented by the ket $|$ JMLS$\rangle$.

It is now necessary to construct simultaneous eigenstates of total angular momentum and of the electronic spin independent Hamiltonian, H^{el}. In the Born-Oppenheimer approximation the electronic Hamiltonian eigenstates are given by ket $|$ n$\Lambda S\Sigma\rangle$ (see Chapter II-3) where n is some electronic energy state quantum number. The simultaneous eigenstates of total angular momentum and the spin independent Hamiltonain are thus represented by the ket $|$ n$\Lambda S\Sigma$JM$\rangle$. To determine the form of these eigenstates they are expanded in terms of the eigenstates of total angular momentum given in equation (1-61) and are given by:

$$\langle\theta,\phi,\psi,\rho \mid n\Lambda S\Sigma JM\rangle = \sum_{L',\Lambda',\Sigma'} C^{n\Lambda S\Sigma JM}_{L'\Lambda'S\Sigma'JM} d^{J*}_{M,\Omega}(\theta\phi\psi)\langle\rho \mid L\Lambda'\rangle \mid S\Sigma'\rangle \qquad (1\text{-}62)$$

where

$$C^{n\Lambda S\Sigma JM}_{L'\Lambda'S\Sigma'JM} = (-1)^{2L'+2S-P+K-J} \left(\frac{2K+1}{4\pi}\right)^{1/2} X$$

$$\langle JML'S \mid n\Lambda S\Sigma JM\rangle\langle L'S\Lambda'\Sigma' \mid L'SP\Omega\rangle\langle KPO-\Omega \mid KPJ-\Omega\rangle \qquad (1\text{-}63)$$

Since these eigenstates are also eigenstates of H^{el}, C has to be of the form

$$C^{n\Lambda S\Sigma JM}_{L'\Lambda'S\Sigma'JM} = \delta_{\Lambda,\Lambda'}\,\delta_{\Sigma,\Sigma'}\,C^{n\Lambda S\Sigma JM}_{L'\Lambda S\Sigma JM} \qquad (1\text{-}64)$$

thus

$$\langle\bar{\rho},\theta,\phi,\psi \mid n\Lambda S\Sigma JM\rangle = \sum_{L} C^{n\Lambda S\Sigma JM}_{L'\Lambda S\Sigma JM} X$$

$$\langle\bar{\rho} \mid L'\Lambda S\Sigma\rangle \, d^{J*}_{M,\Omega}(\theta\phi\psi) \tag{1-65}$$

or

$$\langle\rho,\theta.\phi,\psi \mid n\Lambda S\Sigma JM\Omega\rangle = N\langle\bar{\rho} \mid n\Lambda S\Sigma\rangle \, d^{J*}_{M,\Omega}(\theta\phi\psi) \tag{1-66}$$

where the quantum number Ω is the eigenvalue of $P_\zeta = L_\zeta + S_\zeta$, and as seen later also of J_ζ, and N is a normalization constant. Normalizing the eigenstates and using the integral of the two d matrices from Davydov [14]

$$\int d^{J*}_{M,K}(\theta\phi\psi) d^{J'}_{M',K'}(\theta\phi\psi) d\omega = \delta_{JJ'}\delta_{MM'}\delta_{KK'}\left(\frac{8\pi^2}{2J+1}\right)^{1/2} \tag{1-67}$$

yields the normalized form of the eigenstates;

$$\langle\rho,\theta,\phi,\psi \mid n\Lambda S\Sigma JM\Omega\rangle = \left(\frac{2J+1}{8\pi^2}\right)^{1/2} \langle\rho \mid \eta\Lambda S\Sigma\rangle \, d^{J*}_{M,\Omega}(\theta\phi\psi) \tag{1-68}$$

where

$$\Omega = \Lambda + \Sigma. \tag{1-69}$$

4. TOTAL ANGULAR MOMENTUM IN THE MOLECULAR FIXED SYSTEM AND THE REVERSED ANGULAR MOMENTUM METHOD

In the SFS and on the eigenstates given in equation (1-65) the following relations hold

$$[J_i, J_j] = i\hbar\varepsilon_{ijk}J_k, \tag{1-70}$$

$$J^2 \mid JM\Omega n\Lambda S\Sigma\rangle = J(J+1)\hbar^2 \mid JM\Omega n\Lambda S\Sigma\rangle, \tag{1-71}$$

and

$$J_z \left| JM\Omega n\Lambda S\Sigma \right\rangle = M\hbar \left| JM\Omega n\Lambda S\Sigma \right\rangle. \tag{1-72}$$

It is now helpful to examine these same relations with respect to the total angular momentum components along the axes in the MFS. This is due to the fact that the electronic orbital and spin angular momenta are strongly coupled to the ζ axis in Hund's case A coupling, and due to the appearance of terms such as :

$$\frac{1}{2\mu R^2}(L_+S_- + L_-S_+) + A(R)\ \bar{L}\cdot\bar{S} \tag{1-73}$$

in the Hamiltonian (equation (2-49)). Note that the components of the total angular momentum operator in the SFS are given by J_i where $i = 1, 2, 3$ corresponds to J_x, J_y, and J_z. Now let $\mathcal{J}_i$, where $i = 1, 2, 3$, correspond to the projection of J along the ξ, n, and ζ axes in the MFS, respectively.

The components of total angular momentum along the MFS axes are calculated by expressing the total angular momentum operators in terms of spherical tensor and rotating through the Euler angles. The spherical tensor components in the MFS are thus given by

$$\mathcal{J}^1_q = \sum_{q'=-1}^{1} d^1_{q',q}(\theta\phi\psi)J^1_{q'}, \tag{1-74}$$

where

$$\mathcal{J}^1_{-1} = \frac{1}{\sqrt{2}}(\mathcal{J}_\xi - i\mathcal{J}_n), \tag{1-75}$$

$$\mathcal{J}^1_0 = \mathcal{J}_\zeta\ , \tag{1-76}$$

and

$$\mathcal{J}^1_1 = -\frac{1}{\sqrt{2}}(\mathcal{J}_\xi + i\mathcal{J}_\eta) \tag{1-77}$$

The ζ component of $\bar{\mathcal{J}}$ is given by

$$\mathcal{J}_\zeta = \mathcal{J}_0 = \sum_{q'=-1} d^1_{q',0}(\theta\phi\psi)J^1_{q'} \tag{1-78}$$

Using the form of $\mathcal{J}_\zeta$ in equation (1-78) it is easily shown, on the eigenstates $|\, JM\Omega n\Lambda S\Sigma\rangle$, that

$$[\mathcal{J}_\zeta, J_z] = 0 \tag{1-79}$$

Thus the eigenstates of J^2 and J_z are also simultaneous eigenstates of $\mathcal{J}_\zeta$. Utilizing the form of $\mathcal{J}_\zeta$ in equation (1-78) it can be shown

$$\langle J'M'\Omega'n'\Lambda'S'\Sigma' \,|\mathcal{J}_\zeta|\, JM\Omega n\Lambda S\Sigma\rangle =$$

$$\Omega\delta_{JJ'}\delta_{MM'}\delta_{\Omega\Omega'}\delta_{SS'}\delta_{\Sigma\Sigma'} \tag{1-80}$$

The other components of the total angular momentum on the MFS are investigated by the use of equation (1-74). First note that $J^2(=\mathcal{J}^2)$ commutes with all components of $\bar{J}$ thus

$$[J^2, \mathcal{J}^1_q] = 0 \text{ for all } q \tag{1-81}$$

and therefore

$$\langle J'M'\Omega'n'\Lambda'S'\Sigma' \,|\mathcal{J}^1|\, JM\Omega n\Lambda S\Sigma\rangle =$$

$$\delta_{JJ'}\langle JM'\Omega'n'\Lambda'S'\Sigma' \,|\mathcal{J}^1|\, JM\Omega n\Lambda S\Sigma\rangle. \tag{1-82}$$

The matrix elements of $\mathcal{J}^1_\pm$ using equation (1-82) and the form of $\mathcal{J}^1_{\pm 1}$ in equation (1-74), are given by

$$\langle J'M'\Omega'n'\Lambda'S'\Sigma' \,|\mathcal{J}^1_{\pm 1}|\, JM\Omega n\Lambda S\Sigma\rangle =$$

$$\mp\frac{\hbar}{\sqrt{2}}\delta_{J,J'}\delta_{M,M'}\delta_{\Lambda,\Lambda'}\delta_{S,S'}\delta_{\Sigma,\Sigma'}\delta_{\Omega',\Omega\mp 1}\sqrt{J(J+1) - \Omega(\Omega\mp 1)}. \tag{1-83}$$

From equation (1-83) and equation (1-80) it follows that

$$\langle J'M'\Omega'n'\Lambda'S'\Sigma' \mid [\mathcal{J}_\zeta, \mathcal{J}_\pm] \mid JM\Omega n\Lambda S\Sigma\rangle =$$
$$\mp\hbar\langle J'M'\Omega'n'\Lambda'S'\Sigma' \mid \mathcal{J}_\pm \mid JM\Omega n\Lambda S\Sigma\rangle \qquad (1\text{-}84)$$

thus

$$[\mathcal{J}_\zeta, \mathcal{J}_\pm] = \mp i\hbar \mathcal{J}_\pm. \qquad (1\text{-}85)$$

Therefore from the commutation relation above it is seen that the total angular momentum operators on the eigenstates $\mid JM\Omega n\Lambda S\Sigma\rangle$ obey the commutation relation

$$[\mathcal{J}_i, \mathcal{J}_j] = - i\hbar \, \epsilon_{ijk} \mathcal{J}_k. \qquad (1\text{-}86)$$

The total angular momentum in the MFS, , does not form an angular momentum vector on the eigenstates $\mid JM\Omega n\Lambda S\Sigma\rangle$ since it obeys the anomalous commutation relations in equation (1-86). Thus it is not possible to use directly the usual techniques for evaluating matrix elements containing components of such as the Wigner-Eckart theorem and angular momentum ladder operators. This difficulty is overcome by applying one of two mathematical constructs due to Van Vleck [15], expounded on by Freed [16], and that due to Judd [10].

The Van Vleck approach is to first examine the various angular momentum commutation relations

$$[J_i, J_j] = i\hbar\epsilon_{ijk} J_k, \qquad (1\text{-}87)$$

$$[P_i, P_j] = i\hbar\epsilon_{ijk} P_k, \qquad (1\text{-}88)$$

$$[\mathcal{J}_i, \mathcal{J}_j] = - i\hbar\epsilon_{ijk} \mathcal{J}_k, \qquad (1\text{-}89)$$

and

$$[\bar{P}_m, \bar{\mathcal{J}}] = 0 \qquad (1\text{-}90)$$

where $\bar{P}_m$ is in the MFS. The crux of the procedure by Van Vleck is to consider equations (1-87) and (1-88) as being the anomalous commutation relations. A reversed angular momentum is then formed for $\bar{J}$, $\tilde{\bar{J}}$, and $\bar{P}_m$, $\tilde{\bar{P}}_m$, by

$$\tilde{\bar{J}} = -\bar{J} \tag{1-91}$$

and

$$\tilde{\bar{P}} = -\bar{P} \tag{1-92}$$

thus $\tilde{\bar{J}}$ and $\tilde{\bar{P}}$ now obey the same commutation relations as does $\bar{\mathcal{J}}$. The sign of $i(=\sqrt{-1})$ is then reversed in the commutation relations and the ladder operators and the eigenvalues of the operators are modified so as to be consistent with the usual equations involving angular momenta. This then allows the use of the Clebsch-Gordon coefficients and the Wigner-Eckart theorem with the reversed operators and eigenstates.

The approach taken by Judd (10) is simpler to apply. First note that on the eigenstates $|\, JM\Omega n\Lambda S\Sigma\rangle$ the negative of $\bar{\mathcal{J}}$ obeys the usual commutation relations, that is

$$[-\mathcal{J}_i, -\mathcal{J}_j] = i\hbar\, \varepsilon_{ijk}(-\mathcal{J}_k) \tag{1-93}$$

The operators $-\mathcal{J}_\zeta$ and $-\mathcal{J}_\pm$ do not obey the usual angular momentum relations with respect to the eigenstates but rather obey

$$(-\mathcal{J}_\zeta)\,|\, JM\Omega n\Lambda S\Sigma\rangle = -\Omega\hbar\,|\, JM\Omega n\Lambda S\Sigma\rangle \tag{1-94}$$

and

$$(-\mathcal{J}_\pm)\,|\, JM\Omega n\Lambda S\Sigma\rangle = -\hbar\sqrt{J(J+1) - \Omega(\Omega\mp 1)}\ X$$
$$|\, JM\Omega\mp 1 n\Lambda S\Sigma\rangle. \tag{1-95}$$

Now a reversed angular momentum eigenstate is constructed by

$$\left| JM - \Omega n\Lambda S\Sigma \right\rangle_R = (-1)^{J-\Omega} \left| JM\Omega n\Lambda S\Sigma \right\rangle \tag{1-96}$$

then the angular momentum equations become

$$(-\mathcal{J}_\zeta) \left| JM - \Omega n\Lambda S\Sigma \right\rangle_R = -\Omega\hbar \left| JM - \Omega n\Lambda S\Sigma \right\rangle_R \tag{1-97}$$

and

$$(-\mathcal{J}_\pm) \left| JM - \Omega n\Lambda S\Sigma \right\rangle_R = \sqrt{J\,(J+1) - (-\Omega)(-\Omega\pm 1)}\ X$$
$$\left| JM - \Omega\pm 1 n\Lambda S\Sigma \right\rangle_R \tag{1-98}$$

Thus on the reversed eigenstates the operators of $-\mathcal{J}$ obey the usual angular momentum relations. Note that these reversed eigenstates are also eigenstates of J^2, J_z, and the electronic spin independent Hamiltonian, therefore they can be used as a basis set of eigenstates for a perturbation calculation involving the molecular Hamiltonian.

CHAPTER II

TOTAL MOLECULAR HAMILTONIAN

1. SPIN INDEPENDENT MOLECULAR HAMILTONIAN

The total spin independent Hamiltonian in the SFS is given by

$$H^{total} = \frac{1}{2}\sum_{N}\frac{\bar{P}_N^2}{M_N} + \frac{1}{2m}\sum_{t}\bar{P}_t^2 + Vee\,(\bar{r})$$

$$+ V_{Ne}\,(\bar{R},\bar{r}) + V_{NN}(R) \qquad (2\text{-}1)$$

The first two terms are the kinetic energy operators for both nuclei and the electrons, respectively. $\bar{P}_N$ and $\bar{P}_t$ represent the linear momentum operators for nuclus N and electron t, respectively. The potential energy terms V_{ee}, V_{ne}, and V_{NN} are the electron-electron, nuclus-electron, and nuclus-nuclus coulomb interactions.

The transformation of coordinates relations given in equations (1-7) - (1-16) applied to the Hamiltonian allow it to be cast into the form

$$H^{total} = H^{el} + T^N + T^T. \qquad (2\text{-}2)$$

H^{el}, T^N, and T^T are the electronic Hamiltonian, nuclear kinetic energy operator, and translational kinetic energy operator, respectively, given by;

$$H^{el} = -\frac{\hbar^2}{2\mu'}\sum_{t}\bar{\nabla}_{tc}^2 - \frac{\hbar^2}{2(M_A + M_B)}\sum_{t\neq v}\bar{\nabla}_{tc}\cdot\bar{\nabla}_{vc}$$

$$+ e^2\sum_{t\neq v}\frac{1}{|\bar{r}_{tc} - \bar{r}_{vc}|}$$

$$+ \frac{Z_A Z_B e^2}{R_{BA}} - e^2\sum_{t,N}\frac{Z_N}{|\bar{R}_{Nc} - \bar{r}_{tc}|}\,, \qquad (2\text{-}3)$$

$$T^N = -\frac{\hbar^2}{2\mu}\bar{\nabla}^2_{BA} \quad , \tag{2-4}$$

and

$$T^T = -\frac{\hbar^2}{2(M_A + M_B + nm)}\bar{\nabla}^2_0 \tag{2-5}$$

where

$$\mu = \frac{M_A M_B}{(M_A + M_B)} \tag{2-6}$$

and

$$\mu' = \frac{m(M_A + M_B)}{M_A + M_B + nm}. \tag{2-7}$$

The nuclear kinetic energy operator can be separated into a vibrational and rotational kinetic energy operator;

$$T^N = T^V + T^R \tag{2-8}$$

where

$$T^V = -\frac{\hbar^2}{2\mu R^2}\frac{\partial^2}{\partial R^2}(R^2\ \partial/\partial R) \tag{2-9}$$

$$T^R = \frac{1}{2\mu R^2}K^2 = \frac{1}{2\mu R^2}(\bar{J} - \bar{P})^2 \tag{2-10}$$

and R is the magnitude of $\bar{R}_{BA}$. Ignoring the translational motion the Schroedinger equation becomes

$$[H^{el}(\bar{r},\bar{R}) + T^V(R) + T^R(\bar{R})]\ \Psi(\bar{r},\bar{R}) = E^{Total}\ \Psi(\bar{r},\bar{R}) \tag{2-11}$$

where $\bar{r}$ denotes all electron coordinates.

The Born-Oppenheimer approximation is used to separate the nuclear and electronic portions of the Hamiltonian [12,17,18].

Assuming a solution of the electronic Schroedinger equation, $\Phi_n^{el}(\bar{r},\bar{R})$, i.e.:

$$H^{el}(\bar{r},\bar{R})\ \Phi_n^{el}(\bar{r},\bar{R}) = E_n^{el}(R)\ \Phi_n^{el}(\bar{r},\bar{R}) \tag{2-12}$$

the total molecular wavefunction is then approximated by

$$\psi^{Total}(\bar{r},\bar{R}) = \Phi_n^{el}(\bar{r},\bar{R})\ \psi_{v,\{K\}}(\bar{R}) \tag{2-13}$$

where $\psi_{v\{K\}}$ satisfies the equation

$$[E_n^{el}(R) + T^v(R) + T^R(R)]\ \psi_{v,\{K\}}(\bar{R}) = E^{Total}\psi_{v,\{K\}}(\bar{R}). \tag{2-14}$$

The quantum number n describes some electronic state, v describes the vibrational state, and $\{K\}$ is some set of quantum numbers describing the rotational states. $E_n^{el}(R)$ is approximated by the sum of the Morse potential [10] and an electronic state energy E_n^{el} thus

$$E_n^{el}(R) = E_n^{el} + D_n(1 - e^{-\beta_n(R-R_e)})^2 \tag{2-15}$$

where R_e is the equilibrium internuclear distance.

The nuclear Hamiltonian is reduced further by ignoring, in zeroth order, the coupling between the vibrational and rotational portions of the nuclear Hamiltonian or, as is done in Chapter III, by ignoring the rotational energy entirely. By expanding the R^{-2} term, in T^R, in terms of x where $x = R - R_e$ and keeping only the first term of the expansion, the coupling between vibration and rotation can be ignored in zeroth order. The nuclear Schroedinger equation then splits into a vibrational part

$$[V_N(R) + T^v(R)]\ \psi_v(R) = E^{vib}\psi_v(R) \tag{2-16}$$

where $V_n(R)$ is the Morse potential of the n^{th} electronic state, and a rotational portion

$$T^R(R_e,\phi,\theta,\psi)\psi_{\{K\}} = E^{Rot}_{\{K\}}\ \psi_{\{K\}} \tag{2-17}$$

where the total energy is given by

$$E^{Total} = E_n^{el} + E_{n,v}^{vib} + E_{\{K\}}^{rot} \tag{2-18}$$

and the total wavefunction by

$$\psi^{Total} = \Phi_n^{el}\, \psi_v \psi_{\{K\}} \tag{2-19}$$

It is advantageous at this point to examine the commutation relations of the Hamiltonian and the angular momenta. The rotational and internal angular momenta commute with all terms of the total Hamiltonian, equation (2-1), with the exception of the electron-nuclear interaction term V_{Ne}. Closer examination shows that

$$[\bar{L}, V_{Ne}] = -[\bar{K}, V_{Ne}] \neq 0 \tag{2-20}$$

and for Hund's case A coupling where $\bar{P} = \bar{L} + \bar{S}$ it can be shown that

$$[\bar{P} \cdot \hat{R}_{BA},\ V_{Ne}] = [\bar{K} \cdot \hat{R}_{BA},\ V_{Ne}] = 0 \tag{2-21}$$

which leads to the obvious result

$$[\bar{J}, H^{total}] = 0 \tag{2-22}$$

Since $\bar{J}$ commutes with the total Hamiltonian, eigenstates of J^2, J_z, and J_ζ are used to form, in part, a perturbation calculation basis set for the Hamiltonian which includes the rotational kinetic energy.

2. TOTAL MOLECULAR HAMILTONIAN IN THE MOLECULAR FIXED SYSTEM

The Born-Oppenheimer approximation allows the electronic Hamiltonian to be solved treating $\bar{R}$ as a parameter. Since only one component of the total internal angular momentum commutes with H^{total}, L_ζ, and since $\bar{L}$ and $\bar{S}$ are strongly coupled to the ζ axis in Hund's case A coupling it is advantageous to express the Hamiltonian in the rotated MFS. This rotation of axes will be such that the

new z axis (ζ axis) lies along the vector $\bar{R}_{BA}$. This transformation applied to the electronic Hamiltonian, as was done in Chapter I when considering the angular momentum operator, yields:

$$H^{el}(\bar{\rho},\bar{R}) = -\frac{\hbar^2}{2\mu'}\sum_t \bar{\nabla}^2_{\rho t} - \frac{\hbar^2}{2(M_A + M_B)}\sum_{t\neq v}\bar{\nabla}_{\rho t}\cdot\bar{\nabla}_{\rho v}$$

$$+ \sum_{t\neq v}\frac{e^2}{|\bar{\rho}_{tc} - \bar{\rho}_{vc}|}$$

$$+ \frac{Z_A Z_B e^2}{R_{BA}} - e^2\sum_{t,N}\frac{Z_N}{|R_N\hat{\zeta} - \bar{\rho}_t|} \qquad (2\text{-}23)$$

The vibrational kinetic energy operator is invariant under such a transformation. The rotational kinetic energy operator, equation (2-10), is now expressed in terms of the total angular momentum and internal angular momentum in the MFS, i.e.

$$T^R = \frac{1}{2\mu R^2}(\bar{\mathcal{J}} - \bar{P}_m)^2 \qquad (2\text{-}24)$$

3. ELECTRONIC HAMILTONIAN

The eigenstates of the electronic Hamiltonian are simultaneous eigenstates of operators which commute with H^{el}. One of the operators already discussed is the ζ component of the total electronic orbital angular momentum, another is the total electronic spin, $\bar{S}$, since H^{el} is assumed spin independent. Three more such operators are the parity operator, , which commutes with the total Hamiltonian, the reflection operator i_γ, which reflects the electron's coordinates in a plane containing the internuclear axis, and the intrinsic parity, I, which performs a reflection of a plane perpendicular to the ζ axis

that contains the center of symmetry, if any. Since H^{el} commutes with L_ζ and $\bar{S}$ the following relations hold for the eigenstates of H^{el};

$$H^{el} \mid n\Lambda S\Sigma\rangle = E_{n\Lambda}(R) \mid n\Lambda S\Sigma\rangle, \tag{2-25}$$

$$L_\zeta \mid n\Lambda S\Sigma\rangle = \Lambda\hbar \mid n\Lambda S\Sigma\rangle, \tag{2-26}$$

$$S^2 \mid n\Lambda S\Sigma\rangle = S(S+1)\hbar^2 \mid n\Lambda S\Sigma\rangle, \tag{2-27}$$

and

$$S_\zeta \mid n\Lambda S\Sigma\rangle = \Sigma\hbar \mid n\Lambda S\Sigma\rangle. \tag{2-28}$$

The electronic eigenstates exhibit two degenercies, a degenercy in the sign of Λ and a spin degenercy. The degenercy in the sign of Λ is demonstrated by noting from Appendix A that

$$i_\gamma \mid n\Lambda\rangle = \delta_\gamma \mid n - \Lambda\rangle \tag{2-29}$$

where δ_γ is a phase factor, and using the commutation relation

$$[H^{el}, i_\gamma] \mid n\Lambda\rangle = 0. \tag{2-30}$$

Expanding the above commutation relation and using equation (2-29) yields

$$(E_{n\Lambda} - E_{n-\Lambda}) \mid n - \Lambda\rangle = 0, \tag{2-31}$$

therefore

$$E_{n\Lambda} = E_{n} - \Lambda \tag{2-32}$$

The spin degenercy is in the value of Σ since the electronic Hamiltonian is assumed spin independent.

4. VIBRATIONAL HAMILTONIAN

The vibrational Hamiltonian in equation (2-16) was arrived at by ignoring in zeroth order the rotational kinetic energy in the nuclear

Hamiltonian. The vibrational Schroedinger equation from equation (2-16) is given by

$$\left[-\frac{\hbar^2}{2\mu R^2}\frac{d^2}{dR^2}\left(R^2\frac{d}{dR}\right) + E_n(R)\right]\psi_v(R) = E_v^{vib}\,\psi_v(R) \tag{2-33}$$

where $E_n(R)$ is assumed to be the Morse potential and μ the nuclear reduced mass. This equation was first solved by Morse [19] who found the energy eigenvalue term values to be given by

$$F_v = \frac{E_v}{hc} = \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2 \tag{2-34}$$

where

$$\omega_e = \frac{\beta}{4\pi c}\sqrt{\frac{D}{2\mu}} \tag{2-35}$$

and

$$\omega_e x_e = \frac{h\beta^2}{8\pi^2 c\mu}. \tag{2-36}$$

The eigenfunction of this Schroedinger equation is given by

$$\psi_v(R) = N_v \frac{e^{-z/2}}{R} z_v^{Cv/2} L^{Cv}(z) \tag{2-37}$$

where

$$C_v = \frac{2}{\hbar\beta}\sqrt{2\mu(D - E_v)} \tag{2-38}$$

$$N_v = \sqrt{\frac{C_v v!}{\Gamma(C_v + v + 1)}} \tag{2-39}$$

$$z = 2\sqrt{b}\, e^{-\beta(R-R_e)}, \tag{2-40}$$

$$b = \frac{2\mu D}{\beta^2 h^2} \tag{2-41}$$

and $L_v^{Cv}(z)$ is the associated Lagurre polynomial defined by [20]:

$$L_n^c(z) = \sum_{m=0}^{n} (-1)^m \binom{c+n}{n-m} \frac{z^m}{m!} . \tag{2-42}$$

It has been pointed out by Ter Haar [21] that Morse's solution is an approximation, although a good one, in which the actual boundary conditions on the eigenfunctions given by:

$$\psi_v (R = 0) = \psi_v(R = \infty) = 0 \tag{2-43}$$

are replaced by the approximate boundary conditions

$$\psi_v (R = \infty) = 0 \tag{2-44}$$

and

$$\psi_v (R = 0) \approx \psi_v(R = -\infty) = 0. \tag{2-45}$$

In order to solve the vibrational Schroedinger equation exactly using the Morse potential it is necessary to impose the boundary condition in equation (2-45) exactly which results in finding the zeroes of a confluent hypergeometric function given by:

$$F\left(\frac{C_v + 1}{2} - b;\ C_v + 1;\ Z_0\right) = 0 \tag{2-46}$$

where

$$Z_0 = 2\sqrt{b}\ e^{\beta R_e} \tag{2-47}$$

and

$$C_v = \frac{2}{\beta\hbar}\sqrt{2\mu(D-Ev)} \tag{2-48}$$

5. ROTATIONAL HAMILTONIAN AND SPIN COUPLING TERMS

The rotational Hamiltonian or rotational kinetic energy operator is given in equation (2-24). Expanding the terms of the Hamiltonian

with the use of $\bar{P} = \bar{L} + \bar{S}$ yields:

$$T^R = \frac{1}{2\mu R^2}\left(\mathcal{J}^2 + P_\zeta^2 + S^2 - S_\zeta^2 - 2\mathcal{J}_\zeta P_\zeta + L_\xi^2 + L_\eta^2\right.$$

$$\left. - \mathcal{J}_+ S_- - S_+ \mathcal{J}_- - \mathcal{J}_- L_+ - L_- \mathcal{J}_+ + L_+ S_- + L_- S_+\right). \qquad (2\text{-}49)$$

Thus far various angular momentum coupling terms have been ignored here. These include the spin-orbit, spin-spin, and spin-rotation interactions. The spin-orbit interaction has been discussed by several investigators most notably Fontana [22] and Veseth [23]. Veseth has pointed out that the spin-orbit interaction can be approximated to a high degree of accuracy by the phenomenological term;

$$H^{SO} = A(R)\ \bar{L}\cdot\bar{S} \qquad (2\text{-}50)$$

where A(R) is the spin-orbit coupling constant. The spin-spin interaction was investigated by Fontana [22], Hebb [24], and Kayama [25], who suggested that the interaction can be represented by;

$$H^{SS} = \varepsilon(R)(3S_\zeta^2 - S^2). \qquad (2\text{-}51)$$

The phenomenological spin-rotation interaction term used is that used by Zare, et al. [26] and suggested by Kovacs [27] and Hougen [28];

$$H^{SR} = \gamma(R)\bar{N}\cdot\bar{S} \qquad (2\text{-}52)$$

where

$$\bar{N} = \bar{J} - \bar{S} = \bar{R} + \bar{L} \qquad (2\text{-}53)$$

CHAPTER III

ROTATIONAL ENERGY EIGENVALUES AND EIGENSTATES

1. A BASIS SET OF EIGENSTATES

The diagonalization of the molecular Hamiltonian using perturbation theory requires an initial basis set of eigenstates. The basis set used consists of the simultaneous eigenstates of the observables which commute with the total Hamiltonian in the Born-Oppenheimer approximation. These eigenstates are the simultaneous eigenstates of total angular momentum, the electronic Hamiltonian, the vibrational Hamiltonian, and the parity operator. For the case of homonuclear molecules another operator which commutes with the Hamiltonian is the operator R_I which exchanges nuclei.

The simultaneous eigenstates of total angular momentum and the electronic Hamiltonian were derived in Chapters I and II. Parity eigenstates are formed from the eigenstates of total angular momentum and the operator R_I given in Appendix A and are given by

$$|\, pn\Lambda S\Sigma q_e JM-\Omega\rangle = \frac{1}{\sqrt{2}}\,[\,|\, n\Lambda S\Sigma q_e JM-\Omega) + p\,|\, n-\Lambda S-\Sigma q_e JM\Omega\rangle]. \qquad (3\text{-}1)$$

The p appearing above is what is designated in this work as the "partial parity" and has a value of plus or minus unity. The symbol q_e is a label denoting whether the state is gerade (g state) or ungerade (u state) (see Appendix A). Kronig symmetry is represented by the symbol q which has a value of plus one for a Σ^{-1} state and a value of zero otherwise.

The parity eigenstate of equation (3-2) behaves, when operated on by the parity operator, as

$$P \mid pn\Lambda S\Sigma q_e JM-\Omega\rangle = p(-1)^{J+S+q} \mid pn\Lambda S\Sigma q_e JM-\Omega\rangle. \qquad (3-2)$$

Note that above and hereafter all angular momentum eigenstates are assumed to be reversed angular momentum ones. Therefore, the subscript R will be dropped from the bra and ket vectors except where needed to resolve any ambiguity. Since q_e does not contribute to the parity eigenvalue it is dropped and can from here on be thought of as being incorporated into the electronic state running quantum number n, as with the label q. To make these eigenstates simultaneous eigenstates of the vibrational Hamiltonian requires only multiplication of the two since the vibrational Hamiltonian commutes with the other observables on this basis set. Thus the basis set is then given by:

$$\mid pn\Lambda S\Sigma JM-\Omega v\rangle = \mid pn\Lambda S\Sigma JM-\Omega\rangle \mid v\rangle \qquad (3-3)$$

where $\mid v\rangle$ is an eigenstate of the vibrational Hamiltonian. It should be noted that the values of Λ and Ω in the basis set are positive definite due to the construction of the parity eigenstates in equation (3-1).

2. THE LAMBDA DOUBLING TERMS

The total molecular Hamiltonian from Chapter II has the form:

$$H^{total} = H^{el} + T^{v} + T^{R} + H^{SS} + H^{SO} + H^{SR} \qquad (3-4)$$

The electronic Hamiltonian, H^{el}, is given by equation (2-3) and has eigenstates in the Born-Oppenheimer approximation given by the ket $\mid n\Lambda S\Sigma\rangle$ which makes up, in part, the basis set eigenstates in equation (3-3). There are $2(2S+1)$ degenerate eigenstates which belong to the

same energy state for non-Σ state diatomics. These eigenstates are represented by the same electronic quantum number n and are given by:

$$|n-|\Lambda|S-S\rangle, |n-|\Lambda|S-S+1\rangle \cdots$$
$$|n-\Lambda|SS-1\rangle, |n-|\Lambda|SS\rangle,$$
$$|n|\Lambda|S-S\rangle, |n|\Lambda|S-S+1)\rangle, \cdots$$
$$|n|\Lambda|SS-1\rangle, |n|\Lambda|SS\rangle. \quad (3\text{-}5)$$

It is the values of S and $|\Lambda|$ which determine the electronic state to zeroth order, but not uniquely. That is, there can exist two states represented by $|n\Lambda S\Sigma\rangle$ and $|n'\Lambda S\Sigma\rangle$ which belong to the different energy eigenstates n and n'. The ground electronic state of NO being a $^2\pi$ state implies that it can exist in any of the four basis set eigenstates, of the form of equation (3-3), given by:

$$|1, 0, 1, 1/2, -1/2, J, M, -1/2, v\rangle, \quad (3\text{-}6a)$$
$$|1, 0, 1, 1/2, 1/2, J, M, -3/2, v\rangle, \quad (3\text{-}6b)$$
$$|-1, 0, 1, 1/2, -1/2, J, M, -1/2, v\rangle, \quad (3\text{-}6c)$$

or

$$|-1, 0, 1, 1/2, 1/2, J, M, -3/2, v\rangle. \quad (3\text{-}6d)$$

The rotational portion of the Hamiltonian, along with the additive angular momentum coupling interactions, contains terms which are not diagonal in the electronic eigenstates. These terms give rise to lambda doubling in non Σ state diatomics and are denoted as lambda doubling terms. These terms, designated with a subscript Λ, are given by:

$$T_\Lambda^R = B(R)\ (L_+ S_- + L_- S_+ - \mathcal{J}_- L_+ - \mathcal{J}_+ L_-) \quad (3\text{-}7)$$

and

$$H_\Lambda^{SO} = 1/2\ A(R)(L_+ S_- + L_- S_+). \quad (3\text{-}8)$$

Neglecting the lambda doubling terms, which connect different electronic states differing in Λ values by unity, the total Hamiltonian becomes:

$$H_0^{total} = H^{total} - H_\Lambda^{SO} - T_\Lambda^R$$

$$= H^{el} + T^V + T_0^R + H^{SS} + H^{SR} + H_0^{SO} \tag{3-9}$$

where

$$T_0^R = T^R - T_\Lambda^R = B(R)(\mathcal{J}^2 + P_\zeta^2 + S^2 - S_\zeta^2 - 2\mathcal{J}_\zeta P_\zeta$$

$$+ L_\xi^2 + L_\eta^2 - \mathcal{J}_+ S_- - S_+ \mathcal{J}_-), \tag{3-10}$$

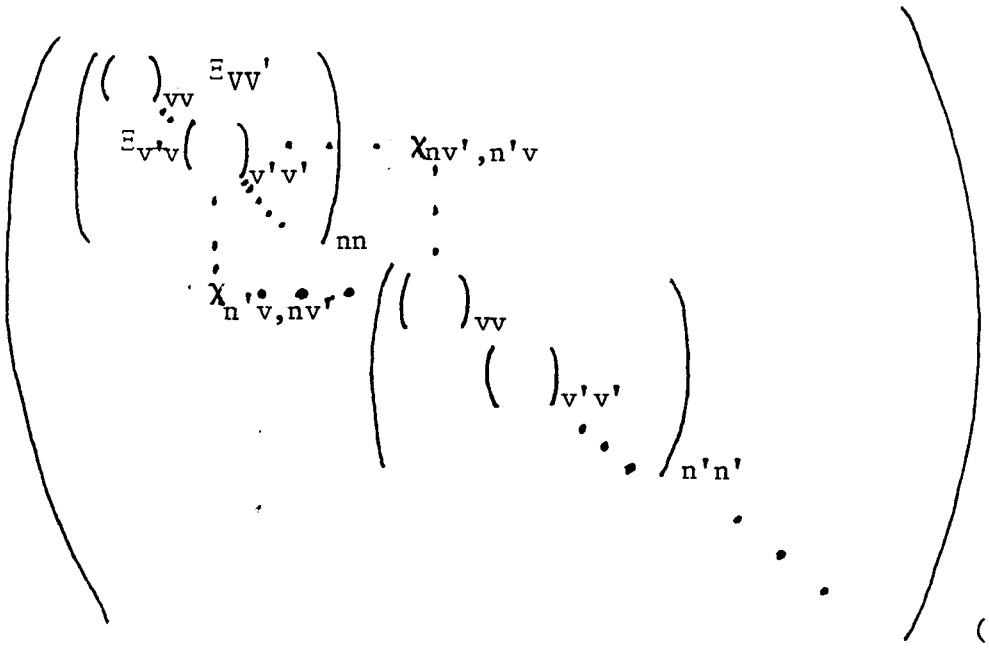
and

$$H_0^{SO} = H^{SO} - H_\Lambda^{SO} = A(R) L_\zeta S_\zeta \tag{3-11}$$

The rotational kinetic energy operator and the spin coupling terms also contains an R dependence. This R dependence connects different vibrational states since the eigenstate $|v\rangle$ is an eigenstate of the vibrational Hamiltonian given in equation (2-33) where only the Morse potential was considered and not the R^{-1} rotational terms. This coupling between vibrational and rotational states gives rise to the centrifugal distortion matrix elements of the Hamiltonian which are considered later.

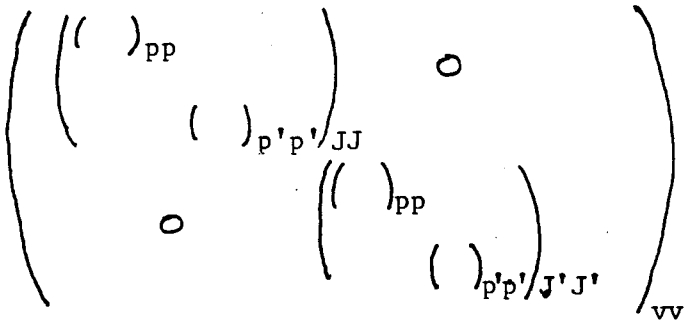
3. VAN VLECK TRANSFORMATION APPLIED TO THE MOLECULAR HAMILTONIAN

The diagonalization of the total Hamiltonian discussed in Section 3B is virtually impossible without making some approximations. This is seen by examining the Hamiltonian matrix given by:



(3-12)

where each vibrational block consist of smaller blocks of matrix elements in the eigenstates of total angular momentum, spin, and parity given by:



(3-13)

Each parity block is a (2S+1) by (2S+1) matrix of spin states. The matrix elements denoted by χ in the matrix of equation (3-12) represents matrix elements due to lambda doubling terms which connect

different electronic states. The matrix elements denoted by ≡ represents those which couple different vibrational states, in the same electronic state, due to the R dependence in the rotational and spin coupling terms of the Hamiltonian. The diagonalization of the Hamiltonian matrix, equation (3-12), would be possible if it were not for matrix elements such as ≡ and χ, since each block of matrix elements in the simultaneous eigenstates of total angular momentum, spin, and parity could be diagonalized independent of a block of another vibrational or electronic state.

An unitary transformation due to Van Vleck [29] and derived in Appendix B, can be used to remove matrix elements, to second order, which connect the block of matrix elements of interest to other blocks [30-32]. The Van Vleck transformation assumes the Hamiltonian to be of the form

$$H = H_0 + \lambda H_1 \tag{3-14}$$

where H_0 is diagonal in the block of interest and may contain one or more degenerate groups of states. The matrix elements of H_1 lie outside the block of interest but may also have some matrix elements inside, and possibly on the diagonal.

The Van Vleck transformation transforms the Hamiltonian H in equation (3-14) into G, that is:

$$G = T^{-1}HT \tag{3-15}$$

where G has the form

$$G = G_0 + \lambda G_1 + \lambda^2 G_2 \tag{3-16}$$

and

$$G_0 = H_0 \tag{3-17}$$

As seen from Appendix B, the matrix elements of H_1 which lie inside the block of interest are equal to those same matrix elements of G_1, whereas those matrix elements of H_1 outside the block of interest contribute to the matrix elements of G inside the block of interest only in second order or higher. The matrix elements of G of order two or higher which lie outside the block of interest contribute to the energy in fourth order or higher and to the eigenstates to second order or higher, thus they are ignored here. It should be noted that the eigenstates of H, $|N\rangle$, and G, $|K\rangle$, are not equal but are related by the Van Vleck transformation:

$$|N\rangle = T|K\rangle \tag{3-18}$$

4. HAMILTONIAN MATRIX ELEMENTS NEGLECTING LAMBDA DOUBLING

The Hamiltonian excluding lambda doubling terms given in equation (3-9) can be put into the form of equation (3-14) using the basis set given in equation (3-3). The Hamiltonian H_0 must be diagonal on the basis set of interest which leads to the assignment of H_0

$$H_0 = H^{el} + T^v. \tag{3-19}$$

The rotational kinetic energy operator is not included since it contains an R dependence which mixes vibrational states. The remaining portion of the Hamiltonian, H_1, is then given by

$$H_1 = T^R + H^{SS} + H^{SR} + H^{SO}. \tag{3-20}$$

The H_1 term mixes both vibrational and electronic states thus it has matrix elements which connects the block of states of interest to other vibrational and electronic blocks. Neglecting the lambda doubling terms H_1 is reduced to

$$H_1' = H_1 - H_1^{\Lambda} = T_0^R + H^{SS} + H^{SR} + H_0^{SO}. \tag{3-21}$$

The matrix elements of the transformed Hamiltonian, neglecting lambda doubling, are calculated using the formulas of Appendix B which relate the matrix elements of G to those of H. The matrix elements of G_0 or H_0, which are diagonal on the basis set, are calculated, using equation (2-12) and (2-16), and are given by

$$\langle pn\Lambda S\Sigma JM\text{-}\Omega \mid \langle v \mid H_0 \mid v\rangle \mid pn\Lambda S\Sigma JM\text{-}\Omega\rangle =$$
$$E_n^{el} + \langle v \mid E_n(R) + T_v \mid v\rangle = E_n^{el} + E_v^{vib}. \tag{3-22}$$

Again utilizing the results of Appendix B the matrix elements of the various terms contributing to G_1 are calculated to be

$$\langle pn\Lambda S\Sigma JM\text{-}\Omega v \mid T_0^R \mid pn\Lambda S\Sigma JM\text{-}\Omega v\rangle =$$
$$B_v[J(J+1) + S(S+1) - \Omega^2 - \Sigma^2], \tag{3-23}$$

$$\langle pn\Lambda S\Sigma JM\text{-}\Omega v \mid H^{SS} \mid pn\Lambda S\Sigma JM\text{-}\Omega v\rangle =$$
$$\varepsilon_v[3\Sigma^2 - S(S+1)], \tag{3-24}$$

$$\langle pn\Lambda S\Sigma JM\text{-}\Omega v \mid H^{SO} \mid pn\Lambda S\Sigma JM\text{-}\Omega v\rangle =$$
$$A_v\Lambda\Sigma, \tag{3-25}$$

$$\langle pn\Lambda S\Sigma JM\text{-}\Omega v \mid H^{SR} \mid pn\Lambda S\Sigma JM\text{-}\Omega v\rangle =$$
$$-\gamma_v[S(S+1) - \Omega\Sigma], \tag{3-26}$$

$$\langle pn\Lambda S\Sigma JM\text{-}\Omega v \mid T_0^R \mid pn\Lambda S\Sigma\pm 1 JM\text{-}\Omega\mp 1 v\rangle =$$
$$B_v\sqrt{J(J+1)-\Omega(\Omega\pm 1)}\ \sqrt{S(S+1) - \Sigma(\Sigma\pm 1)} \tag{3-27}$$

and

$$\langle pn\Lambda S\Sigma JM-\Omega v \mid H^{SR} \mid pn\Lambda S\Sigma\pm 1JM-\Omega\mp 1v\rangle =$$

$$-\frac{\gamma_v}{2}\sqrt{J(J+1) - \Omega(\Omega\pm 1)}\quad\sqrt{S(S+1) - \Sigma(\Sigma\pm 1)} \tag{3-28}$$

where

$$B_v = \langle v \mid R^{-2} \mid v\rangle \frac{\hbar}{8\pi^2\mu c}\,, \tag{3-29}$$

$$\varepsilon_v = \langle v \mid \varepsilon(R) \mid v\rangle, \tag{3-30}$$

$$A_v = \langle v \mid A(R) \mid v\rangle, \tag{3-31}$$

and

$$\gamma_v = \langle v \mid \gamma(R) \mid v\rangle. \tag{3-32}$$

The term given by

$$B_v \langle pn\Lambda S\Sigma JM-\Omega \mid L_\xi^2 + L_\eta^2 \mid pn\Lambda S\Sigma JM-\Omega\rangle \tag{3-33}$$

which is diagonal in the electronic energy eigenstates is incorporated into the Morse potential implicitly in equation (2-15) and therefore does not appear in equation (3-23).

The matrix elements of G_2 within the block of parity and spin eigenstates are calculated using equation (B-19). The energy terms in equation (B-19) are reduced by using

$$\frac{1/2(E^0_{m'} - E^0_m) - E^0_n}{(E^0_m - E^0_n)(E^0_{m'} - E^0_n)} = \frac{1}{E^0_m - E^0_n} \tag{3-34}$$

since $E^o_m = E^o_{\hat{m}}$ i.e. the matrix elements of H_o are diagonal and equal in the block of states of interest. The product of matrix elements of H_1 in the expression for the matrix elements of G_2 cause the mixing of the various interactions that make up H. Therefore each interaction

cannot be considered separately. The matrix elements of G_2, using equations (3-43), (B-19), and the expression for their coefficients are listed below where use has been made of the notation of Zare et al. [26];

$$\langle pn\Lambda S\Sigma JM-\Omega v \mid G_2 \mid pn\Lambda S\Sigma JM-\Omega v\rangle =$$

$$- D_v[f_1(\Omega,\Sigma) + f_2(\Omega,\Sigma) + f_3(\Omega,\Sigma) + A_{D_V} f_1(\Omega,\Sigma)\Lambda\Sigma$$

$$+ a_{D_v}\Lambda^2\Sigma^2 + \varepsilon_{D_V} f_1(\Omega,\Sigma)\,[3\Sigma^2 - S(S+1)]$$

$$+ \gamma_{D_v}\{f_1(\Omega,\Sigma)[\Omega\Sigma - S(S+1)] - 1/2\, f_2(\Omega,\Sigma) - 1/2 f_3(\Omega,\Sigma)\}$$

$$+ \varepsilon_v'[3\Sigma^2 - S(S+1)]^2 + \varepsilon_{A_v}\Lambda\Sigma\,[3\Sigma^2 - S(S+1)]$$

$$+ \varepsilon_{\gamma_v}\,[\Omega\Sigma - S(S+1)][3\Sigma^2 - S(S+1)] + A_{\gamma_v}\Lambda\Sigma[\Omega\Sigma - S(S+1)]$$

$$+ \gamma_v'\{[\Omega\Sigma - S(S+1)]^2 + 1/4 f_2(\Omega,\Sigma) + 1/4 f_3(\Omega,\Sigma)\}, \qquad (3\text{-}35)$$

$$\langle pn\Lambda S\Sigma JM-\Omega v \mid G_2 \mid pn\Lambda S\Sigma\pm 1 - 1\mp\Omega v\rangle =$$

$$- D_v[f_4(\Omega,\Sigma)f_1(\Omega,\Sigma) + f_4(\Omega,\Sigma)\, f_1(\Omega\pm1,\Sigma\pm1)]$$

$$+ A_{D_V}\, f_4(\Omega,\Sigma)(\Sigma\pm1/2)\Lambda$$

$$- 1/4\, A_{\gamma_v}\, f_4(\Omega,\Sigma)\Lambda[2\Sigma\pm1]$$

$$+ 1/4\, \gamma_{D_v}\{2f_4(\Omega.\Sigma)[(\Omega\pm1)(\Sigma\pm1) - S(S+1)]$$

$$+ 2[\Omega\Sigma - S(S+1)]f_4(\Omega,\Sigma) - f_1(\Omega,\Sigma)\, f_4(\Omega,\Sigma)$$

$$- f_4(\Omega,\Sigma)\, f_1(\Omega\pm1,\ \Sigma\pm1)\}$$

$$+ 1/2\, \varepsilon_{D_v}\, f_4(\Omega,\Sigma)[3\Sigma^2 + 3(\Sigma\pm1)^2 - 2S(S+1)]$$

$$- 1/4\, \varepsilon_{\gamma_v} f_4(\Omega,\Sigma)\ x$$

$$[3(\Sigma\pm1)^2 + 3\Sigma^2 - 2S(S+1)] - 1/2\, \gamma_v'\, f_4(\Omega,\Sigma)[\Omega\Sigma - S(S+1)$$

$$+ (\Omega \pm 1)(\Sigma\pm1) - S(S+1)], \qquad (3\text{-}36)$$

and

$$\langle pn\Lambda S\Sigma JM-\Omega v \mid G_2 \mid pn\Lambda S\Sigma\pm 2 JM - \Omega\mp 2v\rangle =$$

$$- D_v f_4(\Omega,\Sigma)f_4(\Omega\pm1,\ \Sigma\pm1) - 1/2\gamma_{D_v} f_4(\Omega,\Sigma)f_4(\Omega\pm1,\Sigma\pm1)$$

$$+ 1/4\, \gamma_v'\, f_4(\Omega,\Sigma)\, f_4\,(\Omega\pm1,\Sigma\pm1) \qquad (3\text{-}37)$$

where

$$a_{D_v} = \sum_{v'} \frac{|\langle v | A(R) | v' \rangle|^2}{E_v - E_{v'}} \tag{3-38}$$

$$\gamma_{D_v} = 2 \sum_{v'} \frac{\langle v | B(R) | v' \rangle \langle v' | \gamma(R) | v \rangle}{E_v - E_{v'}} \tag{3-39}$$

$$\varepsilon'_v = \sum_{v'} \frac{|\langle v | \varepsilon(R) | v' \rangle|^2}{E_v - E_{v'}} \tag{3-40}$$

$$A_{D_V} = 2 \sum_{v'} \frac{\langle v | A(R) | v' \rangle \langle v' | B(R) | v \rangle}{E_v - E_{v'}} \tag{3-41}$$

$$\varepsilon_{\gamma_v} = 2 \sum_{v'} \frac{\langle v | \varepsilon(R) | v' \rangle \langle v' | \gamma(R) | v \rangle}{E_v - E_{v'}} \tag{3-42}$$

$$\gamma'_v = \sum_{v'} \frac{|\langle v | \gamma(R) | v' \rangle|^2}{E_v - E_{v'}} \tag{3-43}$$

$$\varepsilon_{A_v} = \sum_{v'} \frac{\langle v | \varepsilon(R) | v' \rangle \langle v' | A(R) | v \rangle}{E_v - E_{v'}} \tag{3-44}$$

$$A_{\gamma_v} = 2 \sum_{v'} \frac{\langle v | A(R) | v' \rangle \langle v' | \gamma(R) | v \rangle}{E_v - E_{v'}} \tag{3-45}$$

$$\varepsilon_{\gamma_v} = 2 \sum_{v'} \frac{\langle v | B(R) | v' \rangle \langle v' | \varepsilon(R) | v \rangle}{E_v - E_{v'}} \tag{3-46}$$

$$D_v = -\sum_{v'} \frac{|\langle v | B(R) | v' \rangle|^2}{E_v - E_{v'}} \tag{3-47}$$

$$f_1(\Omega,\Sigma) = J(J+1) - \Omega^2 + S(S+1) - \Sigma^2, \tag{3-48}$$

$$f_2(\Omega,\Sigma) = [J(J+1) - \Omega(\Omega+1)][S(S+1) - \Sigma(\Sigma+1)], \tag{3-49}$$

$$f_3(\Omega,\Sigma) = [J(J+1) - \Omega(\Omega-1)][S(S+1) - \Sigma(\Sigma-1)], \tag{3-50}$$

and

$$f_4(\Omega,\Sigma) = [J(J+1) - \Omega(\Omega \pm 1)]^{1/2}[S(S+1) - \Sigma(\Sigma \pm 1)]^{1/2}. \quad (3\text{-}51)$$

The matrix elements of G_3 within the block of interest are calculated using equation (B-20). Since the magnitude of the G_3 matrix elements is small compared to the lower order terms and since only the term T_0^R grows in magnitude as J(J+1), only it is considered in the calculation of the matrix elements of G_3. The resulting matrix elements are listed below;

$$\langle pn\Lambda S\Sigma JM\text{-}\Omega v \mid T_0^R \mid pn\Lambda S\Sigma JM\text{-}\Omega v\rangle =$$

$$H_v\{f_1{}^3(\Omega,\Sigma) + 2f_1(\Omega,\Sigma)[f_2(\Omega,\Sigma) + f_3(\Omega,\Sigma)] +$$

$$f_2(\Omega,\Sigma)f_1(\Omega+1,\ \Sigma+1) + f_1(\Omega-1,\ \Sigma-1)\ f_3(\Omega,\Sigma)\}, \quad (3\text{-}52)$$

$$\langle pn\Lambda S\Sigma JM\text{-}\Omega v \mid T_0^R \mid pn\Lambda S\Sigma\pm 1JM\text{-}\Omega\mp 1v\rangle =$$

$$H_v\{f_1^2(\Omega,\Sigma) + f_1(\Omega\pm 1,\ \Sigma\pm 1)f_1(\Omega,\Sigma) + f_2^2(\Omega\pm 1,\ \Sigma\pm 1)$$

$$+f_4^2(\Omega\pm 1,\ \Sigma\pm 1) + f_4^2(\Omega,\Sigma) + f_4^2(\Omega\mp 1,\ \Sigma\mp 1)\}\ f_4(\Omega,\Sigma), \quad (3\text{-}53)$$

$$\langle pn\Lambda S\Sigma JM\text{-}\Omega v \mid T_0^R \mid pn\Lambda S\Sigma\pm 2JM\text{-}\Omega\mp 2v\rangle =$$

$$H_v f_4(\Omega,\Sigma)f_4(\Omega\pm 1,\Sigma\pm 1)\{f_1(\Omega,\Sigma) + f_1(\Omega\pm 1,\Sigma\pm 1)$$

$$+f_1(\Omega\pm 1,\Sigma\pm 2)\}, \quad (3\text{-}54)$$

and

$$\langle pn\Lambda S\Sigma JM\text{-}\Omega v \mid T_0^R \mid pn\Lambda S\Sigma\pm 3JM\text{-}\Omega\mp 3v\rangle =$$

$$H_v f_4(\Omega,\Sigma)f_4(\Omega\pm 1,\Sigma\pm 1)f_4(\Omega\pm 2,\Sigma\pm 2) \quad (3\text{-}55)$$

where

$$H_v = \sum_{v'v''} \frac{\langle nv \mid B(R) \mid nv' \rangle \langle nv' \mid B(R) \mid nv'' \rangle \langle nv'' \mid B(R) \mid nv \rangle}{(E_v - E_{v''})(E_v - E_{v'})}$$

$$- \frac{1}{2} \{ \sum_{v'} \frac{\langle nv \mid B(R) \mid nv \rangle \mid \langle nv \mid B(R) \mid nv' \rangle \mid 2}{(E_v - E_{v'})^2}$$

$$+ \frac{\mid \langle nv \mid B(R) \mid nv' \rangle \mid^2 \langle nv \mid B(R) \mid nv \rangle}{(E_v - E_{v'})^2} \} \qquad (3\text{-}56)$$

The matrix elements of G_3 and G_2 given above are called the centrifugal distortion matrix elements. They describe the coupling of the vibrational and rotational motions through the R dependence of various interaction terms. The coefficients of the centrifugal distortion matrix elements for the rotational and spin-orbit terms dominate those due to the other interactions. The matrix elements of the rotational kinetic energy operator also contains a $J^n(J+1)^n$ dependence, where n is the order of the transformed Hamiltonian, which forces the rotational energy matrix elements to be the predominate ones for even modest J values. Thus the only centrifugal distortion coefficients usually quoted are D_v, A_{Dv} and H_v.

5. LAMBDA DOUBLING MATRIX ELEMENTS

The lambda doubling interaction from Chapter III-2 of this chapter is given by

$$H_\Lambda = T^R_\Lambda + H^{SO}_\Lambda$$

$$= (B(R) + 1/2A(R))(L_+S_- + L_-S_+)$$

$$- B(R)(L_+ \mathcal{J}_- + L_- \mathcal{J}_+). \qquad (3\text{-}57)$$

Due to the L_+ and L_- operators this interaction connects electronic states differing in Λ by unity.

The Van Vleck transformation can again be used to remove the matrix elements connecting the block of states of interest to blocks within other electronic states. It is shown in Appendix B that in the Van Vleck transformation matrix elements of G_1 that lie outside the block of states of interest vanish and those inside are equal to those of H_1 inside. Since H_1, in this case H_Λ, has no non-vanishing matrix elements within the electronic states of interest all matrix elements of G_1 vanish. The matrix elements of the second order transformed Hamiltonian, G_2, are calculated using equation (B-19) of Appendix B rewritten here

$$\langle m \mid G_2 \mid m' \rangle = \sum_n \frac{\langle m \mid H_1 \mid n \rangle \langle n \mid H_1 \mid m' \rangle}{(E_m^0 - E_n^0)(E_{m'}^0 - E_n^0)} \left[\frac{1}{2} (E_m^0 - E_{m'}^0) - E_n^0 \right] \qquad (3\text{-}58)$$

where m denotes states within the block of states of interest and n represents those outside. Just as in section D of this chapter equation (3-58) reduces to

$$\langle m \mid G_2 \mid m' \rangle = \frac{\langle m \mid H_1 \mid n \rangle \langle n \mid H_1 \mid m' \rangle}{E_m - E_n} \qquad (3\text{-}59)$$

since

$$\langle m \mid G_0 \mid m' \rangle = \langle m \mid H_0 \mid m' \rangle = E_m \delta_{mm'} \qquad (3\text{-}60)$$

or more specifically

$$\langle n'v' \mid H_0 \mid nv \rangle = \langle n'v' \mid G_0 \mid nv \rangle = (E_n^{el} + E_v^{vib}) \delta_{nn'} \delta_{vv'}. \qquad (3\text{-}61)$$

Because the lambda doubling interaction is small compared to the other interactions third order terms are not considered.

The NO molecule whose ground electronic state is a $^2\pi$ state can be connected by means of the lambda doubling interaction to either a $^2\Delta$ or $^2\Sigma$ state. Herzberg [33] shows the nearest $^2\Sigma$ state as being $A^2\Sigma^+$ at 43965.7 cm^{-1} followed by several other $^2\Sigma^+$ states at 52148.0, 53083.0, and 60628.5 cm^{-1}. The nearest $^2\Delta$ state according to Gilmore [34] lies at approximately 60495.0 cm^{-1}. Since there are four $^2\Sigma^+$ states close to the $X^2\pi$ state relative to the nearest $^2\Delta$ state, the $^2\Sigma^+$ states are assumed to be the only contributors to the interaction.

The use of equation (3-59) and the basis set represented in equation (3-3) yields the following formula for the matrix elements of G_2:

$$\langle pn\Lambda S\Sigma JM-\Omega v \mid G_2 \mid pnv\Lambda S\Sigma''JM-\Omega''\rangle =$$

$$\sum_{\substack{n'\Lambda'p' \\ \Omega'v'\Sigma'}} (A_1 + A_2)(B_1 + B_2) \frac{1}{E^0_{nv} - E^0_{n'v'}} \tag{3-62}$$

where

$$A_1 = \langle nv\Lambda S\Sigma JM-\Omega \mid H_1 \mid n'v'\Lambda'S\Sigma'JM-\Omega'\rangle + p'\langle nv\Lambda S\Sigma JM-\Omega \mid H_1 \mid n'v'\Lambda S-\Sigma'JM\Omega'\rangle, \tag{3-63}$$

$$A_2 = p\langle nv-\Lambda S-\Sigma JM\Omega \mid H_1 \mid n'v'\Lambda S\Sigma'JM-\Omega'\rangle + pp'\langle nv-\Lambda S-\Sigma JM\Omega \mid H_1 \mid n'v'\Lambda S-\Sigma'JM\Omega'\rangle, \tag{3-64}$$

$$B_1 = \langle n'v'\Lambda S\Sigma'JM-\Omega' \mid H_1 \mid nv\Lambda S\Sigma''JM-\Omega''\rangle + p\langle n'v'\Lambda'S\Sigma'JM-\Omega' \mid H_1 \mid nv-\Lambda S-\Sigma''JM\Omega''\rangle, \tag{3-65}$$

and

$$B_2 = p'\langle n'v'\Lambda'S-\Sigma'JM\Omega' \mid H_1 \mid nv\Lambda S\Sigma''JM-\Omega''\rangle + pp'\langle n'v'\Lambda S-\Sigma'JM\Omega' \mid H_1 \mid nv-\Lambda S-\Sigma''JM\Omega''\rangle. \tag{3-66}$$

The assumption that all the perturbing states are $^2\Sigma^+$ states would imply $\Lambda'' = 0$, therefore the Λ' designation is replaced by Σ^s. This indicates a Σ electronic state with a Kronig symmetry of s = + or s = −. Use is made of the results of the parity operator acting on the above states, from appendix A, by inserting unity in the appropriate matrix elements in the form of the parity operator times its adjoint. The parity operator acting on states to both the left and right results in matrix elements which can be combined with others to yield:

$$\langle pn\Lambda S\Sigma JM-\Omega v \mid G_2 \mid pn\Lambda S\Sigma''JM-\Omega''\rangle =$$

$$1/4 \sum_{n'v'\Lambda'} \sum_{\Sigma'\Omega'p'} \frac{(C_1 + C_2 + C_3 + C_4)}{E^0_{nv} - E^0_{n'v'}} \tag{3-67}$$

where

$$C_1 = \langle nv\Lambda S\Sigma JM-\Omega \mid H_1 \mid n'v'\Sigma^S S-\Sigma'JM-\Omega'\rangle,$$

$$(1+pp's)^2\langle n'\Sigma^S S\Sigma'JM-\Omega'v' \mid H_1 \mid nv\Lambda S\Sigma''JM-\Omega''\rangle, \tag{3-68}$$

$$C_2 = \langle nv\Lambda S\Sigma JM-\Omega \mid H_1 \mid n'v'\Sigma^S S\Sigma'JM-\Omega'\rangle\ (1+pp's)\ x$$

$$(p'+ps)\langle n'v'\Sigma^S-\Sigma'JM\Omega' \mid H_1 \mid nv\Lambda S\Sigma''JM-\Omega''\rangle, \tag{3-69}$$

$$C_3 = \langle nv\Lambda S\Sigma JM-\Omega \mid H_1 \mid n'v'\Sigma^S-\Sigma'JM\Omega'\rangle(p'+ps)x$$

$$\langle n'v'\Sigma^S S\Sigma'JM-\Omega' \mid H_1 \mid nv\Lambda S\Sigma''JM-\Omega''\rangle(1+pp's), \tag{3-70}$$

and

$$C_4 = \langle nvS\Sigma JM-\Omega \mid H_1 \mid n'v'\Sigma^S S-\Sigma'JM\Omega'\rangle(p'+ps)^2\ x$$

$$\langle n'\Sigma^S S-\Sigma'JM\Omega'v' \mid H_1 \mid n\Lambda S\Sigma''JM-\Omega''v\rangle. \tag{3-71}$$

Performing the sum over p' and using the following designation for the set of quantum numbers

$$\Lambda = 0,\ \Sigma = 1/2,\ \Omega = 1/2 \rightarrow {}^2\Sigma, \tag{3-72a}$$

$$\Lambda = 1,\ S = 1/2,\ \Omega = 3/2 \rightarrow {}^2\pi_{3/2}, \tag{3-72b}$$

$$\Lambda = 1,\ \Sigma = -1/2.\ \Omega = 1/2 \rightarrow {}^2\pi_{1/2}, \tag{3-72c}$$

the matrix elements are then obtained from equation (3-67) through (3-71) and are given by

$$\langle pnv^2\pi_{1/2}JM \mid G_2 \mid pnv^2\pi_{1/2}JM\rangle = O_v^\pi$$

$$+ \frac{q_v^\pi}{2}\left[(J+1/2)^2 + ps2(J+1/2)+1\right] + \frac{p_v^\pi}{2}\left[1+ps(J+1/2)\right] + O_v^\pi, \tag{3-73}$$

$$\langle pnv^2\pi_{3/2}JM \mid G_2 \mid pnv^2\pi_{3/2}JM\rangle = \frac{q_v^\pi}{2}\left[(J+1/2)^2 - 1\right], \tag{3-74}$$

and

$$\langle pnv^2\pi_{3/2}JM \mid G_2 \mid pnv^2\pi_{1/2}\ JM\rangle =$$

$$\langle pnv^2\pi_{1/2}JM \mid G_2 \mid pnv^2\pi_{3/2}JM\rangle = \frac{p_v^\pi}{4}(J+1/2)^2-1]^{1/2}$$

$$+ \frac{q_v^\pi}{2}\left[1 + ps(J+1/2)\right]\left[(J + 1/2)^2 - 1\right]^{1/2}. \tag{3-75}$$

The three coefficients p_v^π, q_v^π, and O_v^π are given by

$$p_v^\pi = 4 \sum_{n'v'} \frac{\langle nv^2\pi \mid B(R)L_+ \mid n'v'^2\Sigma\rangle\langle n'v'^2\Sigma \mid \frac{A(R)}{2} L_- \mid nv^2\pi\rangle}{E^0_{nv} - E^0_{n'v'}} \tag{3-76}$$

$$q_v^\pi = 2 \sum_{v'n'} \frac{\left| \langle nv^2\pi \mid B(R)L_+ \mid n'v'^2\Sigma\rangle \right|^2}{E^0_{nv} - E^0_{n'v'}} \tag{3-77}$$

and

$$O_v^\pi = \sum_{n'v'} \frac{\left| \langle nv^2\pi \mid 1/2A(R)L_+ \mid n'v'^2\Sigma\rangle \right|^2}{E^0_{nv} - E^0_{n'v'}} \tag{3-78}$$

6. ROTATIONAL ENERGIES AND ENERGY EIGENSTATES

The vibrational molecular constants of NO in the ground electronic state have been measured [35, 36] or calculated [37] by several workers. One of the best sets of vibrational constants is that of Henry, et al., [36] who examined data from the 1-0, 2-0, and 3-0 bands of NO and arrived at the set of constants in Table 3-1.

The rotational molecular constants of NO have also been the subject of several works [35-41]. Likewise, there has been several investigations of the lambda doubling parameters [36, 40-42] since the advent of very high resolution and doppler limited spectroscopy. One of the most complete works on the v = 0 and v = 1 vibrational states is that of Valentin et al. [41] whose results appear in Table 3-2. It is this set of constants that was used in this work.

The rotational energies were calculated using the matrix elements given in equations (3-23) through (3-28), (3-35) through (3-37), and (3-52) through (3-55). The matrix elements given in equation (3-22), which are those of the electronic and vibrational Hamiltonian, were ignored since they are diagonal and constant in a given electronic and vibrational state. The Hamiltonian matrix is a four-by-four matrix made up of the matrix elements of $\bar{G}$ in the states of $|\Omega|$ (1/2,3/2) and p (= ±1). The four-by-four matrix consist of two two-by-two matrices each of which belong to a definite parity eigenstate. The four-by-four reduces to two identical two-by-two matrices when lambda doubling is ignored.

Table 3-1

Vibrational Molecular Constants for
the Ground Electronic State of NO

Constant	Value (cm^{-1})
w_e	1904.1113 ± .0026
$w_e x_e$	14.833 ± .001
$w_e y_e$	.00836 ± .00017

Table 3-2

Rotational Molecular Constants for the $X^2\pi$ 1-0 Band of NO

Constant	Value (cm^{-1})	
	v = 0	v = 1
B_v	$1.6961359 \pm 31 \times 10^{-7}$	$1.6785671 \pm 30 \times 10^{-7}$
D_v	$0.547403 \times 10^{-5} \pm 56 \times 10^{-10}$	$.549223 \times 10^{-5} \pm 50 \times 10^{-10}$
H_v	$0.1279 \times 10^{-10} \pm 30 \times 10^{-13}$	$0.1173 \times 10^{-10} \pm 25 \times 10^{-13}$
A_v	$123.02772 \pm .00011$	$122.78248 \pm .00011$
A_{D_v}	$3.47573 \pm .0051$	$3.37135 \pm .0050$
p_v^π	$-11.668 \times 10^{-3} \pm 7 \times 10^{-6}$	$-11.667 \times 10^{-3} \pm 8 \times 10^{-6}$
q_v^π	$9.303 \times 10^{-5} \pm 8 \times 10^{-7}$	$-9.383 \times 10^{-5} \pm 8 \times 10^{-7}$
o_v^π	-0.10579	-0.10668
ω_o	$1875.97233 \pm 7 \times 10^{-5}$	

The rotational constants in Table 3-2 were used in calculating the Hamiltonian matrix which was then diagonalized to yield the energy eigenstates and eigenvalues. The calculations were performed for both v = 0 and v = 1 vibrational states with and without lambda doubling ($p\pi_v = q\pi_v = 0\pi_v = 0$) for J values of 0.5 to 40.5. The results of these calculations appear in Table C-1 through C-4 of Appendix C.

Table C-1 through C-4 also list the eigenvectors of the transformed Hamiltonian. These eigenvectors determine the eigenstates of the transformed Hamiltonian in terms of the basis set of eigenvectors by the relation.

$$|\, pnJMg\rangle = \sum_{\Omega} C(J,g,\Omega,p)\, |\, pn\Lambda SDJM\text{-}\Omega\rangle \qquad (3\text{-}79)$$

where the $C(J,g,\Omega,p)$'s are the eigenvector components of the transformed Hamiltonian matrix.

CHAPTER IV

COUPLED SPECTRAL LINE BROADENING THEORY

1. ANDERSON-TSAO-CURNUTTE THEORY

A. Radiator-Perturber-Field Hamiltonian

The starting point in the introduction to the Anderson-Tsao-Curnutte (ATC) boadening theory is the radiator-perturber-field Hamiltonian.[6-8] The Hamiltonian is expressed as

$$H = H_0 + H_c(t) + H_{1R} \tag{4-1}$$

where

$$H_0 = H_1 + H_2 + H_R. \tag{4-2}$$

The unperturbed Hamiltonian H_0 consist of three parts, the Hamiltonian of the radiating molecule (molecule 1), H_1, that of the perturbing molecule (molecule 2), H_2, and that of the quantitized radiation field, H_R. The perturbing terms in the total Hamiltonian, $H_c(t)$ and H_{1R}, are the time dependent collision interaction and the interaction of the radiating molecule with the radiation field, respectively.

The unperturbed Hamiltonian has eigenstates which are the products of the eigenstates of H_1, H_2, and H_{1R}. These eigenstates solve the eigenvalue equations:

$$H_0 \left| n_1 n_2 N_{\vec{k}\vec{\lambda}} \right\rangle = (E_{n_1} + E_{n_2} + \hbar\omega_k) \left| N_{\vec{k}\vec{\lambda}} \right\rangle \tag{4-3}$$

where

$$H_1 \left| n_1 \right\rangle = E_{n_1} \left| n_1 \right\rangle \tag{4-4}$$

$$H_2 \left| n_2 \right\rangle = E_{n_2} \left| n_2 \right\rangle \tag{4-5}$$

and

$$H_R \left| N_{\vec{k}\vec{\lambda}} \right\rangle = \hbar\omega_{\vec{k}} \left| N_{\vec{k}\vec{\lambda}} \right\rangle. \tag{4-6}$$

B. Transition Probability

Calculation of the transition probability in the presence of collisions is best understood by first examining the case without collisions. Time dependent perturbation theory indicates that the transition probability for absorption from a state A to a state B at time t later is given by

$$P_{A\to B}(t) = \left| \langle n_A \; N_{\vec{k}\vec{\lambda}} - 1 \left| \; U_0(t) \; U_{1R}(t) \right| n_B \; N_{\vec{k}\vec{\lambda}} \rangle \right|^2 \tag{4-7}$$

where

$$U_{1R}(t) = (e^{-i/\hbar \int_0^t H^I_{1R}(t')dt'})+. \tag{4-8}$$

The term H^I_{1R} above is the radiation interaction Hamiltonian in the interaction representation defined by

$$H^I_{1R}(t) = U_0^{-1}(t) \; H_{1R} U_0(t) \tag{4-9}$$

where

$$U_0(t) = e^{-iH_0 t/\hbar}. \tag{4-10}$$

For the present case $H_c(t)$ is zero and molecule 1 states are the only ones considered.

The expression for the transition probability can also be written in terms of the time development operator for the total Hamiltonian (see Appendix D)

$$P_{A\to B}(t) = \left| \langle n_A \; N_{\vec{k}\vec{\lambda}} - 1 \left| \; U(t) \right| n_B \; N_{\vec{k}\vec{\lambda}} \rangle \right|^2 \tag{4-11}$$

where

$$U(t) = U_0(t) \; U_{1R}(t) = (e^{-i/\hbar \int_0^t H(t')dt'})+.^1 \tag{4-12}$$

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[1] The + following the expression for the time development operator implies that it is a time ordered product time development operator.[2]

The approach taken in the ATC theory to include the addition of collisions is to calculate the transition probability for a transition between two "collision smeared states". In order to construct these smeared states it is first necessary to make the impact approximation. This approximation assumes the duration of a collision is much smaller than the time between collisions. With this assumption the Hamiltonian of the system can be equated to the unperturbed Hamiltonian, H_0, at some time t = 0. At some later time the system is in a collision smeared state given by;

$$| n_1(t)n_2(t)\ N_{\vec{k}\vec{\lambda}}\rangle = U_{0c}(t) | n_1 n_2\ N_{\vec{k}\vec{\lambda}}\rangle \tag{4-13}$$

where

$$U_{0c}(t) = (e^{-i/\hbar\int_0^t H_{0c}(t')dt'})_+ \tag{4-14}$$

and

$$H_{0c}(t) = H_0 + H_c(t). \tag{4-15}$$

The absorption transition probability is now the probability of a transition from a collision smeared state minus a photon given by;

$$| A(t)\rangle \equiv U_{0c}(t) | n_1 n_2\ N_{\vec{k}\vec{\lambda}} - 1\rangle \tag{4-16}$$

to a state time developed under the total Hamiltonian given by;

$$| B(t)\rangle = U(t) | n_1' n_2'\ N_{\vec{k}\vec{\lambda}}\rangle. \tag{4-17}$$

The transition probability is therefore expressed as:

$$\begin{aligned} P_{A\to B}(t) &= | \langle A(t) | B(t)\rangle |^2 \\ &= | \langle n_1 n_2\ N_{\vec{k}\vec{\lambda}} - 1 | U_{0c}^{-1}(t)\ U(t) | n_1'\ n_2'\ N_{\vec{k}\vec{\lambda}}\rangle |^2. \end{aligned} \tag{4-18}$$

It is interesting to note at this point the similarity of equation (4-18) with equation (4-7) for the noncollision case.

The expression for the transition probability is made more palatable by expressing the product of the two TDO's through first order only. To obtain first order terms let V(t) be defined by;

$$V(t) \equiv U_{0c}^{-1}(t)U(t) \tag{4-19}$$

and note that;

$$\dot{V}(t) = -\frac{i}{\hbar} U_{0c}^{-1}(t)H_{1R}U_{0c}(t)V(t). \tag{4-20}$$

A boundary condition on V(t) is easily obtained by noting that at t=0 $U_{0c}^{-1}(t)$ and U(t) go over to $U_0^{-1}(t)$ and $U_0(t)$, respectively, therefore V(t=0) is unity. Utilizing this boundary condition and solving equation (4-20) iteratively through first order yields;

$$V(t) = 1 - \frac{i}{\hbar}\int_0^t U_{0c}(t')H_{1R}U_{0c}(t')dt'. \tag{4-21}$$

Substituting into equation (4-18) for the transition probability yields:

$$P_{A\to B}(t) =$$

$$\frac{1}{\hbar^2}\left| \langle n_1 n_2 N_{\bar{k}\bar{\lambda}}^{--} - 1 \left| \int_0^t U^{\dagger}{}_{0c}(t')H_{1R}U_{0c}(t')dt' \right| n_1' n_2' N_{\bar{k}\bar{\lambda}}^{--} \rangle \right|^2. \tag{4-22}$$

The TDO $U_{0c}(t)$ above continues to carry the free quantitized radiation field Hamiltonian dependency. To "pull" this dependency out of the TDO appearing in the matrix element above a new Hamiltonian is constructed given by;

$$H_m(t) \equiv H_1 + H_2 + H_c(t). \tag{4-23}$$

Now note that the old $H_{0c}(t)$ Hamiltonian can be expressed in terms of the new $H_m(t)$ Hamiltonian by;

$$H_{0c}(t) = H_0 + H_c(t) = H_m(t) + H_R. \tag{4-24}$$

Since H_R has the following commutitive properties;

$$[H_R, H_1] = [H_R, H_2] = [H_R, H_c(t)] = 0 \tag{4-25}$$

the TDO $U_{0c}(t)$ consists of two commuting parts, therefore;

$$U_{0c}(t) = U_R(t)U_m(t) = U_m(t)U_R(t). \tag{4-26}$$

Making use of the above term of $U_{0c}(t)$ in equation (4-22) for the transition probability, yields:

$$P_{A\to B}(t) =$$

$$\frac{1}{\hbar^2}\left| \langle n_1 n_2 N_{\bar{k}\bar{\lambda}} - 1 \right| \int_0^t e^{-i w_{\bar{k}\bar{\lambda}} t} U_m^{-1}(t') H_{1R} U_m(t') dt' \; X$$

$$\left| n_1' n_2' \; N_{\bar{k}\bar{\lambda}} \rangle \right|^2 \tag{4-27}$$

C. Radiation Interaction Hamiltonian and the Dipole Approximation

The specific form of the radiation interaction Hamiltonian which appears in the transition probability is now addressed. From quantum electrodynamics this Hamiltonian is given by;

$$H_{1R} = -\frac{1}{c\sqrt{V}} \sum_{\bar{k}\bar{\lambda}} \left(\bar{j}_{-\bar{k}} \cdot \bar{\lambda} A^{0P}_{\bar{k}\bar{\lambda}} + \bar{j}_{\bar{k}} \cdot \bar{\lambda}^* \, A^{0P\dagger}_{\bar{k}\bar{\lambda}} \right) \tag{4-28}$$

where $\bar{\lambda}$ is the complex polarization vector, $\bar{k}$ the propagation vector ($\bar{k} = \hat{k} wc$), and V is a volume element.[11] The term $\bar{j}_{\bar{k}}$ is the Fourier transform of the paramagnetic current density, that is;

$$\bar{j}_{\bar{k}} = \int e^{-\bar{k}\cdot\bar{r}} \, \bar{j}(\bar{r}) dr^3 \tag{4-29}$$

where;

$$\bar{j}(\bar{r}) = \frac{1}{2} \sum_i q_i [\frac{\bar{P}_i}{m_i} \delta(\bar{r}-\bar{r}_i) + \delta(\bar{r}-\bar{r}_i) \frac{\bar{P}_i}{m_i}]. \tag{4-30}$$

The A^{OP} operator is the photon creation-annihilation operator which exhibit the following properties on the photon field states;

$$A^{OP}_{\bar{k}\bar{\lambda}} \mid N_{\bar{k}\bar{\lambda}}> = \sqrt{\frac{2\pi\hbar c^2}{w}} \sqrt{N_{\bar{k}\bar{\lambda}}} \mid N_{\bar{k}\bar{\lambda}}-1> \tag{4-31}$$

and

$$A^{OP\dagger}_{\bar{k}\bar{\lambda}} \mid N_{\bar{k}\bar{\lambda}}> = \sqrt{\frac{2\pi\hbar c^2}{w}} \sqrt{N_{\bar{k}\bar{\lambda}} + 1} \mid N_{\bar{k}\bar{\lambda}} + 1>. \tag{4-32}$$

Utilizing the interaction Hamiltonian equation (4-28), with the properties of the photon state operators above the transition probability from equation (4-27) becomes;

$$P_{A\to B}(t) = \frac{2\pi\ N_{\bar{k}\bar{\lambda}}}{Vw\hbar} \mid <n_1 n_2 N_{\bar{k}\bar{\lambda}}-1 \mid \int_0^t e^{-iwt} U_m^{-1}(t') \bar{j}_{-\bar{k}} \cdot \bar{\lambda}\ U_m(t')dt'$$

$$\mid n_1' n_2' N_{\bar{k}\bar{\lambda}}^{-1}> \mid^2. \tag{4-33}$$

Since this work is directed toward the investigation of the vibrational rotational fundamental band, only dipole transitions are of concern. The dipole approximation consist of expanding the exponential of equation (4-29) and keeping only the first term, therefore;

$$\bar{j}_{\bar{k}} \sim \sum_i \frac{\bar{P}_i}{m_i} q_i. \tag{4-34}$$

Since $\bar{p}_i$ is the conjugate momentum one has;

$$\bar{j}_{\bar{k}} \sim \sum_i q_i \dot{\bar{r}}_i + \sum_i \frac{q_i^2}{cm_i} \bar{A}(\bar{r}_i, t) \tag{4-35}$$

where, from quantum electrodynamics;

$$\bar{A}(\bar{r},t) = \sum_{\bar{k}\bar{\lambda}} [A^{OP}_{\bar{k}\bar{\lambda}} \bar{\lambda} \frac{e^{i\bar{k}\cdot\bar{\lambda}-iwt}}{\sqrt{V}} + A^{OP\dagger}_{\bar{k}\bar{\lambda}} \bar{\lambda}^* \frac{e^{-i\bar{k}\cdot\bar{\lambda}+iwt}}{\sqrt{V}}]. \qquad (4\text{-}36)$$

Note that the matrix element appearing in equation (4-33) is diagonal in the photon states therefore the vector potential portion of $\bar{j}_k$ in equation (4-35) does not contribute to the transition probability. Dropping the diagonal photon states from the matrix element for convenience, the matrix element then becomes;

$$\sum_i q_i \langle n_1 n_2 \mid U_m^{-1}(t') \dot{\bar{r}}_i \cdot \bar{\lambda} U_m(t') \mid n_1' n_2' \rangle. \qquad (4\text{-}37)$$

The velocity term above together with the TDO, $U_m(t)$, forms the Heisenberg representation of the velocity, that is;

$$\dot{\bar{r}}_i(t) = U_m^{-1}(t)\dot{\bar{r}}_i U_m(t). \qquad (4\text{-}38)$$

From this and the equation for the velocity;

$$\dot{\bar{r}}_i(t) = \frac{d}{dt}\bar{r}_i(t) \qquad (4\text{-}39)$$

one arrives at the equation;

$$U_m^{-1}(t)\dot{\bar{r}}_i U_m(t) = \frac{d}{dt} U_m^{-1}(t)\bar{r}_i U_m(t). \qquad (4\text{-}40)$$

Utilizing the above equation and equation (4-37), the matrix element appearing in the expression for transition probability, after integration by parts, is given by;

$$e^{-iwt}\langle n_1 n_2 \mid U_m(t)\bar{r}_i\cdot\bar{\lambda}U_m(t) \mid n_1' n_2'\rangle - \langle n_1 n_2 \mid \bar{r}_i\cdot\bar{\lambda} \mid n_1' n_2'\rangle$$

$$+ iw \int_0^t e^{-iwt'} \langle n_1 n_2 \mid U_m^{-1}(t')\bar{r}_i\cdot\bar{\lambda}U_m(t') \mid n_1' n_2'\rangle dt' \qquad (4\text{-}41)$$

The last term in the above equation contributes almost entirely at infrared frequencies since w is of the order 10^{14} sec^{-1}. Therefore upon dropping the first two terms in equation (4-41) and after insertion into equation (4-33) the transition probability becomes;

$$P_{A\to B}(t) = \frac{2\pi N \bar{k}\bar{\lambda}}{Vw\hbar^3} \int_0^t \int_0^t \langle n_1 n_2 \mid \bar{\mu}(t') \cdot \bar{\lambda} \mid n_1' n_2' \rangle \; X$$

$$\langle n_1' n_2' \mid \bar{\mu}(t'') \cdot \bar{\lambda} \mid n_1 n_2 \rangle \; e^{iw(t''-t')} dt'dt''. \qquad (4\text{-}42)$$

In the above equation $\bar{\mu}$ is the dipole moment operator defined by;

$$\bar{\mu} = \sum_i q_i \bar{r}_i = -e\sum_t \bar{r}_t + e \sum_\alpha Z_\alpha \bar{R}_\alpha. \qquad (4\text{-}43)$$

where the first sum is over electrons and the last sum over nuclei.

The transition probability just derived is the probability for a transition from the molecular states given by $\mid n_1 n_2 \rangle$ to the states $\mid n_1' n_2' \rangle$ via the absorption of a photon of frequency w and polarization $\bar{\lambda}$. Since the interest of this work is to examine the spectral characteristics of the absorption regardless of the molecular states the transition probability is summed over all final states and summed over all initial states weighted by the Boltzmann distribution. This total transition probability ,P(t), is then given by;

$$P(t) = \sum_{\substack{n_1 n_2 \\ n_1' n_2'}} \rho_{n_1} \rho_{n_2} \; P_{A\to B}(t) \qquad (4\text{-}44)$$

where ρ_n is the Boltzmann distribution function for the state n. Upon performing the above summation utilizing equation (4-42) the total transition probability becomes;

$$P(t) =$$

$$\frac{2\pi N_{k\bar{\lambda}}\, w}{V\hbar} \int_0^t \int_0^t \mathrm{Tr}\,[\rho\bar{\lambda}\cdot\bar{\mu}(t'')\bar{\lambda}\cdot\bar{\mu}(t')e^{iw(t'-t'')}dt'dt'' \qquad (4\text{-}45)$$

where Tr denotes the trace operation.

D. Molecular Dipole Moment

Consider once again the dipole moment operator of equation (4-43). A matrix element of this operator between two molecular states belonging to the same electronic state is given by;

$$\langle nvJ \mid \bar{\mu} \mid nv'J' \rangle = \langle nvJ \mid -e \sum_t \bar{r}_t \mid nv'J' \rangle + e\langle nvJ \mid \sum_\alpha Z_\alpha \bar{R}_\alpha \mid nv'J' \rangle \qquad (4\text{-}46)$$

where the Born-Oppenheimer approximation is assumed. Note that the first matrix element involves electronic coordinates only and therefore is diagonal on the v and J quantum numbers. Since it is diagonal on v and J this term contributes only to the permanent dipole moment. The second matrix element does not depend on the electronic coordinates, however, the internuclear distance is a function of the electronic state. Therefore, the last matrix element above can be written as;

$$\langle nvJ \mid \sum_\alpha Z\alpha\bar{R}\alpha \mid nv'J' \rangle = \langle vJ \mid f_n(\bar{R}) \mid vJ \rangle. \qquad (4\text{-}47)$$

Combining this result with the first matrix element of equation (4-46) allows one to express the dipole moment operator in a form suggested by Levine.[45]

$$\bar{\mu}(R) = \bar{\mu}(R_e) + \bar{\mu}'(R_e)(R-R_e) + \frac{1}{2}\bar{\mu}''(R_e)(R-R_e)^2 + \ldots \qquad (4\text{-}48)$$

For the case of the infrared fundamental band only the second term contributes to the transition probability due to the vibrational selection rules.

It should be noted that due to the symmetry of a diatomic molecule about the internuclear axis the dipole moment necessarily lies along the internuclear axis.

E. Transition Rate and Absorption Coefficient

The aim of this section is to obtain an expression for the transition rate and from that derive an expression for the absorption coefficient. This step will involve commuting TDO's in the trace of equation (4-45), therefore another approximation is needed. This approximation is that the density matrix is stationary, which is a valid approximation neglecting such phenomenon as saturation effects and assuming the gas is in an isothermal bath. Since the density matrix $\rho(t)$ time develops according to;

$$\rho(t) = U_m(t)\rho_0 U_m^{-1}(t) \tag{4-49}$$

and it is assumed;

$$\rho(t) \sim \rho_0, \tag{4-50}$$

the density matrix commutes with $U_m(t)$, that is;

$$[\rho_0, U_m(t)] = 0. \tag{4-51}$$

Examine now the trace appearing in equation (4-45) for the transition probability. Rewriting it utilizing the TDO's yields:

$$\mathrm{Tr}[\rho_0 \bar{\lambda}\cdot\mu(t'')\bar{\lambda}\cdot\bar{\mu}(t')] =$$

$$\mathrm{Tr}[\rho_0 \bar{\lambda}\cdot U_m^{-1}(t'')\bar{\mu}U_m(t'')\ \bar{\lambda}\cdot U_m^{-1}(t')\bar{\mu}U_m(t')] \tag{4-52}$$

Utilizing the commutivity of the density matrix and the cyclic permutational properties of the operators in the trace, the above equation reduces to;

$$Tr[\rho_0 \bar{\lambda}\cdot\bar{\mu}(t")\bar{\lambda}\cdot\bar{\mu}(t')] = Tr[\rho_0\ \bar{\lambda}\cdot\bar{\mu}U_m^{-1}(t"\rightarrow t')\bar{\mu}\cdot\bar{\lambda}U_m(t"\rightarrow t')] \quad (4\text{-}53)$$

where

$$U_m(t"\rightarrow t') = U_m(t')\ U_m^{-1}(t"). \quad (4\text{-}54)$$

Letting $\tau \equiv t' - t"$ the TDO can be rewritten in terms of an initial time, t", and some time interval τ.

$$U_m(t"\rightarrow t') = U_m(t" \rightarrow t" + \tau) \quad (4\text{-}55)$$

Consider now a collision average of the above TDO. If the collisions occur randomly the TDO $U_m(t"\rightarrow t"+\tau)$ can be assumed independent of initial time t", therefore the collision averaged trace can be written as:

$$Tr[\rho_0\bar{\mu}\cdot\bar{\lambda}U_m^{-1}(\tau)\bar{\mu}\cdot\bar{\lambda}U_m(\tau)]_{AVE} \quad (4\text{-}56)$$

The integrand of equation (4-45) is now given by;

$$F(\tau) = e^{-iw\tau}Tr[\rho_0\bar{\lambda}\cdot\bar{\mu}U^{-1}(\tau)\bar{\lambda}\cdot\bar{\mu}U_m(\tau)]_{AVE}. \quad (4\text{-}57)$$

Since the collision averaged term $U_m^{-1}(\tau)\bar{R}U_m(\tau)$ has the property (see Appendix E);

$$U_m^{-1}(-\tau)\bar{\mu}U_m(-\tau)_{AVE} = U_m(\tau)\bar{\mu}U_m^{-1}(\tau)_{AVE} \quad (4\text{-}58)$$

and since the density matrix commutes with the TDO it is easily shown;

$$F(-\tau) = F^*(\tau). \quad (4\text{-}59)$$

In terms of the integrand $F(\tau)$ the transition probability is then given by;

$$P(t) = \frac{2\pi N\bar{\bar{k}}\bar{\lambda}w}{V\bar{n}}\int_0^t\int_0^t F(\tau)dt'dt" \quad (4\text{-}60)$$

where $\tau = t'-t''$. Making a change of integration variables from t' and t" to t" and τ, and using equation (4-59) P(t) becomes;

$$P(t) = \frac{2\pi N_{\bar{k}\bar{\lambda}}\bar{w}}{V\hbar} \; 2Re(T \int_0^T F(\tau)d\tau - \int_0^T F(\tau)\tau d\tau). \tag{4-61}$$

Ignoring the effects of natural broadening the transition rate is calculated from the transition probability using;

$$\Gamma = \lim_{t\to\infty} \frac{P(t)}{t} \tag{4-62}$$

Therefore the transition rate obeys the equation;

$$\Gamma \; \alpha \; \lim_{t\to\infty} [\int_0^t F(\tau)d\tau - \frac{1}{t}\int_0^t F(\tau)\tau d\tau] \; . \tag{4-63}$$

Note that $F(\tau)$ is an exponential times the collision averaged dipole moment correlation function. The dipole correlation function tends to be larger for small τ. As τ becomes large the collision averaged dipole correlation tends to vanish. Thus the transition rate is given by;

$$\Gamma = \frac{4\pi N_{\bar{k}\bar{\lambda}}\bar{w}}{V\hbar} \; Re \int_0^\infty F(\tau)d\tau. \tag{4-64}$$

The absorption coefficient is formulated by first calculating the incident intensity of radiation on a gas. The incident intensity or energy per unit area per unit time of frequency w and polarization $\bar{\lambda}$ is the product of the following; the number of photons of frequency w and polarization $\bar{\lambda}$ per unit volume, the energy per photon, and the photon speed, thus;

$$I^0(w) = \frac{N_{\bar{k}\bar{\lambda}}}{V} \hbar w c. \tag{4-65}$$

Now consider the radiant energy absorbed, of frequency w and polarization $\bar{\lambda}$, per unit area per unit time by a gas of n molecules per unit volume. This quantity is equal to the product of the following quantities; the transition rate per molecule for absorption of a photon of frequency w and polarization $\bar{\lambda}$, the number of absorbing molecules per unit volume, the energy per transition, and the optical path length, therefore:

$$dI = -\Gamma n\hbar w d\ell \tag{4-66}$$

After some rearranging of terms the above equation becomes;

$$dI(w) = -I^0(w)k(w)d\ell \tag{4-67}$$

where;

$$k(w) = \frac{4\pi nw}{c\hbar} \text{Re} \int_0^\infty F(\tau)d\tau. \tag{4-68}$$

Integration of equation (4-67) then yields Beer's law:

$$I(w) = I^0(w)e^{-k(w)\ell} \tag{4-69}$$

F. Resolved Line Approximation

A new time development operator $T(\tau)$ given by Anderson as;

$$T(\tau) = U_0^{-1}(\tau)U_m(\tau) \tag{4-70}$$

is now introduced.[36-38] This TDO is necessary for both the following discussion of the resolved line approximation and in the derivation of the coupled line form of the absorption coefficient. From its definition it is easily seen that $T(\tau)$ solves the differential equation;

$$\dot{T}(t) = -i/\hbar\ U_0^{-1}(t)\ H_c(t)\ U_0(t)\ T(t) \tag{4-71}$$

with boundary condition;

$$T(t=0) = U^{-1}(0)U_m(0) = U^{-1}(0)U_0(0) = 1. \tag{4-72}$$

Solving equation (4-71) iteratively yields:

$$T(t) = \left(e^{-i/\hbar \int_0^t U^{-1}(t')H_c(t')U_0(t')dt'}\right)_+ \tag{4-73}$$

Writing $U_m(t)$ in terms of $U_0(t)$ and $T(t)$ from equation (4-70) and substituting into equation (4-57) for $F(\tau)$ one obtains;

$$F(\tau) = e^{-iw\tau} Tr[\rho_0 \bar{\mu}\cdot\bar{\lambda} T^{-1}(\tau)U_0^{-1}(\tau)\bar{\mu}\cdot\bar{\lambda}U_0(\tau)T(\tau)]_{AVE} \tag{4-74}$$

Expanding the trace in terms of states a, b, c, and d gives:

$$F(\tau) = e^{-iw\tau} \sum_{a,b,c,d} e^{-iw_{dc}\tau} \rho_{aa} \langle a \mid \bar{\mu}\cdot\bar{\lambda} \mid b\rangle$$
$$\langle b \mid T^{-1}(\tau) \mid c\rangle\langle c \mid \bar{\mu}\cdot\bar{\lambda} \mid d\rangle\langle d \mid T(\tau) \mid a\rangle_{AVE} \tag{4-75}$$

It is this form of $F(\tau)$ which is used in the following discussion of the resolved line approximation.

The applicability of the resolved line approximation or lack thereof is illustrated by utilizing the approach of Tsao and Curnutte. [36] Since it is assumed the duration of collisions is much smaller than the time between collisions (impact approximation) the TDO $T(\tau)$ can be expressed as the product of TDO's for individual collisions in the time interval τ, that is;

$$T(\tau) = \prod_{\alpha} T_\alpha(\tau) \tag{4-76}$$

where α is an index of collisions. Consider an individual collision,

using terms of $T_\alpha(\tau)$ through first order, in which case the product of the last three matrix elements in equation (4-75) become;

$$\langle b \mid T_\alpha^{-1} \mid c\rangle\langle c \mid \bar{\mu}\cdot\bar{\lambda} \mid d\rangle\langle d \mid T_\alpha \mid a\rangle = \delta_{bc}\delta_{da}\langle b \mid \bar{\mu}\cdot\bar{\lambda} \mid a\rangle$$

$$+ \delta_{bc}\langle b \mid \bar{\mu}\cdot\bar{\lambda} \mid d\rangle\langle d \mid T_{1\alpha} \mid a\rangle$$

$$+ \delta_{da}\langle b \mid T_{1\alpha}^{-1} \mid c\rangle\langle c \mid \bar{\mu}\cdot\bar{\lambda} \mid d\rangle$$

$$+ \langle c \mid \bar{\mu}\cdot\bar{\lambda} \mid d\rangle\langle b \mid T_{1\alpha}^{-1} \mid c\rangle\langle d \mid T_{1\alpha} \mid a\rangle \qquad (4\text{-}77)$$

where;

$$T_\alpha = -T_\alpha^{-1} = i/\hbar \int_0^\tau U_0^{-1}(t)H_c(t)U_0(t)dt. \qquad (4\text{-}78)$$

It is interesting to note at this point that if $H_c(t)$ vanishes the only term remaining in equation (4-77) is the diagonal term. When this term is substituted into equation (4-68), via equation (4-75), there results an absorption coefficient which consists of a delta function in frequency centered at w_{ba}. The first order terms will be shown later to contribute only to the spectral line shift and not the line width, therefore they will be neglected in the following argument.

Tsao and Curnutte argue that for an individual collision starting at time t_0 with duration δ the second order term in equation (4-77) is given by;

$$\int_{t_0}^{t_0+\delta} e^{itw_{bc}}\langle b \mid H_{c,\alpha}(t) \mid c\rangle\, dt \int_{t_0}^{t_0+\delta} e^{iw_{da}t}$$

$$\langle d \mid H_{c,\alpha}(t) \mid a\rangle dt. \qquad (4\text{-}79)$$

Since δ is assumed much smaller than the time between collisions of type σ, τ_σ, to obtain a collision averaged quantity for collisions of type σ the initial time, t_0, needs to be averaged over τ_σ. Making use of the fact that the form of $H_{c,\sigma}(t)$ is independent of the actual

starting time, and by making a change of variable of integration in equation (4-79), the time average is found proportional to;

$$(1/\tau_\sigma) \int_0^{\tau_\sigma} e^{i(w_{bc}+w_{da})t} dt. \tag{4-80}$$

The above integral for $w_{bc} + w_{da}$ equal to zero is unity and for a non-zero exponent the integral is equal to;

$$\frac{e^{i(w_{bc} + w_{da})\tau_\sigma - 1}}{(w_{bc} + w_{da})\ \tau_\sigma} . \tag{4-81}$$

The interaction term $H_c(t)$ is assumed independent of vibrational states since the intermolecular potentials considered here are those due to permanent electric multipole moments which are a function of molecular orientation and distance only. Therefore for a zero spin $\sum$-state diatomic molecule the states a,b,c, and d can be assigned the total angular momentum quantum numbers:

$$\begin{aligned} &\text{a: } J_i,\ J_2 && \text{b: } J_f,\ J_2 \\ &\text{c: } J_f,\ J_2, && \text{d: } J_i,\ J_2, \end{aligned} \tag{4-82}$$

Using the above notation and noting that the rotational energy depends only on the J quantum number one can easily obtain:

$$w_{bc} + w_{da} = 2\pi c[(E_{J_f} - E_{J_i}) + (E_{J_i,} - E_{J_f,})] \tag{4-83}$$

Now note that the individual energy difference terms can take on the same range of values, those corresponding to $\Delta J = \pm 1$. From this one concludes that equation (4-83) is either zero or some non-zero multiple of;

$$E = 2\pi c \cdot 2B_v \tag{4-84}$$

where B_v is the molecular rotational term value constant. Assuming a multiple of unity and a typical B_v value of 1.5 cm^{-1}, the frequency

difference term would have a value of 5.6×10^{11} sec^{-1}. Using as a collision time that of N_2 at a temperature of 300K and pressure of one atmosphere, $\tau_\sigma = 1.37 \times 10^{-10}$ sec, the denominator of equation (4-81) is found to have a value of 76.9, and therefore the absolute value of (4-81) is approximately 10^{-2} as opposed to 1 for a vanishing exponent. [46]

The above argument due to Tsao and Curnutte implies one can ignore, to an approximation, all non-zero values of the energy difference terms for zero spin Σ state diatomics. This implies $J_f = J_{f'}$ and $J_i = J_{i'}$, and leads to a formulation of the absorption coefficient which is the sum of Lorentz pressure broadened absorption profiles, hence the "resolved line approximation". Although a zero spin Σ state diatomic was used in the above argument the approximation is by no means limited to just those type molecules. Any molecule whose energy levels would lead to a situation where $(w_{bc}+w_{da})\tau_\sigma$ is either zero or a "large" value would qualify for the resolved line approximation.

Chapter III demonstrated that the zeroth order approximation of the rotational energy eigenvalues of NO for a given J quantum number consisted of two values. One of these is that belonging to the $^2\pi_{1/2}$ electronic state the other belonging to the $^2\pi_{3/2}$ state, with the $^2\pi_{3/2}$ state lying approximately 120 cm^{-1} higher in energy. The dipole selection rules on the zeroth order eigenstates forbid transitions between rotational states belonging to different spin states, that is between the $^2\pi_{1/2}$ and $^2\pi_{3/2}$ state. Hence only energy levels within a particular subband need be considered. Therefore, from examining the energy levels of NO one can conclude the resolved line approximation

is valid for the NO fundamental band in zeroth order. Therefore, the ATC theory, as given by Tsao and Curnutte for symmetric top molecules utilizing the resolved line approximation, can be used for the calculation of NO pressure broadening parameters when incorporating zeroth order NO eigenstates.

The first order eigenstates of NO consist of two pairs of states. Each eigenstate in the pair has definite parity and is comprised of an admixture of rotational states of both the $^2\pi_{1/2}$ and $^2\pi_{3/2}$ electronic states. Due to this admixture, two transitions are now allowed in each subband, each having different ground state parity. These pairs of lines, lambda doublets, are extremely closely spaced, 10^{-4}-10^{-3}cm^{-1}, and their ground state energies are separated by approximately 10^{-2}-1 cm^{-1} depending on the J value.

Examination of the criterion for the resolved line approximation does not clearly indicate that pressure broadening effects on the doublets of NO can necessarily be calculated using the resolved line approximation. Consider the $P(2.5)_{1/2}$ + parity line of NO. From equation (4-83) the first energy difference term yields a value for this transistion, of 8.3302 cm^{-1}. The second term could be an energy difference between the J=5/2, g = 1/2, P = -1 state and the J = 3/2, g = 1/2, P = -1 state in which case it has a value of 8.3893 cm^{-1}. This leads to a total frequency difference of 1.11 X 10^{10} sec^{-1}. Utilizing again the time between collisions of N_2 molecules of 1.37 X 10^{-10} sec the denominater of equation (4-81) would have a value 1.53 thereby increasing the value of the integral, equation (3-81), by a factor of approximately 50.

2. GERSTEN-FOLEY THEORY

A theory was developed by Gersten and Foley which took into account the effects of overlapping spectral lines.[9] This theory has recently been employed by Braun to examine the overlapping effects of the ν_2 band of CO_2 utilizing only the quadrupole-quadrupole intermolecular interactions.[47]

The Gersten-Foley work starts out by assuming a system Hamiltonian given by;

$$H = H_0 + V \tag{4-85}$$

where H_0 is the unperturbed Hamiltonian and V is a time dependent collision interaction. The dipole moment operator in the Heisenberg representation, $\mu(t)$, which is given by;

$$\mu(t) = U^{-1}(t)\mu U(t) \tag{4-86}$$

is then said to solve the following equation of motion;

$$\frac{d\mu(t)}{dt} = i[H,\mu(t)]. \tag{4-87}$$

Since H_0 is stationary the above equation holds only in the case that V(t) obeys;

$$[V(t), V(t')] = 0 \text{ for } t \neq t'. \tag{4-88}$$

Although this assumption is made later in their work the intermediate results are formulated starting with equation (4-87) (equation 4 of Reference 47).

Gersten and Foley are able to demonstrate that in the resolved line approximation their coupled line formulation reduces to a sum of

Lorentz lines as does the ATC theory. Examination of Braun's work reveals that in the resolved line approximation his results, based on the Gersten-Foley theory, yield exactly those of the ATC theory for the line widths.

3. A COUPLED LINE THEORY UTILIZING THE ATC THEORY

A. Dipole Moment Reduced Matrix Element Differential Equation

This section is the starting point for the calculation of the coupled line absorption coefficient. No assumption as to the commutable behavior of the collision interaction is made at this point nor is it assumed until the introduction of the approximate form of the collision operator. The starting point for the coupled line absorption coefficient formulation is equation (4-57) from the ATC theory. Utilizing this equation together with some of the methods applied by Tsao and Curnutte an expression for the collision operator is derived. This collision operator is the counterpart of the S matrix arrived at by Gersten and Foley.[49] After the development of the collision operator the work given in this and the next few sections essentially parallels that of Braun with the exception of allowing for non-$\sum$ state diatomic eigenstates.

The $F(\tau)$ function of equation (4-57) can be rewritten, using the results of Appendix F, as;

$$F(\tau) = \frac{1}{3} e^{-iw\tau} \mathrm{Tr}[\rho_0 \bar{\mu} \cdot U_m^{-1}(\tau) \bar{\mu} U_m(\tau)]_{AVE}. \qquad (4\text{-}89)$$

Since the density matrix is assumed to commute with the TDO $U_m(t)$ (equation 4-51), $F(\tau)$ can be written;

$$F(\tau) = \frac{1}{3} e^{-iwt} \mathrm{Tr}[\rho_0 \tilde{\bar{\mu}}(t) \cdot \bar{\mu}]_{AVE} \tag{4-90}$$

where $\tilde{\bar{\mu}}(t)$ is defined by;

$$\tilde{\bar{\mu}}(t) = U_m(t) \bar{\mu} U_m^{-1}(t). \tag{4-91}$$

Note that the operator $\bar{\mu}$ is diagonal on molecule 2 states since $\tilde{\bar{\mu}}$ transforms like a scalar with respect to $\bar{J}_2$. Therefore, with the aid of Appendix F;

$$F(t) = (\tfrac{1}{3}) e^{-iwt} \sum_{\substack{J_i,\alpha_i,M_i \\ J_f,\alpha_f,M_f}} \rho_{J_i\alpha_i} (-1)^q$$

$$\sum_{J_2,M_2,\alpha_2} \rho_{J_2\alpha_2} \langle J_i M_i \alpha_i \; J_2 M_2 \alpha_2 \mid \tilde{\mu}_q^1(t) \mid J_f M_f \alpha_f J_2 M_2 \alpha_2 \rangle_{AVE}$$

$$\langle J_f M_f \alpha_f \mid \mu_q^1 \mid J_i M_i \alpha_i \rangle. \tag{4-92}$$

Applying more results of Appendix F;

$$F(\tau) = (\tfrac{1}{3}) e^{-iwt} \sum_{\substack{J_i,\alpha_i \\ J_f,\alpha_f}} \rho_{J_i\alpha_i} (-1)^{J_f - J_i}$$

$$\sum_{J_2 M_2 \alpha_2} \rho_{J_2\alpha_2} \langle J_2 M_2 \alpha_2 \mid \langle J_i \alpha_i \mid\mid \tilde{\mu}_q^1(t) \mid\mid J_f \alpha_f \rangle \mid J_2 M_2 \alpha_2 \rangle_{AVE}$$

$$\langle J_f \alpha_f \mid\mid \mu^1{}_q \mid\mid J_i \alpha_i \rangle. \tag{4-93}$$

Since the collision averaged matrix element of $\tilde{\mu}^1(t)$ is independent of molecule 2 states the sum of the Boltzmann factor $\rho_{J_2\alpha_2}$ becomes unity, and therefore:

$$F(\tau) = (\tfrac{1}{3})\, e^{-iwt} \sum_{\substack{J_i,\alpha_i \\ J_f,\alpha_f}} (-1)^{J_f - J_i}\, \rho_{J_i\alpha_i}$$

$$\langle J_i\alpha_i \,||\, \tilde{\mu}^1(t) \,||\, J_f\alpha_f\rangle_{AVE} \langle J_f\alpha_f \,||\, \mu^1 \,||\, J_i\alpha_i\rangle \qquad (4\text{-}94)$$

Now the function $F(\tau)$ is in terms of the reduced matrix elements of the dipole moment function.

An expression is now needed for the collision averaged reduced matrix exlement of $\tilde{\bar{\mu}}(t)$ in terms of the reduced matrix element of $\bar{\mu}$ and the collision interaction. To obtain just such an expression consider the derivative of a component of the operator $\tilde{\bar{\mu}}(t)$;

$$\frac{d}{dt}\tilde{\mu}^1_q(t) = \frac{d}{dt} U_0(t)\, T(t)\, \mu^1_q\, T(t)^{-1}\, U_0^{-1}(t) \qquad (4\text{-}95)$$

where Anderson's T(t) TDO operator, defined in equation (4-70), has been introduced.[6-8] Performing the derivative on the right hand side yields:

$$\frac{d}{dt}\tilde{\bar{\mu}}^1_q(t) = i\hbar\,[\tilde{\mu}^1_q(t),\, H_0]$$

$$+\, U_0(t)\, \frac{d}{dt}\,[T(t)\mu^1_q T^{-1}(t)]\, U_0^{-1}(t) \qquad (4\text{-}96)$$

The time derivative appearing on the right hand side of equation (4-96) is now payed close attention. Consider first a change in the quantity $T(t)\mu^1_q T^{-1}(t)$ in going from time t to $t+\Delta$;

$$dT(t)\mu^1_q T^{-1}(t) = T(t+\Delta)\mu^1_q T^{-1}(t+\Delta) - T(t)\mu^1_q T^{-1}(t) \qquad (4\text{-}97)$$

rewriting the TDO's this expression becomes:

$$dT(t)\mu_q^1 T^{-1}(t) = T(t\to t+\Delta)\ T(t)\mu_q^1(t)T^{-1}(t)T^{-1}(t\to t+\Delta)$$
$$-T(t)\mu_q^1 T^{-1}(t) \qquad (4\text{-}98)$$

The time differential of equation (4-97) is now collision averaged. Since the collisions are assumed random the collision average in the time interval t to t + Δ is assumed independent of that prior to t. Therefore performing the averages separately in equation (4-98) yields:

$$d(T(t)\mu_q^1 T^{-1}(t))_{AVE} = [T(t\to t+\Delta)(T(t)\mu_q^1 T^{-1}(t))_{AVE}\ T^{-1}(t\to t+\Delta)$$
$$-\ (T(t)\mu^1 T^{-1}(t))_{AVE}]_{AVE\ in\ \Delta} \qquad (4\text{-}99)$$

Let Δ_σ be a time interval much longer than the duration of a collision but short enough to allow at most one collision of type σ. Then the probability of a collision occuring in time Δ_σ with an impact parameter between b and b + db would be given by;

$$p(d\sigma\ in\ \Delta_\sigma) = nvd\sigma\Delta_\sigma \qquad (4\text{-}100)$$

where v is the mean relative speed of the radiator and perturber molecules and;

$$d\sigma = 2\pi bdb. \qquad (4\text{-}101)$$

Therefore averaging over the time interval Δ_σ for collisions of type σ utilizing the collision probability of equation (4-101) yields:

$$d(T(t)\mu_q^1 T(t))_{AVE} = nv\Delta_\sigma\int [T_\sigma(t\to t+\Delta_\sigma)(T(t)\mu_q^1 T^{-1}(t))_{AVE}\ T^{-1}(t\to t+\Delta_\sigma)$$
$$-\ (T(t)\mu_q^1 T^{-1}(t))_{AVE}]d\sigma \qquad (4\text{-}102)$$

The differential equation for $\tilde{\mu}_q^1(t)$, equation (4-96), is now collision averaged and the above expression for the time differential

used to form the time derivative of $T(\tau)\mu_q^1 T^{-1}(\tau)_{AVE}$. Thus the following equation follows:

$$\frac{d}{dt}\tilde{\mu}^1_{q_{AVE}}(t) = ih\,[\tilde{\mu}^1_{q_{AVE}}(t),\ H_0] + nv\int [U_0(t)T(t\to t+\Delta_\sigma)U_0^{-1}(t)\tilde{\mu}^1_{q_{AVE}}(t)U_0(t)T^{-1}(t\to t+\Delta_\sigma)U_0^{-1}(t) - \tilde{\mu}^1_{q_{AVE}}(t)]d\sigma \quad (4\text{-}103)$$

Applying the results of Appendix G the above equation is put into the form;

$$\frac{d}{dt}\tilde{\mu}^1_{q_{AVE}}(t) = i\hbar\,[\tilde{\mu}^1_{q_{AVE}}(t),\ H_0] + nv\int [B(\sigma)\tilde{\mu}^1_{q_{AVE}}(t)B^{-1}(\sigma) - \tilde{\mu}^1_{q_{AVE}}(t)]d\sigma \quad (4\text{-}104)$$

where the collision operator $B(\sigma)$ is given by;

$$B(\sigma) = \left(e^{-i/\hbar\int_{-\infty}^{\infty} U_0^{-1}(t)H_{c,\sigma}(t)U_0(t)dt}\right)_+. \quad (4\text{-}105)$$

Now that a differential equation for $\mu^1_{q_{AVE}}(t)$ has been found the differential equation for its reduced matrix element is formulated. First examine the time derivative of a quantity appearing in equation (4-92):

$$\frac{d}{dt}\sum_{J_2\alpha_2M_2}\rho_{J_2\alpha_2}\langle J_i\alpha_iM_iJ_2\alpha_2M_2\,|\,\tilde{\mu}^1_q(t)\,|\,J_f\alpha_fM_fJ_2\alpha_2M_2\rangle_{AVE} \quad (4\text{-}106)$$

Since the collision averaged matrix element is independent of molecule 2 states the above expression reduces, with the aid of the Wigner-Eckart theorem, to:

$$\frac{\langle 1J_fqM_f\,|\,J_iM_i\rangle}{\sqrt{2J_i+1}}\frac{d}{d\tau}\langle J_i\alpha_i\,||\,\tilde{\mu}^1_{AVE}(t)\,||\,J_f\alpha_f\rangle \quad (4\text{-}107)$$

Consider again equation (4-106) this time using equation (4-104) for the time derivative of $\mu^1_{q_{AVE}}(t)$, and applying the Wigner Eckart theorem, in which case equation (4-106) becomes:

$$i\, w_{fi} \frac{\langle 1 J_F q M_f \mid J_i M_i \rangle}{\sqrt{2J_i + 1}} \langle J_i \alpha_i \,||\, \tilde{\mu}^1_{AVE}(t) \,||\, J_f \alpha_f \rangle$$

$$+ nv \sum_{J_2 M_2 \alpha_2} \rho_{J_2 \alpha_2} \int \langle J_i \alpha_i M_i J_2 M_2 \alpha_2 \mid B(\sigma)\, \tilde{\mu}^1_{q_{AVE}}(t) B(\sigma)^{-1}$$

$$- \tilde{\mu}^1_{q_{AVE}}(t) \mid J_f \alpha_f M_f J_2 M_2 \alpha_2 \rangle d\sigma \qquad (4\text{-}108)$$

The last term in the above expression is expanded by inserting unity in the form of a sum over intermediate states and applying the Wigner-Eckart theorem. After expansion equation (4-107) and (4-108) are equated yielding:

$$\frac{\langle 1 J_f q M_f \mid J_i M_i \rangle}{\sqrt{2J_i + 1}} \frac{d}{d\tau} \langle J_i \alpha_i \,||\, \tilde{\mu}^1_{AVE}(t) \,||\, J_f \alpha_f \rangle =$$

$$i w_{fi} \frac{\langle 1 J_f q M_f \mid J_i M_i \rangle}{\sqrt{2J_i + 1}} \langle J_i \alpha_i \,||\, \tilde{\mu}^1_{AVE}(t) \,||\, J_f \alpha_f \rangle$$

$$- nv \sum_{J_2 M_2 \alpha_2} \rho_{J_2 \alpha_2} \int \Bigg[\frac{\langle 1 J_f q M_f \mid J_i M_i \rangle}{\sqrt{2J_i + 1}} \langle J_i \alpha_i \,||\, \tilde{\mu}^1_{AVE}(t) \,||\, J_f \alpha_f \rangle$$

$$- \sum_{\substack{J_i', M_i', \alpha_i', \\ J_f', M_f', \alpha_f', \\ J_2', M_2', \alpha_2'}} \langle J_i M_i \alpha_i J_2 M_2 \alpha_2 \mid B(\sigma) \mid J_i', M_i', \alpha_i', J_2', M_2', \alpha_2' \rangle \times$$

$$\frac{\langle 1 J_f' q M_f' \mid J_i' M_i' \rangle}{\sqrt{2J_i + 1}} \langle J_i' \alpha_i' \,||\, \tilde{\mu}^1_{AVE}(t) \,||\, J_f' \alpha_f' \rangle \times$$

$$\langle J_f' M_f' \alpha_f' J_2' M_2' \alpha_2' \mid B^{-1}(\sigma) \mid J_f M_f \alpha_f J_2 M_2 \alpha_2 \rangle \Bigg] d\sigma \qquad (4\text{-}109)$$

Multiplying both sides of the above equation by $(-1)^q\langle 1J_i\text{-}qM_i \mid J_fM_f\rangle$, summing over M_i and M_f, and rearranging terms finally yields:

$$\frac{d}{d\tau}\langle J_i\alpha_i \| \tilde{\mu}^1_{AVE}(t) \| J_f\alpha_f\rangle = iw_{fi}\langle J_i\alpha_i \| \tilde{\mu}^1_{AVE}(t) \| J_f\alpha_f\rangle$$

$$\sum_{\substack{J_i',\alpha_i' \\ J_f',\alpha_f'}} A(J_i\alpha_i J_f\alpha_f : J_i',\alpha_i', J_f',\alpha_f')\langle J_i'\alpha_i' \| \tilde{\mu}^1_{AVE}(t) \| J_f'\alpha_f'\rangle \qquad (4\text{-}110)$$

where

$$A(J_i\alpha_i J_f\alpha_f : J_i',\alpha_i', J_f',\alpha_f') = nv\,(-1)^{J_f-J_i}\sum_{M_iM_f}\sum_{J_2M_2\alpha_2}\sum_{M_i'M_f'}\rho_{J_2\alpha_2}\,X$$

$$\int\Big[\delta_{ii'}\,\delta_{ff'} - \sum_{J_2'M_2'\alpha_2'}\langle J_iM_i\alpha_iJ_2M_2\alpha_2 \mid B(\sigma) \mid J_i'M_i'\alpha_i'J_2'M_2'\alpha_2'\rangle\,X$$

$$\langle J_f'M_f'\alpha_f'J_2'M_2'\alpha_2' \mid B(\sigma) \mid J_fM_f\alpha_fJ_2M_2\alpha_2\rangle\Big]d\sigma\,X$$

$$\sum_q (-1)^q\,\frac{\langle 1J_f'qM_f' \mid J_i'M_i'\rangle\langle 1J_i\text{-}qM_i \mid J_fM_f\rangle}{\sqrt{(2J_i'+1)(2J_i+1)}} \qquad (4\text{-}111)$$

B. Coupled Line Spectrum

Once a solution is found for the dipole moment differential equation, of the previous section, the spectrum can be readily calculated. Note that equation (4-111) is a coupled first order differential equation. Letting the indicies a and b represent a set of quantum numbers $\{J_i, \alpha_i, J_f, \alpha_f\}$ and $\{J_i', \alpha_i', J_f', \alpha_f'\}$ respectively, equation (4-111) can be put into the form;

$$\frac{d}{dt}X_a = i\,w_{0a}X_a - \sum_b A_{ab}X_b \qquad (4\text{-}112)$$

where

$$X_a = \langle J_i\alpha_i \| \tilde{\mu}^1(t) \| J_f\alpha_f\rangle. \qquad (4\text{-}113)$$

Writing this equation in matrix form yields;

$$\frac{d}{dt}\bar{X} = (i\bar{w}_0 - \bar{A})\bar{X} \tag{4-114}$$

where $\bar{w}_0$ is the diagonal matrix:

$$\bar{w}_0 = \begin{pmatrix} w_{oa} & & \\ & w_{ob} & \\ & & \ddots \end{pmatrix} \tag{4-115}$$

The differential equation is found to have a solution given by;

$$\bar{X}(t) = e^{(i\bar{w}_0 - \bar{A})t}\bar{X}(0). \tag{4-116}$$

The spectrum can now be calculated from the function F(t). Substituting the above solution into equation (4-94) yields the following from F(t):

$$F(t) = \frac{1}{3} e^{-iwt} \sum_{\substack{J_i\alpha_i \\ J_f\alpha_f}} \rho_{J_i\alpha_i} (-1)^{J_f - J_i} \langle J_f\alpha_f \| \mu^1 \| J_i\alpha_i \rangle X \sum_{\substack{J_i',\alpha_i' \\ J_f',\alpha_f'}} [e^{(i\bar{w}_0 - \bar{A})t}]_{i,f:i',f'} \langle J_i'\alpha_i' \| \mu^1 \| J_f'\alpha_f' \rangle \tag{4-117}$$

where the subscripts i and f denote all quantum numbers with subscripts of i or f, respectively. Inserting the above form of F(t) into equation (4-68) the absorption coefficient is found to be given by;

$$k(w) = \frac{4\pi nw}{3c\hbar} \sum_{\substack{J_i\alpha_i \\ J_f\alpha_f}} (-1)^{J_f - J_i} \rho_{J_i\alpha_i} \langle J_f\alpha_f \| \mu^1 \| J_i\alpha_i \rangle X \sum_{\substack{J_i',\alpha_i' \\ J_f',\alpha_f'}} \mathrm{Re} \int_0^\infty [e^{(i(\bar{w}_o - \bar{w}) - \bar{A})t}]_{i,f:i',f'} \langle J_i',\alpha_i' \| \mu^1 \| J_f',\alpha_f' \rangle \tag{4-118}$$

where w is the diagonal matrix given by:

$$\bar{w} = w\bar{1} \tag{4-119}$$

Performing the integration yields the following form for the absorption coefficient:

$$k(w) = \frac{4\pi nw}{3c\hbar} \sum_{\substack{J_i\alpha_i \\ J_f\alpha_f}} \rho_{J_i\alpha_i} (-1)^{J_f-J_i+1} \langle J_f\alpha_f \,||\, \mu^1 \,||\, J_i\alpha_i\rangle \; X$$

$$\sum_{\substack{J_i',\alpha_i' \\ J_f',\alpha_f'}} \mathrm{Re}[i(\bar{w}_o-\bar{w}) - A]^{-1}_{i,f:i',f'} \langle J_i',\alpha_i' \,||\, \mu^1 \,||\, J_f',\alpha_i'\rangle \tag{4-120}$$

A conversion is now made from frequency, $w(sec^{-1})$, to wavenumbers, $\omega(cm^{-1})$. The ideal gas law is also applied in order that the number density, n, can be written in terms of the partial pressure of the absorbing species and the temperature. Thus, the absorption coefficient is given by;

$$k(w) = C \sum_{\substack{J_i\alpha_i \\ J_f\alpha_f}} \rho_{J_i\alpha_i} (-1)^{J_f-J_i+1} \langle J_f\alpha_f \,||\, \mu^1 \,||\, J_i\alpha_i\rangle$$

$$\sum_{\substack{J_i',\alpha, \\ J_f',\alpha_f'}} \mathrm{Re}[i(\bar{w}_o-\bar{w}) - \bar{G}]^{-1}_{i,f:i',f'} \langle J_i',\alpha_i' \,||\, \mu^1 \,||\, J_f',\alpha_f'\rangle \tag{4-121}$$

where;

$$C = \frac{P_a \, 8\pi^2 \, \omega d}{3hck_BT} \tag{4-122}$$

P_a = absorbing species partial pressure (atmospheres)

d = 1.01325×10^6 dynes/cm^2/atm

k_B = Boltzmann's constant

and;

$$\bar{G} = \frac{1}{2\pi c}\,\bar{A}. \tag{4-123}$$

The matrix $\bar{G}$ can also be rewritten as;

$$G(J_i\alpha_i J_f\alpha_f : J_i',\alpha_i',J_f',\alpha_f') = \frac{P_B dv}{2\pi c k_B T}(-1)^{J_f-J_i} \sum_{J_2M_2\alpha_2} \rho_{J_2\alpha_2} \; X$$

$$\sum_{\substack{M_i M_f \\ M_i' M_f'}} \int \Big[\delta_{i,i'}\delta_{f,f'} - \sum_{J_2',M_2',\alpha_2'} \langle J_i M_I \alpha_i J_2 M_2 \alpha_2 \mid B(\sigma) \mid J_i',M_i',\alpha_i',J_2',M_2',\alpha_2' \rangle \; X$$

$$\langle J_f',M_f',\alpha_f',J_2',M_2',\alpha_2' \mid B^{-1}(\sigma) \mid J_f M_f \alpha_f J_2 M_2 \alpha_2 \rangle \Big] d\sigma \; X$$

$$\sum_q (-1)^q \frac{\langle 1 J_f', qM_f' \mid J_i',M_i' \rangle \langle 1 J_i - qM_i \mid J_f M_f \rangle}{\sqrt{(2J_i'+1)(2J_f+1)}} \tag{4-124}$$

where P_B is the partial pressure of the broadening gas. Note that it is assumed $P_B >> P_a$.

C. Vibrational and Electronic State Considerations

Thus far the vibrational and electronic state dependency of the absorption coefficient has not been addressed directly. Their quantum numbers have thus far been carried along through the general quantum numbers α appearing in equation (4-121). Since this work considers only the fundamental band spectrum the dipole moment matrix elements are diagonal in the electronic states, as is the $\bar{G}$ matrix. For the electric multipole moment intermolecular potentials considered here there is no internuclear distance dependency, only a directionality dependency. Therefore the $\bar{G}$ matrix is diagonal on the vibrational states and thus the entire inverse matrix in equation (4-121) is diagonal in the vibrational states.

The vibration and electronic state dependency arises out of the product of the vibrational Boltzmann distribution function and the dipole moment matrix elements. The electronic Boltzmann distribution function is set equal to unity since very few upper electronic states are occupied in the temperature range considered in this work (300-1000K). Assuming the Born-Oppenheimer approximation and no rotation vibration coupling the vibrational dipole moment matrix elements of equation (4-121) are of the form;

$$\langle nv_i \mid \mu \mid nv_f \rangle \langle nv_f \mid \mu \mid nv_i \rangle \tag{4-125}$$

where n is some electronic state quantum number. From Chapter IV-1-D the dipole moment matrix element for a given electronic state is given by;

$$\langle n \mid \mu \mid n \rangle = \mu(R_e)\hat{R} + \mu'(R_e)(R-R_e)\hat{R} + \frac{1}{2}\mu''(R_e)(R-R_e)^2\hat{R}. \tag{4-126}$$

Assume now the vibrational eigenstates are those of a simple harmonic oscillator as given by Herzberg.[33] The vibrational matrix elements of the first term of equation (4-126) are diagonal on these states and contributes only to the microwave pure rotational spectra. This term of the dipole moment is the permanent dipole moment and appears in the electric dipole intermolecular potentials later. The second term is given by;

$$\langle v_i \mid \mu'(R_e)(R-R_e)\hat{R} \mid v_f \rangle = \hat{R}\mu'(R_e)\langle v_i \mid R-R_e \mid v_f \rangle \tag{4-127}$$

and is responsible for the fundamental band since it is non-vanishing only for $\mid \Delta v \mid = 1$. The last term contributes to the overtone bands and is usually small in comparison to the second term therefore it is ignored. Utilizing the simple harmonic oscillator eigenstates the matrix element of equation (4-127) is given by;[33,48]

$$\langle v_i \mid R\text{-}Re \mid v_f \rangle = \sqrt{\frac{B_e R_e^2}{\omega_e}}$$

$$[\sqrt{v_i}\ \delta_{v_f, v_{i-1}} + \sqrt{v_i+1}\ \delta_{v_f, v_i+1}]. \qquad (4\text{-}128)$$

Therefore the dipole moment matrix element product of equation (4-125) can be written;

$$\langle v_i \mid \mu \mid v_f \rangle \langle v_f \mid \mu \mid v_i \rangle = \mu'^2(R_e)\ \frac{B_e R_e^2}{\omega_e}\ (v_i + 1) \qquad (4\text{-}129)$$

for absorption.

The results obtained above can now be applied to the absorption coefficient as given in equation (4-121) thereby giving;

$$k(w) = C_1 \sum_{\substack{J_i \alpha_i v_i \\ J_f \alpha_f}} \rho_{J_i \alpha_i} \rho_{v_i}\ (v_i+1)(-1)^{J_f - J_i + 1} \langle J_f \alpha_f \,||\, \mu^1 \,||\, J_i \alpha_i \rangle\ X$$

$$\sum_{\substack{J_i', \alpha_i' \\ J_f', \alpha_f'}} \mathrm{Re}[i(\bar{w}_o - \bar{w}) - \bar{G}]^{-1}_{i,f:i'f'} \langle J_i', \alpha_i' \,||\, \mu^1 \,||\, J_f', \alpha_f' \rangle \qquad (4\text{-}130)$$

where

$$C_1 = C\ \frac{B_e R_e^2}{\omega_e}\ \mu'^2(R_e). \qquad (4\text{-}131)$$

The above equation is now understood to have all electronic and vibrational state dependency removed from the reduced dipole matrix elements. Now note that for microwave spectra equation (4-130) is still applicable provided $\mu'(R_e)$ is replaced by $\mu(R_e)$ and ω_e and $B_e R_e^2$ are dropped.

D. Interruption Function

The matrix $\bar{G}$ appearing in the expressions for the absorption coefficient is now the center of attention. The major effort is

equation (4-124). Expanding the collision operator in equation (4-105) through second order yields:

$$B(\sigma) = 1 - i/\hbar \int_{-\infty}^{\infty} U_0^{-1}(t)H_{c,\sigma}(t)U_0(t)dt$$

$$- \frac{1}{2\hbar^2} \int_{-\infty}^{\infty} \int_{-\infty}^{t} U_0^{-1}(t)H_{c,\sigma}(t)U_0(t)U_0^{-1}(t')H_{c,\sigma}(t')U_0(t')dt'dt. \quad (4\text{-}132)$$

Anderson was able to demonstrate that the commutator term;

$$\int_{-\infty}^{\infty} \int_{-\infty}^{t} [H_{c,\sigma}(t), H_{c,\sigma}(t')]dt'dt \quad (4\text{-}133)$$

can be neglected thereby allowing the last term of equation (4-132) to be written as the square of only one of the integrals.[6] Thus the collision operator can be written as;

$$B(\sigma) = 1 - iP - \frac{P^2}{2} \quad (4\text{-}134)$$

and

$$B(\sigma) = 1 + iP - \frac{P^2}{2} \quad (4\text{-}135)$$

where

$$P = \frac{1}{\hbar} \int_{-\infty}^{\infty} U_0^{-1}(t)H_{c,\sigma}(t)U_0(t)dt. \quad (4\text{-}136)$$

Using a somewhat simpler notation the product of collision operator matrix elements found in equation (4-124) can now be expressed through second order as:

$$\langle i2 \mid B(\sigma) \mid i'2' \rangle \langle f'2' \mid B^{-1}(\sigma) \mid f2 \rangle = \delta_{i,i'}\delta_{f,f'}\delta_{2,2'}$$

$$- i\langle i2 \mid P \mid i'2' \rangle \delta_{f,f'}\delta_{2,2'} + i\langle f'2' \mid P \mid i2 \rangle \delta_{f,f'}\delta_{2,2'}$$

$$+ \langle i2 \mid P \mid i'2' \rangle \langle f'2' \mid P \mid f2 \rangle - \frac{1}{2} \langle i2 \mid P^2 \mid i'2 \rangle \delta_{f,f'}\delta_{2,2'}$$

$$- \frac{1}{2} \delta_{i,i'}\delta_{2,2'} \langle f'2 \mid P^2 \mid f2 \rangle \quad (4\text{-}137)$$

The $\bar{G}$ matrix elements can, with the help of the above results, be expressed in terms of a collision cross section which in turn is expressed in terms of the interruption function as given by Tsao and Curnutte. First note that the Boltzmann distribution function of equation (4-124) is the distribution of states, that is;

$$\rho_{J_2\alpha_2} = \frac{e^{E_{J_2,\alpha_2}/kT}}{Q_R(T)} \tag{4-138}$$

where

$$Q_R(T) = \sum_{J_2\alpha_2} (2J_2+1)e^{-E_{J_2,\alpha_2}/kT} . \tag{4-139}$$

By introducing the distribution of energy levels $\rho'_{J_2\alpha_2}$ given by:

$$\rho'_{J_2,\alpha_2} = (2J_2+1)\ \rho_{j_2,\alpha_2} \tag{4-140}$$

summing over M_2, and using the expansion of equation (4-137) the matrix element of $\bar{G}$ can be expressed as;

$$G_{(i,f:i',f')} = F_1 \sum_{J_2,\alpha_2} \rho_{J_2,\alpha_2}\ \sigma_{J_2,\alpha_2} \tag{4-141}$$

where;

$$\sigma_{J_2,\alpha_\alpha} = 2\pi\int S(b)bdb. \tag{4-142}$$

and:

$$F_1 = P_B dv/2\pi ckT \tag{4-143}$$

The function S(b) is what Tsao and Curnutte call the interruption function, since it is a measure of the interruption of the absorbing

process due to collision, and in this case it is given through second order by:

$$S_0(b) = 0 \tag{4-144}$$

$$S_1(b) = i \sum_{M_i, M_2} \frac{\langle J_i M_i \alpha_i J_2 M_2 \alpha_2 \mid P \mid J_i M_i \alpha_i' J_2 M_2 \alpha_2 \rangle}{(2J_2 + 1)(2J_i + 1)} \delta_{f,f'} \delta_{2,2'}$$

$$- i \sum_{M_f, M_2} \frac{\langle J_f M_f \alpha_f' J_2 M_2 \alpha_2 \mid P \mid J_f M_f \alpha_f J_2 M_2 \alpha_2 \rangle}{(2J_f + 1)(2J_2 + 1)} \delta_{i,i'} \delta_{2,2'} \tag{4-145}$$

$$S_2(b) = S_{2,f}(b) + S_{2,i}(b) + S_{2,m}(b) \tag{4-146}$$

$$S_{2,f}(b) = \frac{1}{2} \delta_{J_i, J_i'} \delta_{M_i, M_i'} \delta_{\alpha_i, \alpha_i'} \delta_{J_f, J_f} \delta_{M_f, M_f'} X$$

$$\sum_{M_f, M_2} \frac{\langle J_f M_f \alpha_f, J_2 M_2 \alpha_2 \mid P^2 \mid J_f M_f \alpha_f J_2 M_2 \alpha_2 \rangle}{(2J_f + 1)(2J_2 + 1)} \tag{4-147}$$

$$S_{2,M}(b) = - \sum_{\substack{M_i, M_f, \\ M_i', M_f', \\ M_2, M_2'}} \sum_{J_2', \alpha_2', q}$$

$$\langle J_i M_i \alpha_i J_2 M_2 \alpha_2 \mid P \mid J_i, M_i, \alpha_i, J_2, M_2, \alpha_2, \rangle \; X$$

$$\langle J_f M_f \alpha_f J_2 M_2 \alpha_2 \mid P \mid J_f, M_f, \alpha_f, J_2, M_2, \alpha_2, \rangle^* \; X$$

$$\frac{\langle 1 J_f, q M_f, \mid J_i, M_i, \rangle \langle 1 J_f q M_f \mid J_i M_i \rangle}{\sqrt{(2J_i+1)\,(2J_i, + 1)}\;\; 2J_2 + 1} \tag{4-148}$$

Extensive use of the properties of the Clebsch-Gordon coefficients have been utilized to obtain the above result [49]. Note that use of the fact that P is Hermitian has been made in order to express the last matrix element of equation (4-148) as the complex conjugate of the matrix element of P. The term $S_{2,i}(b)$ is identical to $S_{2,f}(b)$ with all f's and i's exchanged.

E. Anderson's Cutoff Procedure

The intermolecular potentials considered in this work do not take into account close range forces. Anderson approximated the close range potential by a hard sphere collision potential. Consider the matrix $\bar{G}$ given by equation (4-124) for a hard sphere collision, in this case the second term drops out since P vanishes and the only remaining term is the Kronecker delta function term given by;

$$G = \frac{P_B dv}{2\pi ckT} (-1)^{J_f - J_i} \sigma \delta_{i,i'} \delta_{f,f'}. \tag{4-149}$$

This imples that for small b the interruption function is given by;

$$S(b \to 0) = \delta_{i,i'} \delta_{f,f'}. \tag{4-150}$$

Note that the zeroth order term vanishes leaving only the first and second order terms to contribute to S(b) for small b. As will be seen later, the matrix elements of P are real for the interactions considered here and therefore the first order terms are purely imaginary. Therefore, the only contribution to the interruption function for small b through second order is the second order term. The approach taken by Anderson, and applied here also is to use equations (4-146) through (4-148) to solve for an impact parameter b_0 which solves the equation;

$$S_2(b_0) = \delta_{i,i'} \delta_{f,f'} \tag{4-151}$$

for the diagonal matrix elements of $\bar{G}$. The function S(b) is integrated from b_0 to infinity and the hard sphere contribution πb_0^2 is added yielding:

$$2\pi \int_0^\infty S(b) b db \approx \pi b_0^2 \delta_{i,i'} \delta_{f,f'} + 2\pi \int_{b_0}^\infty S_1(b) b db + 2\pi \int_{b_0}^\infty S_2(b) b db \tag{4-152}$$

The Anderson interruption cutoff procedure is graphically illustrated by Figure 4-1.

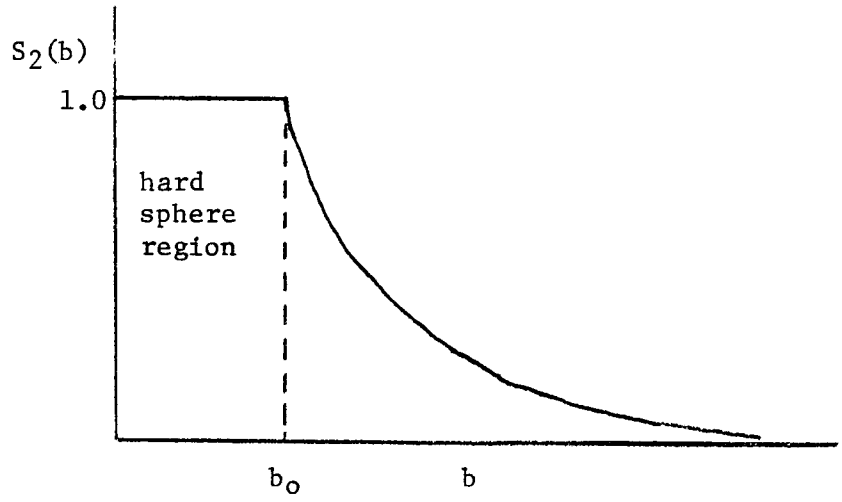

Figure 4-1. Anderson's interruption function cutoff procedure.

For the off diagonal term only the integral of S(b) is calculated since the hard sphere potential does not contribute to the off diagonal matrix elements.

4. EVALUATION OF THE INTERRUPTION FUNCTION

A. Matrix Elements of P and P^2

The next task is the calculation of the matrix elements of P and P^2 which appear in the interruption function, equations (4-144) through (4-148). First examine the form for the matrix elements of P, equation (4-136), given by;

$$\langle J_1 M_1 \alpha_1 J_2 M_2 \alpha_2 \mid P \mid J_1', M_1', \alpha_1', J_2', M_2', \alpha_2' \rangle =$$

$$\frac{1}{\hbar} \int_{-\infty}^{\infty} e^{iw't} H_{c,\sigma}(t)\,dt \qquad (4\text{-}153)$$

where;

$$w' = \frac{1}{\hbar}\left(E_{J_1\alpha_1} + E_{J_2\alpha_2} - E_{J_1',\alpha_1'} - E_{J_2',\alpha_2'}\right). \tag{4-154}$$

Assuming $H_{c,\sigma}(t)$ is of the form;

$$H_{c,\sigma}(t) = \sum_{\substack{k_1k_2\\q_1q_2}} C^{k_1k_2}_{q_1q_2}(t)\; Y^{k_1}_{q_1}\; Y^{k_2}_{q_2} \tag{4-155}$$

where the Y's are the spherical harmonics in the coordinates of molecule 1 and molecule 2, respectively, the matrix element of P then becomes;

$$\langle J_1M_1\alpha_1J_2M_2\alpha_2 \mid P \mid J_1',M_1',\alpha_1',J_2',M_2',\alpha_2'\rangle =$$

$$\sum_{\substack{k_1k_2\\q_1q_2}} a(J_1,J_1',\alpha_1,\alpha_1',J_2,J_2',\alpha_2,\alpha_2',k_1,k_2,q_1,q_2)\ X$$

$$\langle J_1M_1\alpha_1 \mid Y^{k_1}_{q_1} \mid J_1',M_1',\alpha_1'\rangle\langle J_2M_2\alpha_2 \mid Y^{k_2}_{q_2} \mid J_2',M_2',\alpha_2'\rangle \tag{4-156}$$

where;

$$a(J_1,J_1',\alpha_1,\alpha_1',J_2,J_2',\alpha_2\alpha_2',k_1,k_2,q_1,q_2)$$

$$= \frac{1}{\hbar}\int_{-\infty}^{\infty} e^{iw't}\; C^{k_1k_2}_{q_1q_2}(t)dt. \tag{4-157}$$

The general molecular eigenstates used up until this point are now specialized to the eigenstates derived in Chapter III for intermediate Hund's case A and case B coupling. In this case the α's represent, p, the partial parity and, g, the subband quantun number. From Chapter III-6 these eigenstates have the form;

$$\mid pnSJMg\rangle = \sum_{\Omega} C(J,g,\Omega,p) \mid pn\Lambda S\Sigma JM-\Omega\rangle_R \tag{4-158}$$

where g is assigned a value according to the prescription;

$$g = \Omega \text{ for } C(J,g,\Omega,p) > C(J,g,\Omega',p) \text{ for all } \Omega' \neq \Omega. \tag{4-159}$$

Therefore a spherical harmonic matrix element of equation (4-156) has the form;

$$\langle pnSJMg \mid Y^k_q(\theta,\phi) \mid p'n'S'J'M'g' \rangle =$$

$$\sum_{\Omega,\Omega'} C(J,g,\Omega,p)C(J',g',\Omega',p') \; X$$

$$_R\langle npA\Sigma JM{-}\Omega \mid Y^k_q(\theta,\phi) \mid n'p'\Lambda'S'\Sigma'J'M'{-}\Omega' \rangle_R. \tag{4-160}$$

Consider now the matrix elements of equation (4-160). Since both the primed and unprimed states are of the same electronic (ground) state one has:

$$_R\langle npA\Sigma JM{-}\Omega \mid Y^k_q(\theta,\phi) \mid p'n'\Lambda'S'\Sigma'J'M'{-}\Omega' \rangle_R =$$

$$\delta n,n' \delta_{S,S'} \; _R\langle npA\Sigma JM{-}\Omega \mid Y^k_q(\theta,\phi) \mid np'\Lambda'S\Sigma'J'M'{-}\Omega' \rangle_R \tag{4-161}$$

Expanding the parity eigenstates by means of equation (3-1) yields:

$$_R\langle npA\Sigma JM{-}\Omega \mid Y^k_q(\theta,\psi) \mid np'\Lambda'S\Sigma'J'M'{-}\Omega' \rangle_R =$$

$$\frac{1}{2} \{ _R\langle JM{-}\Omega nA\Sigma \mid Y^k_q \mid J'M'{-}\Omega'nA\Sigma \rangle_R \; \delta_{\Lambda,\Lambda'} \; \delta_{\Sigma,\Sigma'}$$

$$+ \; p \, _R\langle JM\Omega n{-}A S{-}\Sigma \mid Y^k_q \mid J'M'{-}\Omega'n{-}\Lambda S{-}\Sigma \rangle_R \delta_{-\Lambda,\Lambda'} \delta_{\Sigma',-\Sigma}$$

$$+ p' \, _R\langle JM{-}\Omega nA\Sigma \mid Y^k \mid J'M'\Omega'nA\Sigma \rangle_R \; \delta_{-\Lambda,\Lambda'} \delta_{-\Sigma,\Sigma'}$$

$$+ \; pp' \, _R\langle M\Omega n{-}\Lambda S{-}\Sigma \mid Y^k_q \mid J'M'\Omega'n{-}\Lambda S{-}\Sigma \rangle \delta_{\Lambda,\Lambda'} \delta_{\Sigma,\Sigma'} \} . \tag{4-162}$$

As mentioned in Chapter I-3 the spherical harmonic can be expressed in terms of a d-matrix as given in equation (1-57). Using this in conjunction with the coordinate representation of the eigenstates given by equation (1-67) the matrix element is expressed as follows:

$$ {}_R\langle JM-\Omega n\Lambda S\Sigma \mid Y^k_q(\theta,\phi) \mid J'M'-\Omega' n\Lambda S\Sigma\rangle_R = $$

$$ (-1)^{J+J'-\Omega-\Omega'+q} \frac{\sqrt{(2J+1)(2J'+1)}}{8\pi^2} \left(\frac{2k+1}{4\pi}\right)^{\frac{1}{2}} X $$

$$ \int d^J_{M',\Omega'}(\theta,\phi,\psi)\, d^k_{-q,0}(\theta,\phi,\psi) d^J_{M,\Omega}(\theta,\phi,\psi) d(\theta,\phi,\psi) \qquad (4\text{-}163) $$

Applying the results of Davydov (Reference 14, p. 172) the matrix element reduces to;

$$ {}_R\langle JM-\Omega n\Lambda S\Sigma \mid Y^k_q(\theta,\phi) \mid J'M'-\Omega' n\Lambda S\Sigma\rangle_R = $$

$$ (-1)^{J+J'-\Omega-\Omega'+q} \sqrt{\frac{(2J+1)(2k+1)}{4\pi}} \langle kJ-qM \mid J'M'\rangle X $$

$$ \langle kJ0\Omega \mid J'\Omega'\rangle. \qquad (4\text{-}164) $$

Applying the properties of the Clebsch-Gordon coefficients the above equation becomes:

$$ {}_R\langle JM-\Omega n\Lambda S\Sigma \mid Y^{k1}_{q1}(\theta,\phi) \mid J'M' - \Omega' n\Lambda S\Sigma\rangle_R = $$

$$ \delta_{\Omega,\Omega'}(-1)^{J+J'-2\Omega} \sqrt{\frac{(2J'+1)(2J+1)}{4\pi(2J+1)}} \langle J'kM'q \mid JM\rangle\langle J'k\Omega 0 \mid J\Omega\rangle \qquad (4\text{-}165) $$

Since the quantum number Ω is positive definite (see Chapter III-1) and the above matrix elements are diagonal on the quantum number Ω, the two middle terms of equation (4-162) vanish.

The two non-vanishing terms of equation (4-162) can be simplified by utilizing the properties of the spherical harmonics and the properties of the eigenstates under the parity operator. By inserting unity in the form of the parity operator times its inverse into the matrix element and using equation (3-2) one finds:

$$ {}_R\langle JM-\Omega n\Lambda S\Sigma \mid Y^k_q \mid J'M'-\Omega' n\Lambda S\Sigma\rangle_R = $$

$$ {}_R\langle JM-\Omega n\Lambda S\Sigma \mid P^\dagger P Y^k_q P^\dagger P \mid J'M'-\Omega' n\Lambda S\Sigma\rangle_R = $$

$$ (-1)^{J+J'+2S+k}\, {}_R\langle JM\Omega n-\Lambda S-\Sigma \mid Y^k_q \mid J'M'\Omega' n-\Lambda S-\Sigma\rangle_R \qquad (4\text{-}166) $$

Combining the above equation, utilizing some Clebsch-Gordon coefficient relations, with equation (4-165) and (4-162) yields the following expression for the two nonvanishing terms of equation (4-162);

$$ {}_R\langle JM-\Omega np\Lambda S\Sigma \mid Y^k \mid J'M'-\Omega' n'p'\Lambda' S'\Sigma'\rangle_R = $$

$$ \delta_{n,n'}\delta_{S,S'}\delta_{\Sigma,\Sigma'}\,\delta_{\Lambda,\Lambda'}\,\delta_{\Omega,\Omega'}\,\beta(J,J',k,\Omega,p,p')\ X $$

$$ \langle J'kM'q \mid JM\rangle \qquad (4\text{-}167) $$

where;

$$ \beta(J,J',k,\Omega,p,p') = \frac{1}{2}\left[1+pp'(-1)^{J+J'+2S+k}\right] X $$

$$ (-1)^{J'+J-2\Omega}\Delta(J',k,J,\Omega) \qquad (4\text{-}168) $$

and Δ is the same as that given by Tsao and Curnutte:

$$ \Delta(J',k,J,\Omega) = \sqrt{\frac{2k+1}{4\pi}}\,(-1)^{J-J'}\,\langle Jk\Omega 0 \mid J'\Omega\rangle \qquad (4\text{-}169) $$

The matrix elements of P can now be formulated using equation (4-156) and the results just derived for the matrix elements of the spherical harmonics. Thus equation (4-156) yields:

$$ \langle J_1M_1g_1p_1J_2M_2g_2p_2 \mid P \mid J_1'M_1'g_1'p_1'\ J_2'M_2'g_2'p_2'\rangle = $$

$$ \sum_{\Omega_1,\Omega_2}\ \sum_{\substack{k_1,k_2\\ q_1,q_2}} C(J_1,g_1,\Omega_1,p_1)\ C(J_1',g_1',\Omega_1,p_1')\ X $$

$$ C(J_2,g_2,\Omega_2,p_2)\ C(J_2',g_2',\Omega_2,p_2')\ X $$

$$ a(J_1,J_1',\alpha_1,\alpha_1',\ J_2,J_2',\alpha_2,\alpha_2',k_1,k_2,q_1,q_2)\ X $$

$$ \beta(J_1,J_1',k_1,\Omega_1,p_1,p_1')\ \beta(J_2,J_2',k_2,\Omega_2,p_2,p_2')\ X $$

$$ \langle J_1,k_1M_1,q_1 \mid J_1M_1\rangle\langle J_2,k_2M_2,q_2 \mid J_2M_2\rangle \qquad (4\text{-}170) $$

where the quantum number α_i represents all other quantum numbers associated with the i^{th} molecule.

The matrix element of P^2 found in equation (4-147) is formulated by inserting unity in the form of a sum over intermediate states;

$$\langle J_1 M_1 \alpha_1 J_2 M_2 \alpha_2 \mid P^2 \mid J_1 M_1 \alpha_1 \cdots J_2 M_2 \alpha_2 \rangle =$$

$$\sum_{\substack{J_1', M_1', \alpha_1' \\ J_2', M_2', \alpha_2'}} \langle J_1 M_1 \alpha_1 J_2 M_2 \alpha_2 \mid P \mid J_1', M_1', \alpha_1', J_2', M_2', \alpha_2' \rangle \times$$

$$\langle J_1', M_1', \alpha_1', J_2', M_2', \alpha_2' \mid P \mid J_1 M_1 \alpha_1 \cdots J_2 M_2 \alpha_2 \rangle \qquad (4\text{-}171)$$

Since P is Hermitian (equation 4-136) the last matrix element above can be re-expressed using;

$$\langle J_1', M_1', \alpha_1', J_2 M_2 \alpha_2 \mid P \mid J_1 M_1 \alpha_1 \cdots J_2 M_2 \alpha_2 \rangle =$$

$$\langle J_1 M_1 \alpha_1 \cdots J_2 M_2 \alpha_2 \mid P \mid J_1', M_1', \alpha_1', J_2 M_2 \alpha_2 \rangle^*. \qquad (4\text{-}172)$$

Now using the results obtained for the matrix elements of P yields:

$$\langle J_1 M_1 g_1 p_1 \; J_2 M_2 g_2 p_2 \mid P^2 \mid J_1 M_1 g_1 \cdots p_1 \cdots J_2 M_2 g_2 p_2 \rangle =$$

$$\sum_{\substack{J_1', g_1', p_1' \\ J_2', g_2', p_2'}} \sum_{\substack{k_1, k_2 \\ q_1, q_2 \\ \Omega_1, \Omega_2}} \sum_{\substack{k_1', k_2' \\ q_1', q_2' \\ \Omega_1', \Omega_2'}}$$

$$D(J_1, J_1', \cdots q_1, q_2, q_1', q_2') \; B(J_1, J_1', \cdots q_1, q_2, q_1', q_2') \qquad (4\text{-}173)$$

where;

$$D(J_1, J_1', \cdots q_1, q_2, q_1', q_2') =$$

$$C(J_1, g_1, \Omega_1, p_1) \; C(J_1', g_1', \Omega_1, p_1') \; C(J_2, g_2, \Omega_2, p_2) \times$$

$$C(J_2', g_2', \Omega_2, p_2') \; C(J_1, g_1'', \Omega_1', p_1'') \; C(J_1', g_1', \Omega_1', p_1') \times$$

$$C(J_2, g_2, \Omega_2', p_2) \; C(J_2', g_2', \Omega_2', p_2') \times$$

$$a(J_1, J_1', \alpha_1, \alpha_1', J_2, J_2', k_1, k_2, q_1, q_2) \times$$

$$a^*(J_1, J_1', \alpha_1'', \alpha_1', J_2, J_2', \alpha_2, \alpha_2', k_1', k_2', q_1', q_2') \times$$

$$\beta(J_2, J_2', k_2, \Omega_2, p_2, p_2') \; \beta(J_1, J_1', k_1, \Omega_1, p_1, p_1') \times$$

$$\beta(J_1, J_1', k_1, \Omega_1', p_1'', p_1') \; \beta(J_2, J_2', k_2', \Omega_2', p_2, p_2') \qquad (4\text{-}174)$$

and;

$$B(J_1,J_1',\ \ldots\ q_1,q_2,q_1',q_2') =$$

$$\sum_{M_1',M_2'} \langle J_1',k_1M_1',q_1 \mid J_1M_1\rangle\langle J_1',k_1',M_1',q_1' \mid J_1M_1\rangle \ X$$

$$\langle J_2',k_2M_2',q_2 \mid J_2M_2\rangle\langle J_2',k_2',M_2',q_2' \mid J_2M_2\rangle. \qquad (4\text{-}175)$$

It is easily seen that the Clebsch-Gordon product above vanish unless $q_1 = q_1'$ and $q_2 = q_2'$, therefore;

$$\langle J_1M_1q_1p_1J_2M_2g_2p_2 \mid P^2 \mid J_1M_1g_1''p_1''J_2M_2q_2p_2\rangle =$$

$$\sum_{\substack{J_1',g_1',p_1'\\ J_2',g_2',p_2'}} \ \sum_{\substack{k_1,k_2\\ \Omega_1,\Omega_2\\ q_1,q_2}} \ \sum_{\substack{k_1',k_2'\\ \Omega_i',\Omega_2'}}$$

$$D(J_1,J_1',\ldots\ q_1,q_2,q_1,q_2)\ B(J_1,J_1',\ldots q_1,q_2,q_1,q_2) \qquad (4\text{-}176)$$

B. First Order Interruption Function

The first order term of the interruption function is calculated utilizing equation (4-145) as the starting point. The matrix elements of P, given in equation (4-170), are substituted into equation (4-145), this yields:

$$S_1(b) = S_{1,i}(b) - S_{1,f}(b) \qquad (4\text{-}177)$$

where

$$S_{1,i}(b) = \frac{i\delta_{f,f'}}{(2J_2+1)(2J_i+1)} \sum_{\substack{M_i,M_2\\ \Omega_i,\Omega_2}} \ \sum_{\substack{k_1,k_2\\ q_1,q_2}} C(J_i,g_i,\Omega_i,p_i)\ X$$

$$C(J_i,g_i,\Omega_i,p_i')\ C(J_2,g_2,\Omega_2,p_2)\ C(J_2,g_2,\Omega_2,p_2)\ X$$

$$\beta(J_i,J_i,k_i,\Omega_i,p_i,p_i')\ \beta(J_2,J_2,k_2,\Omega_2,p_2,p_2)\ a(g_i,g_i',p_i,p_i')\ X$$

$$\langle J_ik_1M_iq_1 \mid J_iM_i\rangle\langle J_2k_2M_2q_2 \mid J_2M_2\rangle. \qquad (4\text{-}178)$$

The first order interruption function term $S_{1,f}(b)$ is the same as $S_{1,i}(b)$ except that f is substituted for i and the "a" function for $S_{1,f}(b)$ is given by;

$$a = a(g_{f'}, g_f, p_{f'}, p_f). \tag{4-179}$$

Only the off diagonal quantum numbers appear in the argument list of the "a" function although it is a function of all non-degenerate quantum numbers. Examination of the Clebsch-Gordon coefficients indicates that only the terms where q_1 and q_2 vanish contributes to the sum. Using the above results together with equations (4-168) and (4-169) $S_{1,i}(b)$ can be expressed as;

$$S_{1,i}(b) = \frac{i}{4\pi(2J_2+1)(2J_i+1)} \sum_{\substack{M_i, M_2 \\ \Omega_i, \Omega_2}} \sum_{k_1, k_2} \sqrt{(2k_1+1)(2k_2+1)}\ X$$

$$C(J_i, g_i, \Omega_i, p_i)\ C(J_i, g_{i'}, \Omega_i, p_{i'})\ C^2(J_2, g_2, \Omega_2, p_2)\ X$$

$$H(J_i, J_i, k_1, p_i, p_{i'})\ H(J_2, J_2, k_2, p_2, p_2)\ a(g_i, g_{i'}, p_i, p_{i'})\ X$$

$$\langle J_1 k_1 \Omega_i 0 \mid J_i \Omega_i \rangle \langle J_i k_1 M_i 0 \mid J_i M_i \rangle \langle J_2 k_2 M_2 0 \mid J_2 M_2 \rangle\ X$$

$$\langle J_2 k_2 \Omega_2 0 \mid J_2 \Omega_2 \rangle \tag{4-180}$$

where;

$$H(J, J', k, \Omega, p, p') = \frac{1}{2}\left[1 + pp'(-1)^{J+J'+2S+k}\right] \tag{4-181}$$

and S is the total electronic spin angular momentum.

The sum of the Clebsch-Gordon coefficient over all possible magnetic quantum numbers appearing in equation (4-180) is now considered. For the case of $k_1=1$ the sum is given by;

$$\sum_{M} \langle J1M0 \mid JM\rangle = \sum_{M=-J}^{J} \frac{M}{\sqrt{J(J+1)}} = 0. \tag{4-182}$$

For the case of $k_2 = 2$ the sum becomes;

$$\sum_{M} \langle J2M0 \mid JM\rangle = \sum_{M=-J}^{J} \frac{3M^2 - J(J+1)}{\sqrt{(2J-1)J(J+1)(2J+3)}} . \tag{4-183}$$

The sum over M^2 is found, in Gradshteyn and Ryzhik (equation 0.121-2 Ref. 20), to be given by; [20]

$$\sum_{M=-J}^{J} M^2 = \frac{1}{3} J(J+1)(2J+1). \tag{4-184}$$

Inserting this result into equation (4-183) yields;

$$\sum_{M} \langle J2M0 \mid JM\rangle = 2J\sqrt{\frac{J(J+1)}{(2J-1)(2J+2)}}$$

$$= - 2J\langle J200 \mid J0\rangle. \tag{4-185}$$

Higher values of k are not considered here since the intermolecular potentials utilized in this work can all be expressed with k values of unity or two.

Therefore, for the potentials considered here only the ones with k_1 and k_2 equal to two contribute to the first order interruption function. Hence, $S_{1,i}(b)$ can be expressed as

$$S_{1,i}(b) = \frac{5i}{\pi} \frac{J_2 J_i}{(2J_i+1)(2J_2+1)} \langle J_2200 \mid J_20\rangle\langle J_i200 \mid J_i0\rangle \; X$$

$$\sum_{\Omega_i,\Omega_2} C(J_i,g_i,\Omega_i,p_i)\; C(J_i,g_i',\Omega_i,p_i')\; C^2(J_2,g_2,\Omega_2,p_2) \; X$$

$$a(g_i,g_i',p_i,p_i',k_1=k_2=2,q_1=q_2=0)\; H(J_i,J_i,2,p_i,p_i') \; X$$

$$H(J_2,J_2,2,p_2,p_2)\; \langle J_i2\Omega_i0 \mid J_i\Omega_i\rangle\langle J_22\Omega_20 \mid J_2\Omega_2\rangle. \tag{4-186}$$

and $S_{1,f}(b)$ is the same as $S_{1,i}(b)$ with f substituted for i and the "a" function of equation (4-179).

C. Second Order Interruption Function

Expressions are derived in this section are for the second order terms of the interruption function as given in equations (4-144) through (4-148). Employing the matrix elements of P^2 derived earlier, equation (4-173), the term $S_{2,i}(b)$, given in equations (4-146) through (4-148), can be written as:

$$S_{2,i}(b) = \frac{\delta_{f,f'}\delta_{J_i,J_i'}}{2(2J_i+1)(2J_f+1)} \sum_{\substack{J_i" g_i" p_i" \\ J_2" g_2" p_2"}} \sum_{\substack{k_1 k_2 \\ k_1', k_2'}} \sum_{\substack{\Omega_i, \Omega_2 \\ \Omega_i', \Omega_{2"}}} \sum_{q_1, q_2}$$

$$C(J_i, g_i, \Omega_i, p_i)\ C(J_i", g_i", \Omega_i, p_i")\ C(J_2, g_2, \Omega_2, p_2)\ X$$

$$C(J_2", g_2", \Omega_2, p_2")\ C(J_i, g_i', \Omega_i', p_i')\ C(J_i", g_i", \Omega_i', p_i")\ X$$

$$C(J_2, g_2, \Omega_2", p_2)\ X$$

$$C(J_2", g_2", \Omega_2", p_2")\ \beta(J_2, J_2", k_2, \Omega_2, p_2, p_2")$$

$$\beta(J_i, J_i", k_1, \Omega_1, p_i, p_i")\ \beta(J_i, J_i", k_i', \Omega_i', p_i', p_i")\ X$$

$$\beta(J_2, J_2", k_2', \Omega_2", p_2, p_2")\ X$$

$$a(J_i, J_i", g_i, g_i", p_i, p_i", J_2, J_2", g_2, g_2", p_2, p_2", k's, q's)\ X$$

$$a^*(J_i, J_i", q_i', g_i", p_i', p_i", J_2, J_2", g_2, g_2", p_2, p_2", k's, q's)\ X$$

$$\sum_{\substack{M_i, M_2 \\ M_i", M_2"}} \langle J_i" k_1 M_i" q_1 \mid J_i M_i \rangle \langle J_i" k_1, M_i" q_1 \mid J_i M_i \rangle\ X$$

$$\langle J_2" k_2 M_2" q_2 \mid J_2 M_2 \rangle \langle J_2" k_2, M_2" q_2 \mid J_2 M_2 \rangle \qquad (4\text{-}187)$$

Utilizing the orthogonality property of the Clebsch Gordon coefficients, the sum of the product of Clebsch Gordon coefficients appearing in equation (4-187) can be reduced to:

$$\delta_{k_1',k_1}\ \delta_{k_2',k_2}\ \frac{(2J_1+1)(2J_2+1)}{(2k_1+1)(2k_2+1)}\ . \tag{4-188}$$

The product of the β-functions can also be rewritten by using its definition from equations (4-168) through (4-169), thus;

$$\beta(J_i,J_i'',k_1,p_i,p_i'')\ \beta(J_i,J_i'',k_1,\Omega_i',p_i',p_i'') =$$

$$\frac{2k_1+1}{4\pi}\ H(J_i,J_i'',k_1,p_i,p_i'')\ H(J_i,J_i'',k_1,p_i',p_i'')\ X$$

$$\langle J_i k_1 \Omega_i 0 \mid J_i''\Omega_i\rangle\langle J_i k_1 \Omega_i' 0 \mid J_i''\Omega_i'\rangle. \tag{4-189}$$

and;

$$\beta(J_2,J_2'',k_2,\Omega_2,p_2,p_2'')\ \beta(J_2,J_2'',k_2,\Omega_2'',p_2,p_2'') =$$

$$\frac{2k_2+1}{4\pi}\ H(J_2,J_2'',k_2,p_2,p_2'')\ H(J_2,J_2'',k_2,p_2,p_2'')\ X$$

$$\langle J_2 k_2 \Omega_2 0 \mid J_2''\Omega_2\rangle\langle J_2 k_2 \Omega_2'' 0 \mid J_2''\Omega_2''\rangle. \tag{4-190}$$

Therefore upon applying equation (4-188) through (4-190) $S_{2,i}(b)$, as given in equation (4-187), becomes:

$$S_{2,i}(b) = \frac{1}{32\pi^2} \sum_{\substack{J_i''g_i''p_i'' \\ J_2''g_2''p_2''}} \sum_{\substack{k_1k_2 \\ q_1q_2}} \sum_{\substack{\Omega_i,\Omega_2 \\ \Omega_i',\Omega_2''}} C(J_i,g_i,\Omega_i,p_i)\ X$$

$$C(J_i'',g_i'',\Omega_i,p_i'')\ C(J_i'',g_i'',\Omega_i',p_i'')\ C(J_2,g_2,\Omega_2'',p_2)$$

$$C(J_i,g_i',\Omega_i',p_i')\ C(J_2,g_2,\Omega_2,p_2)\ C(J_2'',g_2'',\Omega_2,p_2'')$$

$$C(J_2'',g_2'',\Omega_2'',p_2'')$$

$$a^*(J_i,J_i'',g_i,g_i'',p_i,p_i'',J_2,J_2'',g_2,g_2'',p_2,p_2'',k'',q'')$$

$$a(J_i,J_i'',g_i',g_i'',p_i',p_i'',J_2,J_2'',g_2,g_2'',p_2,p_2'',k's,q's)\ X$$

$$H(J_i,J_i'',k_1,p_i,p_i'')\ H(J_i,J_i'',k_1,p_i',p_i'')\ H(J_2,J_2'',k_2,p_2,p_2'')$$

$$H(J_2,J_2'',k_2,p_2,p_2'')\langle J_i k_1 \Omega_i 0 \mid J_i''\Omega_i\rangle\langle J_i k_i \Omega_i' 0 \mid J_i''\Omega_i'\rangle$$

$$\langle J_2 k_2 \Omega_2 0 \mid J_2''\Omega_2\rangle\langle J_2 k_2 \Omega_2'' 0 \mid J_2''\Omega_2''\rangle\ \ \delta_{f,f'}\delta_{J_i,J_i'}\delta_{M_i,M_i'}, \tag{4-191}$$

The expression for $S_{2,f}(b)$ is identical to that of $S_{2,i}(b)$ with f substituted everywhere for i.

The middle term of the second order interruption function is somewhat more complicated. Substituting the matrix elements of P calculated in equation (4-170) into the expression for $S_{2,m}(b)$, equation (4-148), yields:

$$S_{2,m}(b) = - \sum_{\substack{M_i, M_f \\ M_i', M_f'}} \sum_{\substack{J_2', g_2', p_2' \\ M_2, M_2'}} \sum_{q} \Bigg[\sum_{\substack{\Omega_i, \Omega_2 \\ k_1, k_2}} \sum_{q_1 q_2} X$$

$$C(J_i, g_i, \Omega_i, p_i)\ C(J_i', g_i', \Omega_i, p_i')\ C(J_2, g_2, \Omega_2, p_2)\ X$$

$$C(J_2', g_2', \Omega_2, p_2')\ \beta(J_i, J_i', k_1, \Omega_i, p_i, p_i')\ \beta(J_2, J_2', k_2, \Omega_2, p_2, p_2')\ X$$

$$a(J_i, J_i', g_i, g_i', p_i, p_i', J_2, J_2', g_2, g_2', p_2, p_2', k's, q's)\ X$$

$$\langle J_i', k_1 M_i', q_1 \mid J_i M_i \rangle \langle J_2', k_2 M_2', q_2 \mid J_2 M_2 \rangle \Bigg] \times$$

$$\Bigg[\sum_{\Omega_f, \Omega_2'} \sum_{\substack{k_1', k_2' \\ q_1', q_2'}} C(J_f', g_f', \Omega_f, p_f')\ X$$

$$C(J_f, g_f, \Omega_f, p_f)\ C(J_2', g_2', \Omega_2', p_2')\ C(J_2, g_2, \Omega_2', p_2)\ X$$

$$\beta(J_f', J_f, k_1', \Omega_f, p_f', p_f)\ \beta(J_2', J_2, k_2, \Omega_2', p_2', p_2)\ X$$

$$a(J_f', J_f, g_f', g_f, p_f', p_f, J_2', J_2, g_2', g_2, p_2', p_2, k's, q's)\ X$$

$$\langle J_f k_1', M_f q_1' \mid J_f', M_f' \rangle \langle J_2 k_2', M_2 q_2' \mid J_2', M_2' \rangle \Bigg]\ X$$

$$\frac{\langle 1 J_f', q M_f' \mid J_i', M_i' \rangle \langle 1 J_f q M_f \mid J_i M_i \rangle}{\sqrt{(2J_i+1)(2J_i'+1)}\ (2J_2+1)} \qquad (4\text{-}192)$$

Equation (4-192) can now be reduced by applying the properties of the Clebsch Gordon coefficients. The Clebsch Gordon coefficient product appearing in equation (4-192), involving molecule 2 quantum numbers, can be shown to obey the equation:

$$\sum_{M_2,M_2'} \langle J_2',k_2M_2',q_2 \mid J_2M_2\rangle\langle J_2k_2M_2q_2' \mid J_2',M_2',\rangle =$$

$$\delta_{q_2',-q_2}\ \delta_{k_2,k_2'}(-1)^{J_2-J_2'+q_2}\ \frac{\sqrt{(2J_2+1)(2J_2'+1)}}{2k_2+1} \qquad (4\text{-}193)$$

Sustituting the above result into equation (4-192) and performing the sum over k_1' and q_1', allows one to extract the following term;

$$Q \equiv \sum_{\substack{M_i,M_f \\ M_i',M_f'}} \sum_{q} \langle J_i',k_1M_i',q_1 \mid J_iM_i\rangle\langle J_fk_1',M_fq_1' \mid J_f',M_f',\rangle\ X$$

$$\langle 1J_f',qM_f' \mid J_i',M_i'\rangle\langle 1J_fqM_f \mid J_iM_i\rangle. \qquad (4\text{-}194)$$

Four equations in the magnetic quantum numbers must be simultaneously satisfied for each non-vanishing term in the above sum. These equations are given by:

$$\begin{aligned} M_i' + q_1 &= M_i & \qquad q + M_f' &= M_i' \\ M_f + q_1' &= M_f' & \qquad q + M_f &= M_i \end{aligned} \qquad (4\text{-}195)$$

Solving these equations leads to the condition;

$$q_1' = -q_1. \qquad (4\text{-}196)$$

Thus one is left with four equations and six unknowns, hence only two of the unknowns are independent. Letting M_f and q be the independent variables, the sum of equation (4-194) can be written with help of the properties of the Clebsch Gordon coefficients as:

$$Q = \left[\frac{(2J_i+1)(2J_i'+1)}{(2k_1+1)(2k_1'+1)}\right]^{1/2} (-1)^{J_i'-J_f+q_1} \sum_{M_f,q} \langle J_f1M_fq \mid J_iM_f+q\rangle\ X$$

$$\langle J_iJ_i',M_f+qq_1-M_f-q \mid k_1q_1\rangle\langle 1J_i',q\ q_1-M_f-q \mid J_f',q_1-M_f\rangle\ X$$

$$\langle J_fJ_f',M_fq_1-M_f \mid k_1q_1\rangle \qquad (4\text{-}197)$$

The sum of the Clebsch Gordon coefficients can now be expressed in terms of a Racah coefficient. First note that the sum in equation (4-197) has the form:

$$\sum_{\alpha,\beta} \langle ab\alpha\beta \mid e\alpha+\beta\rangle\langle ed\alpha+\beta\ \gamma-\alpha-\beta \mid c\gamma\rangle\ X$$

$$\langle bd\beta\gamma-\alpha-\beta \mid f\gamma-\alpha\rangle\langle af\alpha\gamma-\alpha \mid c'\gamma\rangle \qquad (4\text{-}198)$$

By multiplying equation 19 of reference 50 by the Clebsch Gordon coefficient $\langle af\alpha\gamma-\alpha \mid c'\gamma\rangle$ and performing a sum over α yields;

$$\sum_{\alpha,\beta} \langle ab\alpha\beta \mid e\alpha+\beta\rangle\langle ed\alpha+\beta\gamma-\alpha-\beta \mid c\gamma\rangle\ X$$

$$\langle bd\beta\gamma-\alpha-\beta \mid f\gamma-\alpha\rangle\langle af\alpha\gamma-\alpha \mid c'\gamma\rangle =$$

$$\delta_{c,c'}\sqrt{(2e+1)(2f+1)}\ \ W(a,b,c,d:e,f) \qquad (4\text{-}199)$$

where W is the Racah coefficient. Applying the following equation obeyed by the Racah coefficient (equation 42, p. 116, Ref. 5);

$$W(a,b,c,d:e,f) = (-1)^{e+f-b-c}W(e,a,d,f:b,c) \qquad (4\text{-}200)$$

and substituting equations (4-199) and (4-200) in equation (4-197) yields the following final form for Q:

$$Q = \delta_{q_1,-q_1'}\delta_{k_1,k_1'}(-1)^{J_i'+J_f'+q_1-1-k_1}\ X$$

$$\frac{(2J_i+1)(2J_i'+1)^{1/2}(2J_i'+1)^{1/2}}{(2k_1+1)}\ X$$

$$W(J_i,J_f,J_i',J_f':1,k_1) \qquad (4\text{-}201)$$

Now the only remaining term to be considered in arriving at a general expression for $S_{2,m}(b)$ is the product of β functions appearing in equation (4-192). Utilizing the definition of the β function from equations (4-168) and (4-169), the product can be written in terms of Clebsch-Gordon coefficients as:

$$\beta(J_i,J_{i'},k_1,\Omega_i,p_i,p_{i'})\ \beta(J_2,J_{2'},k_2,p_2,p_{2'})$$

$$\beta(J_{f'},J_f,k_1,\Omega_f,p_{f'},p_f)\ \beta(J_{2'},J_2,k_2,\Omega_{2'},p_{2'},p_2) =$$

$$\frac{(2k_1+1)(2k_2+1)}{16\pi^2}\ H(J_i,J_{i'},k_1,p_i,p_{i'})\ H(J_2,J_{2'},k_2,p_2,p_{2'})\ X$$

$$H(J_{f'},J_f,k_1,p_{f'},p_f)\ H(J_{2'},J_2,k_2,p_{2'},p_2)\langle J_i k_1\Omega_i 0 \mid J_{i'},\Omega_i\rangle\ X$$

$$\langle J_{f'},k_1\Omega_f 0 \mid J_f\Omega_f\rangle\langle J_2 k_2\Omega_2 0 \mid J_{2'},\Omega_2\rangle\langle J_{2'},k_2\Omega_{2'},0 \mid J_2\Omega_{2'},\rangle \qquad (4\text{-}202)$$

Thus utilizing equations (4-192), (4-201), and (4-202) the $S_{2,m}(b)$ term can be expressed as:

$$S_{2,m}(b) = \frac{1}{16\pi^2}\ (-1)^{J_{i'}+J_{f'}}\ \sqrt{(2J_i+1)(2J_{f'}+1)}\ X$$

$$\sum_{J_{2'},g_{2'},p_{2'}}\ \sum_{\substack{k_1,k_2\\ q_1,q_2}}\ \sum_{\substack{\Omega_i,\Omega_2\\ \Omega_f,\Omega_{2'}}}\ (-1)^{q_1+q_2+k_1}\ C(J_i,g_i,\Omega_i,p_i)\ X$$

$$C(J_{i'},g_{i'},\Omega_i,p_{i'})\ C(J_2,g_2,\Omega_2,p_2)\ C(J_{2'},g_{2'},\Omega_2,p_2)\ X$$

$$C(J_{f'},g_{f'},\Omega_f,p_{f'})\ C(J_f,g_f,\Omega_f,p_f)\ C(J_{2'},g_{2'},\Omega_{2'},p_{2'})\ X$$

$$C(J_2,g_2,\Omega_{2'},p_2)\ a(J_i,J_{i'},g_i,g_{i'},p_i,p_{i'},J_2,J_{2'},g_2,g_{2'},p_2,p_{2'},$$

$$k_1,k_2,q_1,q_2)\ X$$

$$a(J_{f'},J_f,g_{f'},g_f,p_{f'},p_f,J_{2'},J_2,g_{2'},g_2,p_{2'}p_2,k_1,k_2,-q_1,-q_2)\ X$$

$$H(J_{2'},J_2,k_2,p_{2'},p_2)\ H(J_i,J_{i'},k_1,p_i,p_{i'})\ H(J_2,J_{2'},k_2,p_2,p_{2'})$$

$$H(J_{f'},J_f,k_1,p_{f'},p_f)\langle J_i k_1\Omega_i 0 \mid J_{i'},\Omega_i\rangle\langle J_{f'},k_1\Omega_f 0 \mid J_f\Omega_f\rangle\ X$$

$$\langle J_2 k_2\Omega_2 0 \mid J_{2'},\Omega_2\rangle\langle J_2 k_2\Omega_{2'},0 \mid J_{2'},\Omega_{2'},\rangle\ W(J_i,J_f,J_{i'}J_{f'}:\ 1,k_1> \qquad (4\text{-}203)$$

5. INCLUSION OF THE INTERMOLECULAR POTENTIALS

The a function appearing in the expression for the interruption function, equations (4-191), and (4-203), now contains all the intermolecular potential information. The various a's are calculated

in this section for the four most considered intermolecular potential used in pressure broadening calculations; the electric dipole-dipole, dipole-quadrupole, quadrupole-dipole, and quadrupole-quadrapole interactions. The a functions derived in this section will be general in that they can be used for calculating both diagonal and off diagonal $\bar{G}$ matrix elements. Diagonal matrix elements correspond to the resolved line approximation and the off diagonal matrix element are necerssary for coupled line calculations. A more exhaustive list of interactions and their associated interruption functions, for the diagonal or resolved line case only, is given by Robert et al.[50]

Much of the material utilized for the calculation of the coupled line interruption function given here is obtained from Tsao and Curnutte who worked only in the resolved line approximation [8]. For brevity only the main points of interest are covered here as well as derivations from the specific case of the resolved line approximation considered by Tsao and Curnutte. The classical path, or straight line trajectory, assumption is again made together with the assumption that only binary collisions occur.

A. Dipole-Dipole Interaction

The dipole-dipole interaction $H_{\mu\mu}$ is given by

$$H_{\mu\mu} = \frac{\bar{\mu}_1 \cdot \bar{\mu}_2 - 3(\bar{\mu}_1 \cdot \hat{R})(\bar{\mu}_2 \cdot \hat{R})}{R^3} \qquad (4\text{-}204)$$

where μ_1 is the permanent dipole moment of the radiating molecule and μ_2 is that of the perturbing molecule. The vector $\bar{R}$ points from molecule 1 to molecule 2 as illustrated in Figure 4-2.

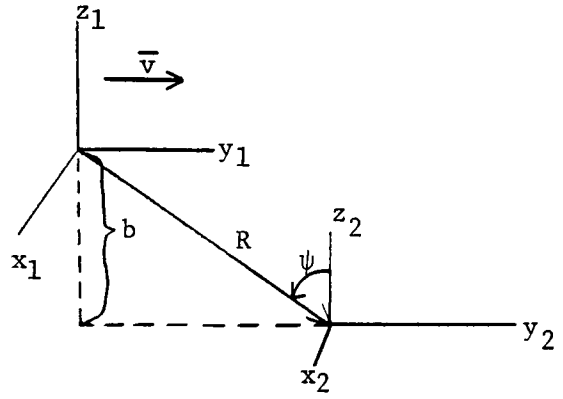

Figure 4-2. Intermolecular potential coordinate system.

In the classical path assumption the distance R is a function of the impact parameter, time, and mean relative speed given by:

$$R = \sqrt{b^2+v^2t^2} \tag{4-205}$$

The angle ψ is also time dependent through the relations;

$$\cos\psi = b/R \tag{4-206}$$

and;

$$\sin\psi = vt/R. \tag{4-207}$$

Utilizing these equations the potential term $H_{\mu\mu}(t)$ can be rewritten as;

$$H_{\mu\mu}(t) = \frac{\mu_1\mu_2}{R^3}(T_1 + \sin\psi\cos\psi T_2 + \cos^2\psi T_3) \tag{4-208}$$

where T_1,T_2, and T_3 are functions of the spherical polar coordinates describing both molecule 1 and molecule 2. Expressing the T's in terms of spherical harmonics, in the coordinates of both molecule 1 and molecule 2, the expression for $H_{\mu\mu}(t)$ in equation (4-208) can be put into the form:

$$H_{\mu\mu}(t) = \sum_{\substack{k_1k_2\\q_1q_2}} C^{k_1k_2}_{q_1q_2}(t) Y^{k_1}_{q_1}(\theta_1,\phi_1) Y^{k_2}_{q_2}(\theta_2,\phi_2). \tag{4-209}$$

For the dipole-dipole interaction only the terms with both k_1 and k_2 equal to unity contribute to the sum. Note that equation (4-209) is of the assumed form of the intermolecular potentials used in deriving the interruption function, equation (4-155).

The "a" function as defined in equation (4-157) can now be calculated using the form of the dipole-dipole interaction given above. Tsao and Curnutte [8] have performed the time integral appearing in equation (4-157) for the case of the dipole-dipole interaction, which leads to the following form for the "a" function;

$$a(J_1,J_1',\alpha_1,\alpha_1',J_2,J_2',\alpha_2,\alpha_2',1,1,q_1,q_2) =$$

$$\frac{4\pi}{3}\ \frac{\mu_1\mu_2}{hv}\ \frac{k^2}{b^2}\ B^{1\ 1}_{q_1q_2}(k) \qquad (4\text{-}210)$$

where;

$$k = \frac{b}{v}\,(E_{J_1\alpha_1} + E_{J_2\alpha_2} - E_{J_1',\alpha_1'} - E_{j_2',\alpha_2'}). \qquad (4\text{-}211)$$

The B's of equation (4-210) are expressed in terms of the modified Bessel functions of the second kind and are repeated here for convenience, from the work of Tsao and Curnutte; [8]

$$B_{1,1} = \frac{3K_1(|k|)}{|k|} - K_2(|k|) \quad B_{1,0} = -\frac{k}{|k|}\sqrt{2}\,K_1(|k|)$$

$$B_{1,-1} = \frac{K_2(|k|)}{|k|} - K_2(|k|) \quad B_{0,1} = -\sqrt{2}\,\frac{k}{|k|}\,K_1(|k|)$$

$$B_{0,0} = \frac{2K_1(|k|)}{|k|} - 2K_2(|k|) \qquad (4\text{-}212)$$

where;

$$B^{1,1}_{-q_1,-q_2} = B^{1,1}_{q_1,q_2} \qquad (4\text{-}213)$$

Note that the B's are real, therefore $S_2^{\mu,\mu}(b)$ is real also.

There is no contribution to the first order interruption function from the dipole-dipole interaction. This is easily seen by noting from equation (4-182) that only potentials where both k_1 and k_2 are equal to two contribute. Therefore of the four potentials utilized here only the quandupole-quadrupole interaction contributes to the first order interruption function.

Consider now the dipole-dipole second order interruption function $S_{i,2}(b)$. Since k_1 and k_2 are both unity the sum of the product of the "a" functions appearing in the expression for $S_{2,i}(b)$, equation (4-191), is given by:

$$\text{Sum} = \sum_{q_i,q_2}$$

$$a(J_i,J_i",g_i,g_i",p_i,p_i",J_2,J_2",g_2,g_2",p_2,p_2",1,1,q_1,q_2)\ X$$

$$a^*(J_i,J_i",g_i',g_i",p_i',p_i",J_2,J_2",g_2,g_2",p_2,p_2",1,1,q_1,q_2). \quad (4\text{-}214)$$

Utilizing equations (4-210) the above sum reduces to;

$$\text{Sum} = \frac{16\pi^2}{9}\left(\frac{\mu_1\mu_2}{h\nu}\right)^2 \frac{k_\alpha^2 \kappa_\beta^2}{b^4} \sum_{q_1q_2} B^{11}_{q_1q_2}(k_\alpha) B^{11}_{q_1q_2}(k_\beta) \quad (4\text{-}215)$$

where;

$$k_\alpha = |\alpha|\, b \qquad k_\beta = |\beta|\, b \quad (4\text{-}216)$$

and;

$$\alpha = (E_{J_i g_i p_i} + E_{J_2 g_2 p_2} - E_{J_i" g_i" p_i"} - E_{J_2" g_2" p_2"})(\tfrac{1}{v})$$

$$\beta = (E_{J_i g_i' p_i'} + E_{J_2 g_2 p_2} - E_{J_i" g_i" p_i"} - E_{J_2" g_2" p_2"})(\tfrac{1}{v}). \quad (4\text{-}217)$$

Defining the sum over q_1 and q_2 of the B's appearing in equation (4-215) as the function $g_1(\alpha,\beta,b)$, $S^{\mu\mu}_{2,i}(b)$ can be expressed as;

$$S^{\mu\mu}_{2,i}(b) = S_i C^{\mu\mu}_i \sum_{J_2" g_2" p_2"} \sum_{J_i" g_i" p_i"} \sum_{\substack{\Omega_i,\Omega_i' \\ \Omega_2,\Omega_2"}} B_i(1,1) g_1(\alpha,\beta,b) \quad (4\text{-}218)$$

where

$$S_i = \delta_{f,f'}\delta_{J_i,J_i'}, \tag{4-219}$$

$$C_i^{\mu\mu} = C_f^{\mu\mu} = \frac{4}{9}\left(\frac{\mu_1\mu_2}{h\nu}\right)^2 \frac{1}{b^4}\ , \tag{4-220}$$

and;

$$B_i(k_1,k_2) = C(J_i,g_i,\Omega_i,p_i)\ C(J_i",g_i",\Omega_i,p_i")C(J_2,g_2,\Omega_2,p_2)\ X$$
$$C(J_2",g_2",\Omega_2,p_2")\ C(J_i,g_i',\Omega_i',p_i')\ C(J_i",g_i",\Omega_i',p_i")$$
$$C(J_2,g_2,\Omega_2",p_2)\ C(J_2",g_2",\Omega_2",p_2")H(J_i,J_i",k_1,p_i,p_i")$$
$$H(J_i,J_i",k_1,p_i',p_i")\ H(J_2,J_2",k_2,p_2,p_2")\ H(J_2,J_2",k_2,p_2,p_2")$$
$$\langle J_ik_1\Omega_i0 \mid J_i"\Omega_i\rangle\langle J_ik_i\Omega_i',0 \mid J_i"\Omega_i',\rangle\langle J_2k_2\Omega_20 \mid J_2"\Omega_2\rangle\ X$$
$$\langle J_2k_2\Omega_2"0 \mid J_2"\Omega_2"\rangle. \tag{4-221}$$

The expression for $S_{2,f}(b)$ is identical to that of $S_{i,f}(b)$ with the exception of all i and f subscripts are interchanged.

By using the B's of equation (4-212) and applying the recurrence relations of the modified Bessel functions the function $g_1(\alpha,\beta,b)$ was found to be given by: [20,51]

$$g_1(\alpha,\beta,b) = \frac{k_\alpha^2 k_\beta^2}{4}\left[K_2(k_\alpha)K_2(k_\beta) + \frac{4\alpha\beta}{|\alpha\beta|}\ K_1(k_\alpha)K_1(k_\beta)\right.$$
$$\left. + 3K_0(k_\alpha)K_0(k_\beta)\right] \tag{4-222}$$

Evaluation of the middle term of the second order interruption function, $S_{2,m}(b)$, differs basically from that of $S_{2,i}(b)$ only in the sum of products of the "a" functions. For the case of $S_{2,m}(b)$, equation (4-203), the sum of the "a" functions is given by

$$\sum_{q_1,q_2} (-1)^{q_1+q_2}$$
$$a(J_i,J_i',g_i,g_i',p_i,p_i',J_2,J_2',g_2,g_2'p_2,p_2',1,1,q_1,q_2)X$$
$$a(J_f',J_f,g_g',g_f,p_f',p_f,J_2,J_2',g_2',g_2,p_2',p_2,1,1,-q_1,-q_2) \tag{4-223}$$

The alternating sign in the sum effects only the terms where q_1+q_2 is odd, but this is negated by reversing the primed and unprimed quantum numbers of the second "a" function of (4-223). Thus by utilizing equation (4-213) the above sum can be shown to be equal to that of the $S^{\mu\mu}_{2,i}(b)$ term. Therefore for the dipole-dipole interaction $S^{\mu\mu}_{2,m}(b)$ is given by;

$$S^{\mu\mu}_{2,m}(b) = C^{\mu\mu}_m \sum_{J_2',g_2',p_2'} \sum_{\Omega_i\Omega_2\Omega_f\Omega_2'} B_m(1,1)g_1(\alpha,\beta,b) \qquad (4\text{-}224)$$

where

$$C^{\mu\mu}_m = \frac{8}{9}\left(\frac{\mu_1\mu_2}{h\nu}\right)^2 \frac{1}{b^4}(-1)^{J_i'+J_f'+1}\sqrt{(2J_i+1)(2J_f'+1)} \qquad (4\text{-}225)$$

and;

$$B_m(k_1,k_2) = C(J_i,g_i,\Omega_i,p_i)\ C(J_i,g_i',\Omega_i,p_i')C(J_2,g_2,\Omega_2,p_2)\ X$$
$$C(J_2',g_2',\Omega_2,p_2)C(J_f',g_f',\Omega_f,p_f')C(J_f,g_f,\Omega_f,p_f)\ X$$
$$C(J_2',g_2',\Omega_2',p_2')C(J_2,g_2,\Omega_2',p_2)H(J_2',J_2,k_2,p_2',p_2)\ X$$
$$H(J_i,J_i',k_1,p_i,p_i')H(J_2,J_2',k_2,p_2,p_2')H(J_f',J_f,k_1,p_f',p_f)$$
$$\langle J_ik_1\Omega_i0 \mid J_i',\Omega_i\rangle\langle J_fk_1\Omega_f0 \mid J_f\Omega_f\rangle\langle J_2k_2\Omega_20 \mid J_2',\Omega_2\rangle\ X$$
$$\langle J_2k_2\Omega_2',0 \mid J_2,\Omega_2',\rangle\ W(J_i,J_f,J_i',J_f':1,k_1). \qquad (4\text{-}226)$$

Evaluation of the matrix elements of $\bar{G}$ necessitate the calculation of the integral of S(b) given by equation (4-142). For $S_{2,i}(b)$, $S_{2,f}(b)$, and $S_{2,m}(b)$ the integral of the b dependent terms reduces to;

$$2\pi\int_{b_0}^{\infty} b^{-3}g_1(\alpha,\beta,b)db = \pi b_0^2 G_1(\alpha,\beta,b_0). \qquad (4\text{-}227)$$

Therefore one has;

$$2\pi\int_{bo}^{\infty} S^{\mu}_{2,i}(b)bdb =$$
$$\pi b_0^2\ S_iC^{\mu\mu}_i \sum_{J_2''g_2''p_2''} \sum_{J_i''p_i''g_i''} \sum_{\substack{\Omega_i,\Omega_i' \\ \Omega_2,\Omega_2''}} B_i(1,1)G_1(\alpha,\beta,b_0) \qquad (4\text{-}228)$$

likewise for $S_{2,f}(b)$, and;

$$2\pi\int_{b_0}^{\infty} S_{2,m}^{\mu\mu}(b)bdb =$$

$$\pi b_o^2 C_m^{\mu\mu} \sum_{J_2',g_2',p_2'} \sum_{\Omega_1,\Omega_2,\Omega_f,\Omega_2'} B_m(1,1)G_1(\alpha,\beta,b_o) \qquad (4\text{-}229)$$

It now remains to consider the functions g_1 and G_1 appearing in dipole-dipole interruption function. The function $g_1(\alpha,\beta,b)$ is given in equation (4-222) and it exhibits the following properties;

$$g_1(0,0,b) = g_1(\alpha,\beta,0) = 1, \qquad (4\text{-}230)$$

$$g_1(0,\beta,b) = \frac{k_\beta^2}{2} K_2(k\beta), \qquad (4\text{-}231)$$

and:

$$g_1(\alpha,0,b) = \frac{k_\alpha^2}{2} K_2(k_\alpha) \qquad (4\text{-}232)$$

Note that for diagonal matrix elements of $\bar{G}$, α and β are identical and g_1 reduces to;

$$f_1(k_\alpha) = g_1(\alpha,\alpha,b) = \frac{k_\alpha^4}{4}[K_2^2(k_\alpha) + 4K_1^2(k_\alpha) + 3K_0^2(k_\alpha)]. \qquad (4\text{-}233)$$

The function $f_1(k_\alpha)$ is that found in the interruption function $S_2^{\mu\mu}(b)$ of Tsao and Curnutte [8] for the resolved line approximation. The function $G_1(\alpha,\beta,b)$ was found to be somewhat more involved. Listed below are the forms of G_1 and some of its properties where α and β are assumed to be distinct:

$$G_1(\alpha,\beta,b) = \frac{k_\alpha^2 k_\beta^2}{8(\beta^2-\alpha^2)}\{ |\alpha\beta| [K_3(k_\alpha)K_1(k_\beta) - K_1(k_\alpha)K_3(k_\beta)]$$

$$+8\alpha\beta[K_2(k_\alpha)K_0(k_\beta) - K_2(k_\beta)K_0(k_\alpha)] + 6\beta^2 K_0(k_\alpha)K_2(k_\beta)$$

$$- 6\alpha^2 K_0(k_\beta)K_2(k_\alpha) - 6(\beta^2-\alpha^2)K_0(k_\beta)K_0(k_\alpha)\} \qquad (4\text{-}234)$$

$$G_1(\alpha,-\alpha,b) = \frac{k_\alpha^4}{4}\left[K_1(k_\alpha)K_3(k_\alpha) - 4K_2(k_\alpha)K_0(k_\alpha) - K_2^2(k_\alpha)\right.$$

$$\left. + 7K_1^2(k_\alpha) - 3K_0^2(k_\alpha)\right] \qquad (4\text{-}235)$$

$$G_1(\alpha,\beta,0) = G_1(0,0,b) = 1 \qquad (4\text{-}236)$$

$$G_1(0,\beta,b) = k_\beta K_1(k_\beta) \qquad (4\text{-}237)$$

$$G_1(\alpha,0,b) = k_\alpha K_1(k_\alpha) \qquad (4\text{-}238)$$

Note again that for diagonal matrix elements of $\bar{G}$ α and β are identical and G_1 becomes

$$F_1(k_\alpha) = G_1(k_\alpha) = \frac{k_\alpha^4}{4}\left[K_3(k_\alpha)K_1(k_\alpha) + 4K_2(k_\alpha)K_0(k_\alpha)\right.$$

$$\left. -K_2^2(k_\alpha) - K_1^2(k_\alpha) - 3K_0^2(k_\alpha)\right]. \qquad (4\text{-}239)$$

This is the function quoted by Tsao and Curnutte [8] which appears in the integrated interruption function for the dipole-dipole interacion in the resolved line approximation. Figures 4-3 and 4-4 illustrate the behavior of g_1 and G_1, respectively.

B. Dipole-Quadrupole Interaction

For the dipole-quadrupole interaction, molecule 1's dipole interacting with molecules 2's quadrupole, the Hamiltonian is written as:

$$H_{\mu,Q}(t) = \frac{3}{4}\frac{\mu_1 Q_2}{R^4}\{-(\hat{R}\cdot\hat{\mu}_1) - (\hat{\mu}_1\cdot\hat{Q}_2)(\hat{R}\cdot\hat{Q}_2)+5(\hat{R}\cdot\hat{\mu}_1)(\hat{R}\cdot\hat{Q}_2)^2\} \qquad (4\text{-}240)$$

The quadrupole moment is assumed to be the linear quadrupole moment component. As done with the dipole-dipole interaction the a function can be expressed as

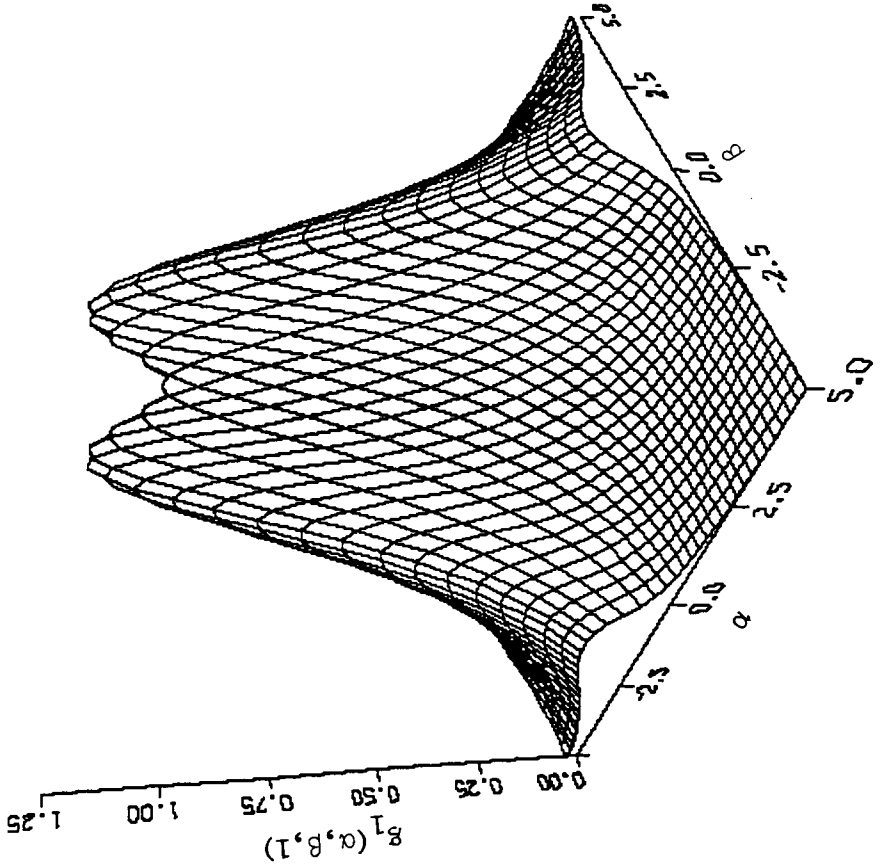

Figure 4-3. The function $g_1(\alpha,\beta,b)$. The value of b has been set to one.

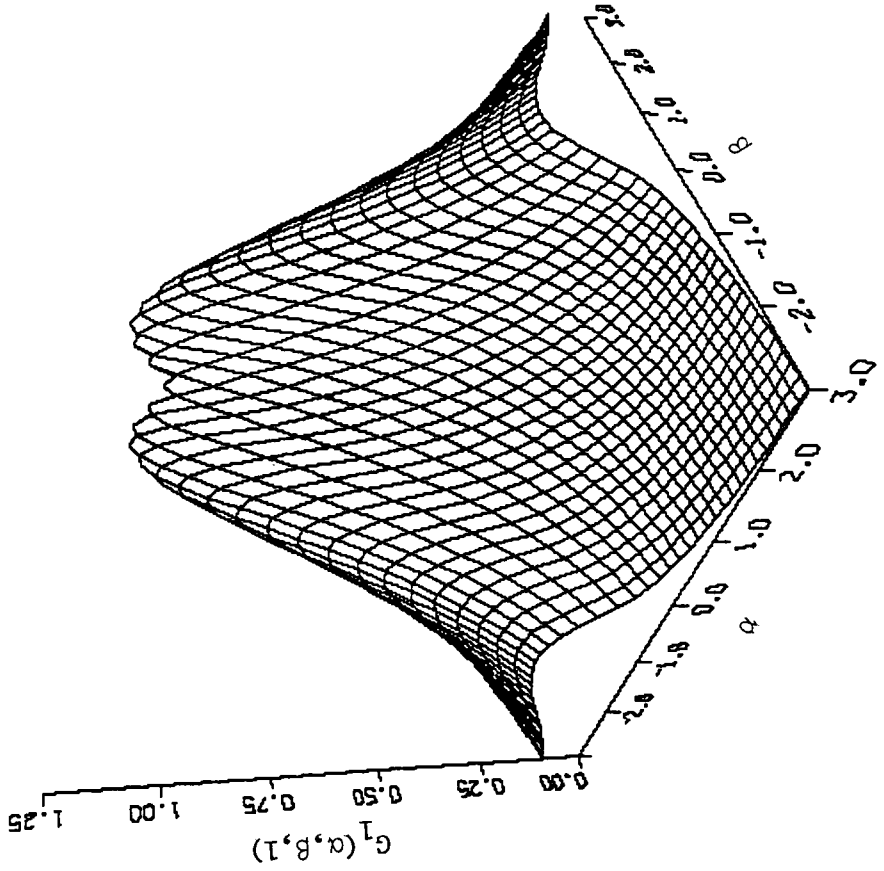

Figure 4-4. The function $G_1(\alpha,\beta,b)$. The value of b has been set to one.

$$a(J_1,J_1',\alpha_1,\alpha_1',J_2,J_2',\alpha_2,\alpha_2',1,2,q_1,q_2) =$$

$$\frac{\sqrt{5}}{15}\frac{\pi\mu_1 Q_2}{hv}\frac{k^3}{b^3}B^{1\ 2}_{q_1\ q_2}(k). \tag{4-241}$$

The B's have been calculated by Tsao and Curnutte [8] and are repeated here for convenience;

$$B_{1,2} = \frac{k}{|k|}\left[5\frac{K_1(|k|)}{|k|} - K_2(|k|)\right]$$

$$B_{1,0} = \frac{k}{|k|}\left[\sqrt{6}\frac{K_1(|k|)}{k} - \sqrt{6}\,K_2(|k|)\right]$$

$$B_{1,-2} = \frac{k}{|k|}\left[\frac{K_1(|k|)}{|k|} - K_2(|k|)\right]$$

$$B_{0,1} = \frac{k}{|k|}\left[2\sqrt{2}\frac{K_1(|k|)}{|k|} - 2\sqrt{2}\,K_2(|k|)\right]$$

$$B_{1,1} = 10\frac{K_2(|k|)}{|k|} - 2K_3(|k|)$$

$$B_{1,-1} = 6\frac{K_2(|k|)}{|k|} - 2K_3(|k|)$$

$$B_{0,2} = 5\sqrt{2}\frac{K_2(|k|)}{|k|} - \sqrt{2}K_3(|k|)$$

and;

$$B_{0,0} = 6\sqrt{3}\frac{K_2(|k|)}{|k|} - 2\sqrt{3}\,K_3(|k|) \tag{4-242}$$

where;

$$B^{1,2}_{q_1,q_2} = B^{1,2}_{-q_1,-q_2}\,. \tag{4-243}$$

As before, the B's are real and therefore $S_2(b)$ is real as they are in the two remaining potentials to be considered. The sum of the product of "a" functions as given in equation (4-191) appears again and this time the sum is given by;

$$\text{Sum} = \frac{128\pi}{45}\left(\frac{\mu_1 Q_2}{h\nu}\right)^2 \frac{1}{b^6}\, g_2(\alpha,\beta,b) \tag{4-244}$$

where $g_2(\alpha,\beta,b)$ is defined by;

$$g_2(\alpha,\beta,b) = \frac{k_\alpha^3 k_\beta^3}{128} \sum_{q_1,q_2} B^{1,2}_{q_1,q_2}(k_\alpha)\, B^{1,2}_{q_1,q_2}(k_\beta). \tag{4-245}$$

Substituting the sum derived above into equation (4-191) yields the following form for the dipole-quadrupole interaction contribution to $S_{2,i}(b)$;

$$S^{\mu,Q}_{2,i}(b) =$$

$$S_i C_i^{\mu Q} \sum_{J_2" g_2" p_2"} \sum_{J_i" g_i" p_i"} \sum_{\substack{\Omega_i,\Omega_2 \\ \Omega_i',\Omega_2"}} B_i(1,2)\, g_2(\alpha,\beta,b) \tag{4-246}$$

where;

$$C_i^{\mu\, Q} = \frac{4}{45}\left(\frac{\mu_1 Q_2}{h\nu}\right)^2 \frac{1}{b^6}\,. \tag{4-247}$$

Again $S^{\mu\ Q}_{2,f}(b)$ is identical with $S^{\mu,Q}_{2,i}(b)$ for all i and f subscripts interchanged. Since equation (4-243) is still obeyed, the same arguments used to show that the sum over q_1 and q_2 appearing in $S^{\mu,\mu}_{2,i}(b)$ is the same as that of $S^{\mu,\mu}_{2,m}(b)$ apply here also.

Therefore;

$$S^{\mu,Q}_{2,m}(b) = C^{\mu Q}_{m} \sum_{J_2',g_2',p_2'} \sum_{\Omega_i,\Omega_2} \sum_{\Omega_f,\Omega_2'} B_{m,2}(1,2) g_2(\alpha,\beta,b) \quad (4\text{-}248)$$

where;

$$C^{\mu Q}_{m} = \frac{8}{45} \left(\frac{\mu_1 Q_2}{h\nu}\right)^2 \frac{1}{b^6} (-1)^{J_i'+J_f'+1} \sqrt{(2J_i+1)(2J_f'+1)} \quad (4\text{-}249)$$

The integrated second order dipole quadrupole interruption function as needed for the calculation of matrix elements of $\bar{G}$, equation (4-142), is given by;

$$2\pi \int_{b_0}^{\infty} S^{\mu\ Q}_{2,i}(b) b\,db =$$

$$\pi b_0^2\ S_i C^{\mu\ Q}_{i} \sum_{J_2'' g_2'' p_2''} \sum_{J_i'' g_i'' p_i''} \sum_{\substack{\Omega_i,\Omega_2 \\ \Omega_i',\Omega_2''}} B_{1,2}(1,2) G_2(\alpha,\beta,b) \quad (4\text{-}250)$$

likewise for $S_{2,f}(b)$, and;

$$2\pi \int_{b_0}^{\infty} S^{\mu\ Q}_{2,m}(b) b\,db =$$

$$\pi b_0^2\ C^{\mu\ 0}_{m} \sum_{J_2',g_2',p_2'} \sum_{\Omega_i\Omega_2} \sum_{\Omega_f\Omega_2'} B_{m,2}(1,2) G_2(\alpha,\beta,b) \quad (4\text{-}251)$$

From the definition of g_2, equation (4-245), and the form of the B's in equation (4-242) the following form and properties of g_2 and G_2 can be derived:

$$g_2(\alpha,\beta,b) = \frac{k_\alpha^3 k_\beta^3}{64} [K_3(k_\alpha)\ K_3(k_\beta) + 6 \frac{\alpha\beta}{|\alpha\beta|} K_2(k_\alpha) K_2(k_\beta)$$

$$+ 15\ K_1(k_\alpha) K_1(k_\beta) + 10 \frac{\alpha\beta}{|\alpha\beta|} K_o(k_\alpha) K_o(k_\beta)] \quad (4\text{-}252)$$

$$G_2(\alpha,\beta,b) = \frac{k_\alpha^3 k_\beta^3}{192(\alpha^2-\beta^2)} \{ |\alpha\beta| [K_4(k_\alpha)K_2(k_\beta)-K_2(k_\alpha)K_4(k_\beta)]$$

$$+ 9\alpha\beta [K_3(K_\alpha)K_1(k_\beta)-K_1(k_\alpha)K_3(k_\beta)]$$

$$+ 45 |\alpha\beta| [K_2(k_\alpha)K_0(k_\beta)-K_0(k_\alpha)K_2(k_\beta)]$$

$$+30 \alpha\beta[\beta^2 K_0(k_\alpha)K_2(k_\beta)-\alpha^2 K_0(k_\beta)K_2(k_\alpha)$$

$$+(\alpha^2-\beta^2)K_0(k_\alpha)K_0(k_\beta)]\}, \qquad (4\text{-}253)$$

$$G_2(\alpha,-\alpha,b) = \frac{k_\alpha^6}{64} \{K_4(k_\alpha)K_2(k_\alpha)-6K_3(k_\alpha)K_1(k_\alpha)$$

$$+ 15 K_2(k_\alpha)K_0(k_\alpha) - K_3^2(k_\alpha)+6K_2^2(k_\alpha)-25K_1^2(k_\alpha)$$

$$+ 10 K_0^2(k_\alpha)], \qquad (4\text{-}254)$$

$$g_2(\alpha,\alpha,b) = f_2(k_\alpha) = \frac{k_\alpha^6}{64} [K_3^2(k_\alpha)+6K_2^2(k_\alpha)+15K_1^2(k_\alpha)$$

$$+ 10 K_0^2(k_\alpha)], \qquad (4\text{-}255)$$

$$G_2(\alpha,\alpha,b) = F_2(k_\alpha) = \frac{k_\alpha^6}{64} [K_4(k_\alpha)K_2(k_\alpha)+6K_3(k_\alpha)K_1(k_\alpha)$$

$$+ 15 K_2(k_\alpha)K_0(k_\alpha)-K_3^2(k_\alpha)-6K_2^2(k_\alpha)-5K_1^2(k_\alpha)-10K_0^2(k_\alpha)] \qquad (4\text{-}256)$$

$$g_2(0,0,b) = g_2(\alpha,\beta,0) = 1 \qquad (4\text{-}257)$$

$$g_2(0,\beta,b) = \frac{k_\beta^3}{8} K_3(k_\beta) \qquad (4\text{-}258)$$

$$g_2(\alpha,0,b) = \frac{k_\alpha^3}{8} K_3(k_\alpha) \qquad (4\text{-}259)$$

$$G_2(\alpha,\beta,0) = G_2(0,0,b) = \frac{1}{2} \tag{4-260}$$

$$G_2(0,\beta,b) = \frac{k_\beta^2}{4} K_2(k_\beta) \tag{4-261}$$

$$G_2(\alpha,0,b) = \frac{k_\alpha^2}{4} K_2(k_\alpha) \tag{4-262}$$

The function $f_2(k)$ and $F_2(k)$ are those arrived at by Tsao and Curnutte [36] in the resolved line approximation, $\alpha=\beta$, for the dipole-quadrupole interaction. Figure 4-5 and 4-6 illustrate the behavior of g_2 and G_2 respectively.

C. Quadrupole-Dipole Interaction

Formulation of the quadrupole-dipole interaction parallels that of the dipole-quadrupole interaction. The collision Hamiltonian for this case is given by;

$$H_{Q,\mu}(t) = -\left(\frac{3}{4}\right) \frac{\mu_2 Q_1}{R^4}$$

$$\left(-(\hat{R}\cdot\hat{\mu}_2)-(\hat{\mu}_1\cdot\hat{\mu}_2)(\hat{R}\cdot\hat{\mu}_1)+5(\hat{R}\cdot\hat{\mu}_2)(\hat{R}\cdot\hat{\mu}_1)^2\right\}. \tag{4-263}$$

As with the dipole-quadrupole interaction the a function becomes;

$$a(J_1,J_1',\alpha_1,\alpha_1',J_2,J_2',\alpha_2,\alpha_2',2,1,q_1,q_2) =$$

$$-\frac{\sqrt{5}\pi}{15}\frac{\mu_2 Q_1}{h\nu}\ \frac{k^3}{b^3}\ B^{2\ 1}_{q_1 q_2}(k) \tag{4-264}$$

where k_1 is now two and k_2 has the value of one. The B's are those as given in equation (4-242) with the k_1 and k_2, and q_1 and q_2, indices interchanged.

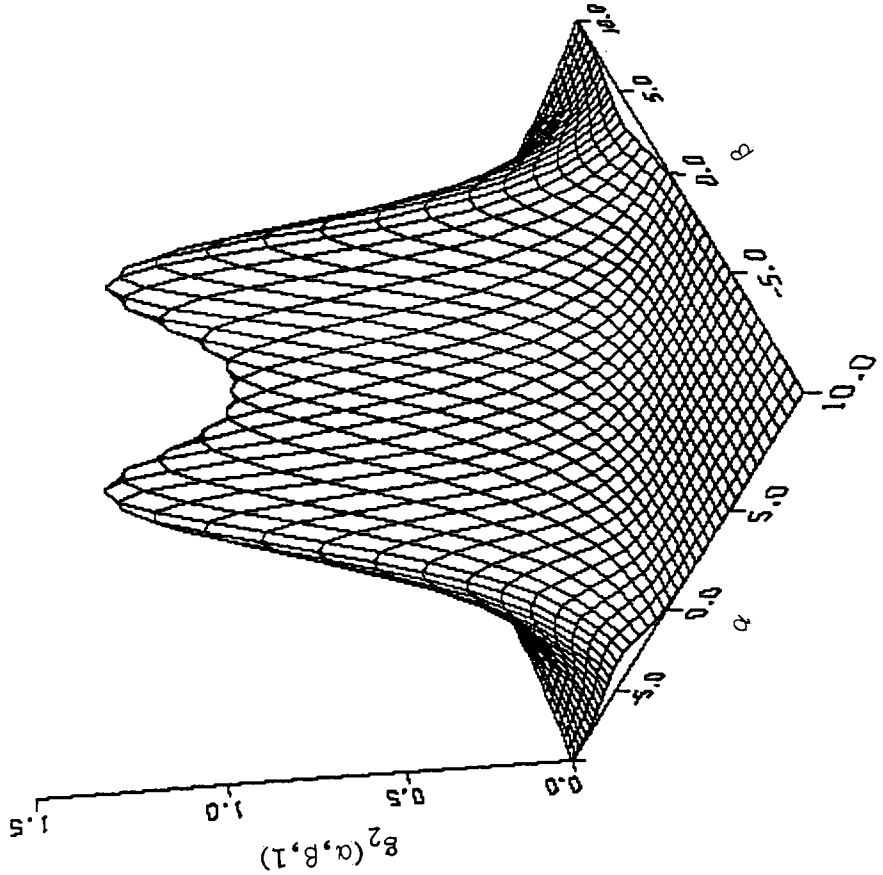

Figure 4-5. The function $g_2(\alpha,\beta,b)$. The value of b has been set to one.

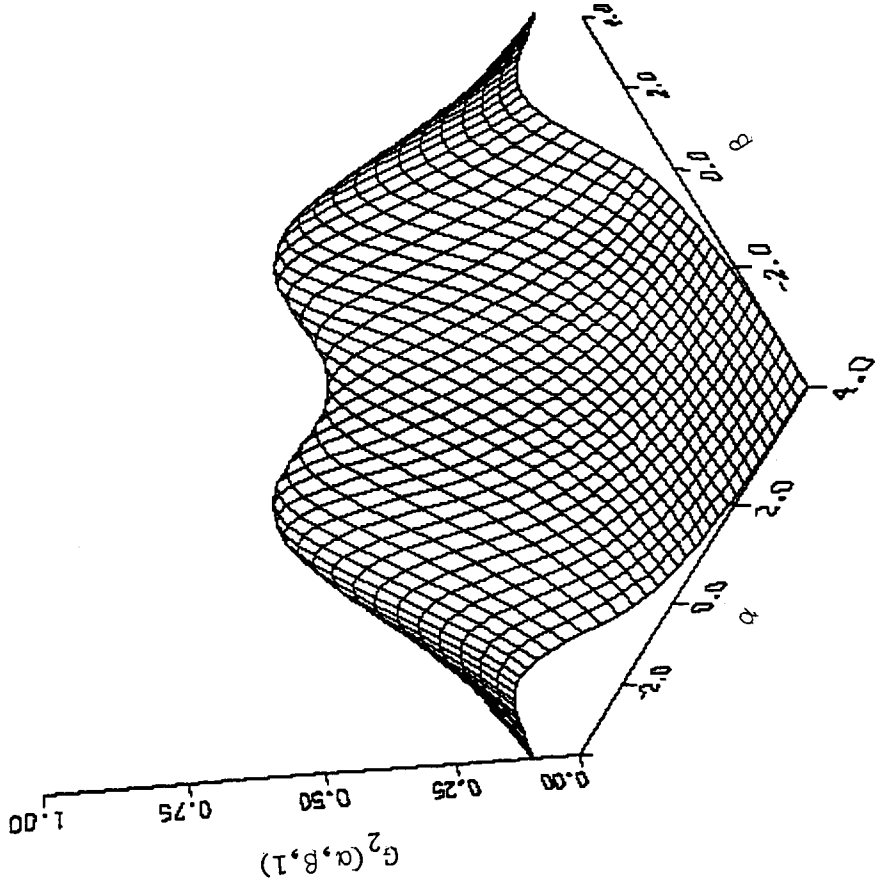

Figure 4-6. The function $G_2(\alpha,\beta,b)$. The value of b has been set to one.

Proceeding as before, quadrupole-dipole interaction contribution to the second order interruption function is found to be given by;

$$S_{2,i}^{Q,\mu}(b) = S_i C_i^{Q\mu} \sum_{J_2" g_2" p_2"} \sum_{J_i" g_i" p_i"} \sum_{\substack{\Omega_i,\Omega_2 \\ \Omega_i',\Omega_2"}} B_{i,2}(2,1) g_2(\alpha,\beta,b) \tag{4-265}$$

and;

$$S_{2,m}^{Q\mu}(b) = C_m^{Q\mu} \sum_{J_2' g_2' p_2'} \sum_{\Omega_i\Omega_2} \sum_{\Omega_f\Omega_2'} B_{m,2}(2,1) g_2(\alpha,\beta,b). \tag{4-266}$$

where;

$$C_i^{Q\mu} = \frac{4}{45} \left(\frac{\mu_2 Q_1}{h\nu}\right)^2 \frac{1}{b^6} \tag{4-267}$$

and:

$$C_m^{Q\mu} = \frac{8}{45} \left(\frac{\mu_2 Q_1}{h\nu}\right)^2 \frac{1}{b^6} (-1)^{J_i'+J_f'} \sqrt{(2J_i+1)(2J_f'+1)} \tag{4-268}$$

The integral over the cross section of these functions likewise follow those of the dipole quadrupole interaction;

$$2\pi \int S_{2,i}^{Q\mu}(b) b db = \pi b^2 C_i^{Q\mu} \sum_{J_2" g_2" p_2"} \sum_{J_i" g_i" p_i"} \sum_{\substack{\Omega_i,\Omega_2 \\ \Omega_i',\Omega_2"}} B_{i,2}(2,1) G_2(\alpha,\beta,b) \tag{4-269}$$

and:

$$2\pi \int S_{2,m}^{Q\mu}(b) b db = \pi b^2 C_m^{Q\mu} X \sum_{J_2' g_2' p_2'} \sum_{\Omega_i\Omega_2} \sum_{\Omega_f\Omega'_2} B_{m,2}(2,1) G_2(\alpha,\beta,b) \tag{4-270}$$

D. Quadrupole-Quadrupole Interaction

For the case of the quadrupole-quadrupole interaction the collision Hamiltonian is given by;

$$H_{QQ} = \frac{3Q_1Q_2}{16R^5}\,[1 - 5(\hat{R}\cdot\hat{Q}_1)^2 - 5(\hat{R}\cdot\hat{Q}_2)^2 + 2(\hat{Q}_1\cdot\hat{Q}_2)^2$$

$$-20(\hat{R}\cdot\hat{Q}_1)(\hat{R}\cdot\hat{Q}_2)(\hat{Q}_1\cdot\hat{Q}_2) + 35(\hat{R}\cdot\hat{Q}_1)^2(\hat{R}\cdot\hat{Q}_2)^2]. \qquad (4\text{-}271)$$

Proceeding as before the "a" function is found to be given by

$$a(J_1,J_1',\alpha_1,\alpha_1',J_2,J_2',\alpha_2,\alpha_2',2,2,q_1,q_2) =$$

$$\frac{\pi}{60}\frac{Q_1Q_2}{h\nu}\frac{k^4}{b^4}B^{2\,2}_{q_1q_2}(k) \qquad (4\text{-}272)$$

The B's have been calculated by Tsao and Curnutte and are given by:

$$B_{22} = 35\frac{K_2(|k|)}{|k|^2} - 14\frac{K_3(|k|)}{|k|} + K_4(|k|)$$

$$B_{20} = 5\sqrt{6}\frac{K_2(|k|)}{|k|^2} - 8\sqrt{6}\frac{K_3(|k|)}{|k|} + \sqrt{6}\,K_4(|k|)$$

$$B_{2,2} = 3\frac{K_2(|k|)}{|k|^2} - 6\frac{K_3(|k|)}{|k|} + K_4(|k|)$$

$$B_{1,1} = 20\frac{K_2(|k|)}{|k|^2} - 32\frac{K_3(|k|)}{|k|} + 4\,K_4(|k|)$$

$$B_{1,-1} = 12\frac{K_2(|k|)}{|k|^2} - 24\frac{K_3(|k|)}{|k|} + 4\,K_4(|k|)$$

$$B_{0,2} = 5\sqrt{6}\frac{K_2(|k|)}{|k|^2} - 8\sqrt{6}\frac{K_3(|k|)}{|k|} + \sqrt{6}\,K_4(|k|)$$

$$B_{0,0} = 18\frac{K_2(|k|)}{|k|^2} - 36\frac{K_3(|k|)}{|k|} + 6\,K_4(|k|)$$

$$B_{2,1} = \frac{k}{|k|}\left[-14\frac{K_2(|k|)}{|k|} + 2\,K_3(|k|)\right]$$

$$B_{2,-1} = \frac{k}{|k|}\left[-6\frac{K_2(|k|)}{|k|} + 2K_3(|k|)\right]$$

$$B_{1,2} = \frac{k}{|k|}\left[-14\frac{K_2(|k|)}{|k|} + 2K_3(|k|)\right]$$

$$B_{1,0} = \frac{k}{|k|}\left[-6\sqrt{6}\frac{K_2(|k|)}{|k|} + 2\sqrt{6}K_3(|k|)\right]$$

$$B_{1,-2} = \frac{k}{|k|}\left[-6\frac{K_2(|k|)}{|k|} + 2K_3(|k|)\right]$$

and

$$B_{0,1} = \frac{k}{|k|}\left[-6\sqrt{6}\frac{K_2(|k|)}{|k|} + 2\sqrt{6}K_3(|k|)\right] \qquad (4\text{-}273)$$

where;

$$B^{2\ 2}_{q_1,q_2} = B^{2\ 2}_{-q_1,-q_2}. \qquad (4\text{-}274)$$

For the quadrupole-quadrupole interaction both k_1 and k_2 are equal to two. From Chapter IV-4-B this implies there is a contribution to the first order interruption function as well as the second order contribution.

The first order contribution is calculated from equations (4-179) and (4-186) utilizing equation (4-272) for the quadrupole-quadrupole "a" function. Thus the first order term $S_1(b)$ is found to be given by;

$$S_1(b) = iD_1\left[C_{1,i}\sum_{\Omega_i,\Omega_2} B_{1,i}\, g_0(k_\alpha) - C_{1,f}\sum_{\Omega_f,\Omega_2} B_{1,f} g_0(k_\beta)\right] \qquad (4\text{-}275)$$

where;

$$D_1 = \frac{3Q_1Q_2}{\hbar v b^4} \qquad (4\text{-}276)$$

$$C_{1,i} = \frac{J_2 J_i}{(2J_2+1)(2J_i+1)} \langle J_2 200 \mid J_2 0\rangle\langle J_i 200 \mid J_i 0\rangle \delta_{f,f'} \qquad (4\text{-}277)$$

$$B_{1,i} = C(J_i,g_i,\Omega_i,p_i)C(J_i,g_i',\Omega_i,p_i') \times$$

$$C^2(J_2,g_2,\Omega_2,p_2)H(J_i,J_i,2,p_i,p_i')H(J_2,J_2,2,p_2,p_2) \times$$

$$\langle J_i 2\Omega_i 0 \mid J_i\Omega_i\rangle\langle J_2 2\Omega_2 0 \mid J_2\Omega_2\rangle. \qquad (4\text{-}278)$$

$$g_0(k) = \frac{k^4}{48}[K_4(\mid k \mid) + 4K_2(\mid k \mid) + 3K_0(\mid k \mid) \qquad (4\text{-}279)$$

$$k_\alpha = \frac{b}{v}[E(J_i,g_i,p_i)-E(J_i,g_i',p_i')] \qquad (4\text{-}280)$$

and;

$$k_\beta = \frac{b}{v}[E(J_f,g_f,p_f)-E(J_f,g_f',p_f')]. \qquad (4\text{-}281)$$

The terms $C_{1,f}$ and $B_{1,f}$ are identical to those of $C_{1,i}$ and $B_{1,i}$ with i replaced everywhere by f. The cross sectional integral of $S_1(b)$, which appears in the matrix elements of $\bar{G}$, is given by;

$$2\pi\int S_1(b)bdb = i\pi b^2 D_1[C_{1,i}\sum_{\Omega_i,\Omega_2} B_{1,i}G_0(k_\alpha)$$

$$- C_{1,f}\sum_{\Omega_f,\Omega_2} B_{1,f}G_0(k_\beta)] \qquad (4\text{-}282)$$

where;

$$G_0(k) = \frac{k^6}{6}[K_0(\mid k \mid)+2\mid k \mid K_1(\mid k \mid)+3K_2(\mid k \mid)]. \qquad (4\text{-}283)$$

As with previously considered interactions, calculations of the second order interruption function terms $S_{2,i}(b)$, $S_{2,f}(b)$, and $S_{2,m}(b)$ necessitates evaluation of the sum of products of "a"

functions found in equation (4-191). Using equation (4-272), for the quadrupole-quadrupole "a" function, this sum of products can be expressed as;

$$\text{Sum} = \frac{32}{25}\pi^2 \frac{Q_1Q_2}{\hbar v} \frac{1}{b^8} g_3(\alpha,\beta,b) \tag{4-284}$$

where:

$$g_3(\alpha,\beta,b) = \frac{k_\alpha^4 k_\beta^4}{4608} \sum_{q_1 q_2} B_{q_1 q_2}^{2\ 2} \tag{4-285}$$

Substituting equation (4-284) into equation (4-191) yields the following form for the quadrupole-quadrupole interaction contribution $S_{2,i}(b)$;

$$S_{2,i}^{QQ}(b) = S_i C_i^{QQ} \sum_{J_2" g_2" p_2"} \sum_{J_i" g_i" p_i"} \sum_{\substack{\Omega_i,\Omega_2 \\ \Omega_i',\Omega_{2'}}} B_i(2,2) g_3(\alpha,\beta,b) \tag{4-286}$$

where;

$$C_i^{QQ} = \frac{1}{25}\left(\frac{Q_1Q_2}{\hbar v}\right)^2 \frac{1}{b^8} . \tag{4-287}$$

As before, $S_{2,f}(b)$ is identical to $S_{2,i}(b)$ with f substituted everywhere for i. The middle term $S_{2,m}(b)$ is likewise given by;

$$S_{2,m}^{QQ}(b) = C_m^{QQ} \sum_{J_2', g_2', p_2'} \sum_{\Omega_i,\Omega_2} \sum_{\Omega_f,\Omega_{2'}} B_{m,2}(2,2) g_3(\alpha,\beta,b) \tag{4-288}$$

where:

$$C_m^{QQ} = \frac{2}{25}\left(\frac{Q_1Q_2}{\hbar v}\right)^2 \frac{1}{b^8} (-1)^{J_i'+J_f'} \sqrt{(2J_i+1)(2J_f'+1)} \tag{4-289}$$

The cross sectional integral of these second order terms are calculated as with previous interaction and are given by;

$$2\pi\int_{b_0}^{\infty} S_{2,i}^{QQ}(b)bdb = \pi b_0^2 S_i C_i^{QQ} \sum_{J_2'' g_2'' p_2''} \sum_{J_i'' g_i'' p_i''} \sum_{\substack{\Omega_i,\Omega_2 \\ \Omega_i',\Omega_2''}} X$$

$$B_i(2,2)G_3(\alpha,\beta,b) \tag{4-290}$$

likewise with $S_{2,f}(b)$ and;

$$2\pi\int_{b}^{\infty} S_{2,m}^{QQ}(b)bdb = \pi b^2 C_m^{QQ} \sum_{J_2' g_2' p_2'} \sum_{\Omega_i,\Omega_2} \sum_{\Omega_f,\Omega_2'} X$$

$$B_m(2,2)G_3(\alpha,\beta,b). \tag{4-291}$$

Listed below are the equations found for g_3, G_3, g_0, and G_0, together with their properties:

$$g_3(\alpha,\beta,b) = \frac{k_\alpha^4 k_\beta^4}{2304}\left[K_4(k_\alpha)K_4(k_\beta)+8\left\lceil\frac{\alpha\beta}{\alpha\beta}\right\rceil K_3(k_\alpha)K_3(k_\beta)\right.$$

$$\left. + 28\, K_2(k_\alpha)K_2(k_\beta)+56\left\lceil\frac{\alpha\beta}{\alpha\beta}\right\rceil K_1(k_\alpha)K_1(k_\beta)+35K_0(k_\alpha)K_0(k_\beta)\right] \tag{4-292}$$

$$f_3(k_\alpha) = g_3(\alpha,\alpha,b)$$

$$= \frac{k_\alpha^8}{2304}[K_4^2(k_\alpha)+8K_3^2(k_\alpha)+28K_2^2(k_\alpha)+56K_1^2(k_\alpha)+35K_0^2(k_\alpha)] \tag{4-293}$$

$$g_3(0,\beta,b) = \frac{k_\beta^4}{48} K_4(k_\beta) \tag{4-294}$$

$$g_3(\alpha,0,b) = \frac{k_\alpha^4}{48} K_4(k_\alpha) \tag{4-295}$$

$$g_3(0,0,b) = g_3(\alpha,\beta,0) = 1 \tag{4-296}$$

$$G_3(\alpha,\beta,b) = \frac{k_\alpha^4 k_\beta^4}{27648(\beta^2-\alpha^2)}\{3\,|\,\alpha\beta\,|\,K_5(k_\alpha)K_3(k_\beta)-K_3(k_\alpha)K_5(k_\beta))$$

$$+ 32\,\alpha\beta\,(K_4(k_\alpha)K_2(k_\beta)-K_2(k_\alpha)K_4(k_\beta))$$

$$+ 168\,|\,\alpha\beta\,|\,(K_3(k_\alpha)K_1(k_\beta)-K_1(k_\alpha)K_3(k_\beta))$$

$$+ 672\,\alpha\beta\,(K_2(k_\alpha)K_0(k_\beta)-K_0(k_\alpha)K_2(k_\beta))$$

$$+ 420\,[\beta^2K_0(k_\alpha)K_2(k_\beta)-\alpha^2K_0(k_\beta)K_2(k_\alpha)$$

$$+(\alpha^2-\beta^2)(K_0(k_\alpha)K_0(k_\beta)]\} \qquad (4\text{-}297)$$

$$G_3(\alpha,-\alpha,b) = \frac{k_\alpha^8}{2304}\,[K_5(k_\alpha)K_3(k_\alpha)-8K_4(k_\alpha)K_2(k_\alpha)+28K_3(k_\alpha)K_1(k_\alpha)$$

$$- 56K_0(k_\alpha)K_2(k_\alpha)-K_4^2(k_\alpha)+8K_3^2(k_\alpha)-28K_2^2(k_\alpha)$$

$$+91K_1^2(k_\alpha)-35K_0^2(k_\alpha)] \qquad (4\text{-}298)$$

$$F_3(k_\alpha) = G_3(\alpha,\alpha,b) = \frac{k_\alpha^8}{2304}\,[K_5(k_\alpha)K_3(k_\alpha)+8K_4(k_\alpha)K_2(k_\alpha)$$

$$+ 28K_3(k_\alpha)K_1(k_\alpha)$$

$$+ 56\,K_2(k_\alpha)K_0(k_\alpha)-K_4(k_\alpha)-8K_3(k_\alpha)$$

$$- 28\,K_2(k_\alpha)-21K_1(k_\alpha)-35K_0(k_\alpha)] \qquad (4\text{-}299)$$

$$G_3(0,\beta,b) = \frac{k_\beta^3}{24}\,K_3(k_\beta) \qquad (4\text{-}300)$$

$$G_3(\alpha,0,b) = \frac{k_\alpha^3}{24}\,K_3(k_\alpha) \qquad (4\text{-}301)$$

$$G_3(0,0,b) = G_3(\alpha,\beta,0) = \frac{1}{3} \qquad (4\text{-}302)$$

$$g_0(0) = 1 \qquad (4\text{-}303)$$

$$G_0(0) = 1 \qquad (4\text{-}304)$$

The functions $f_3(k)$ and $F_3(k)$ are the functions calculated by Tsao and Curnutte when using the resolved line approximation. The functional form of g_3 and G_3 is graphically illustrated in Figures 4-7 and 4-8, respectively. Figures 4-9 and 4-10 are graphs of the function g_0 and G_0, respectively.

6. THE COUPLED LINE FORMULATION ASSUMING A SIGMA STATE PERTURBER

Thus far the deviation of the interruption function has been kept general in nature. Both the radiating and perturbing molecules have not been restricted to any particular electronic state, but have been assumed to be described by the general eigenstate of section III - 6. For the remaining work it will be assumed the perturber is in a $^1\Sigma$ electronic state. This allows for such combinations of radiator and perturber as NO-CO and NO-N_2, however a calculation of NO self broadening or NO-O_2 ($^3\Sigma_g$) broadening would necessitate the use of the general form of $S_1(b)$ and $S_2(b)$ already developed. Note that for a $^1\Sigma$ state perturber ($S = \Sigma=\Lambda=\Omega=0$) the sum over the quantum numbers Ω_2 and g_2 are no longer required and can be dropped. Since there is zero spin the form of the H function given in equation (4-181) is simpler. Examining the formulas previously derived for the general interruption function one notices that an H function involving J_2 always appears simultaneously with a Clebsch-Gordon coefficient also involving J_2. Closer examination indicates that the Clebsch-Gordon coefficients now reproduce the parity selection role of the H functions for zero spin, thus the H function can be dropped.

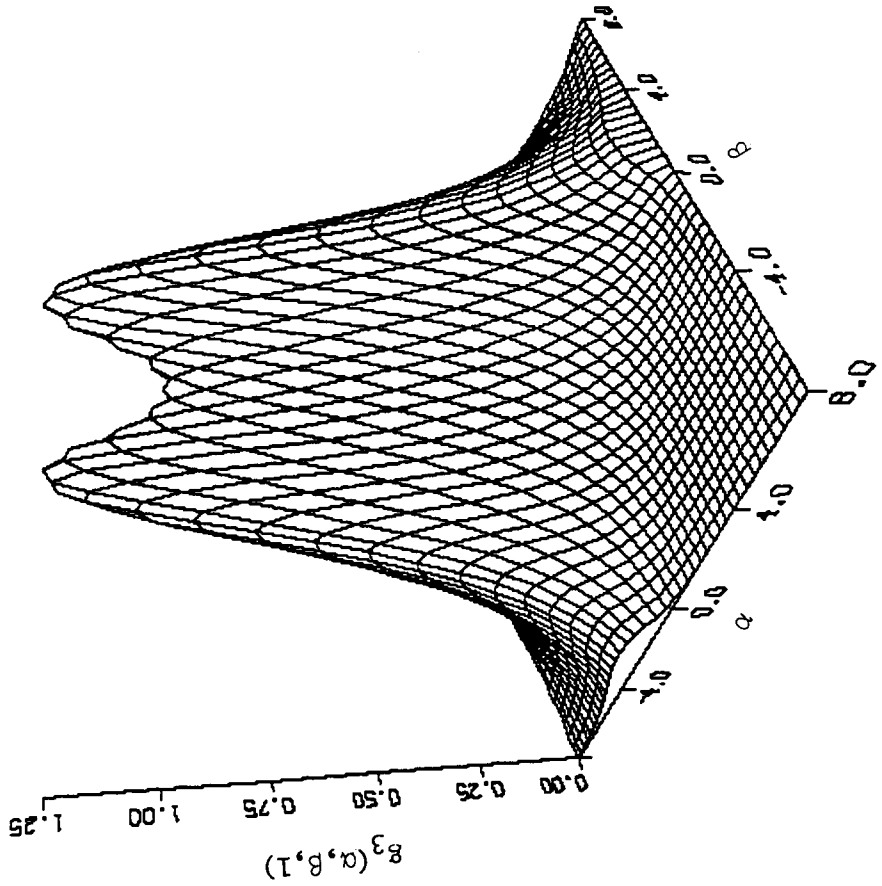

Figure 4-7. The function $g_3(\alpha,\beta,b)$. The value of b has been set to one.

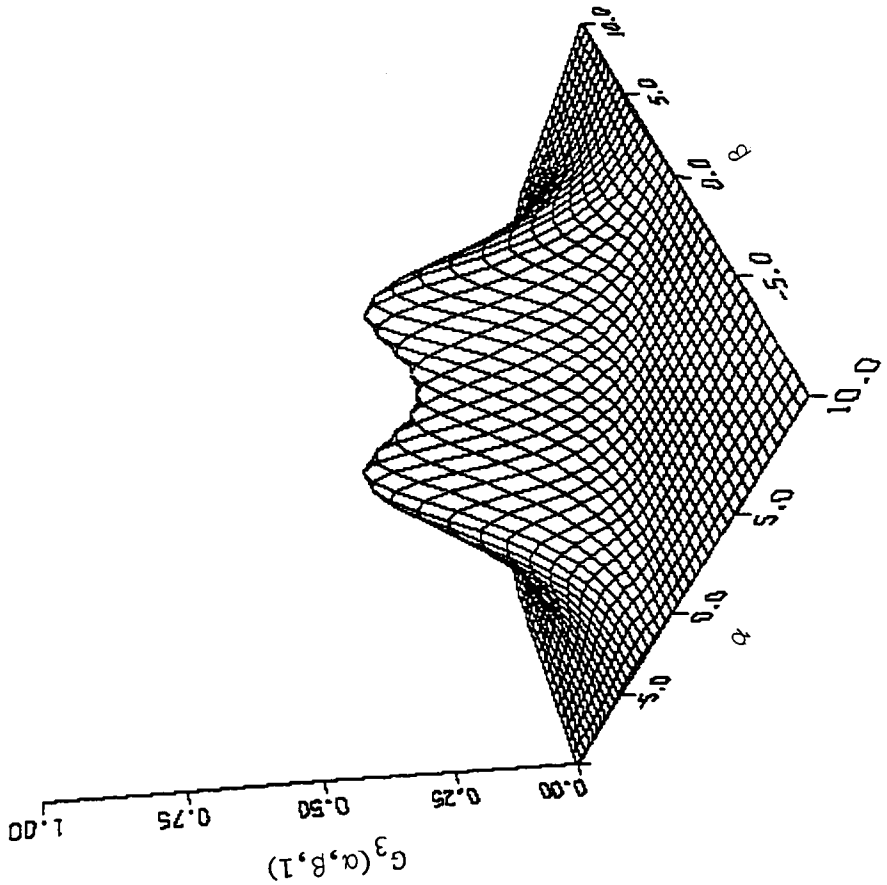

Figure 4-8. The function $G_3(\alpha,\beta,b)$. The value of b has been set to one.

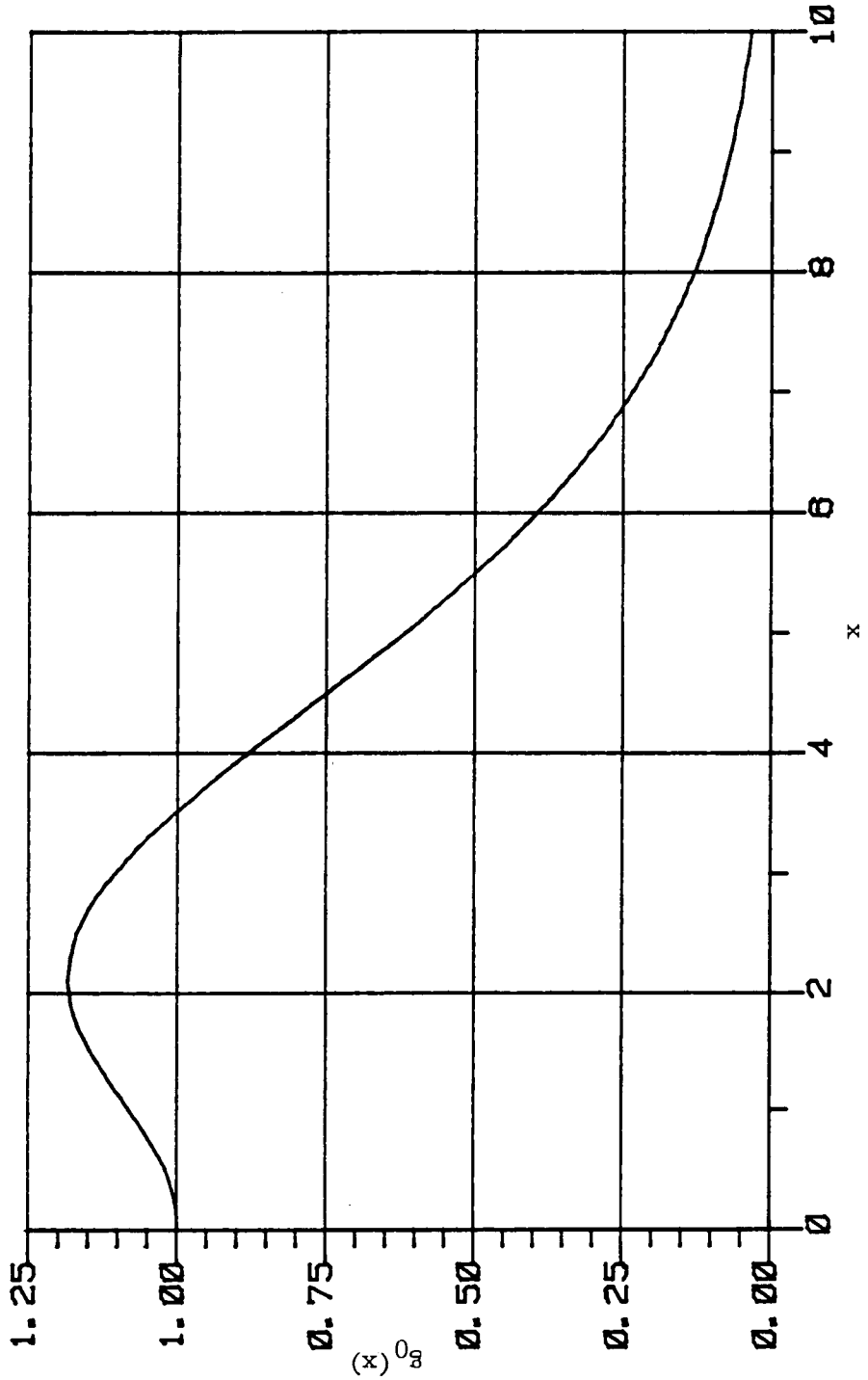

Figure 4-9. The function $g_0(x)$.

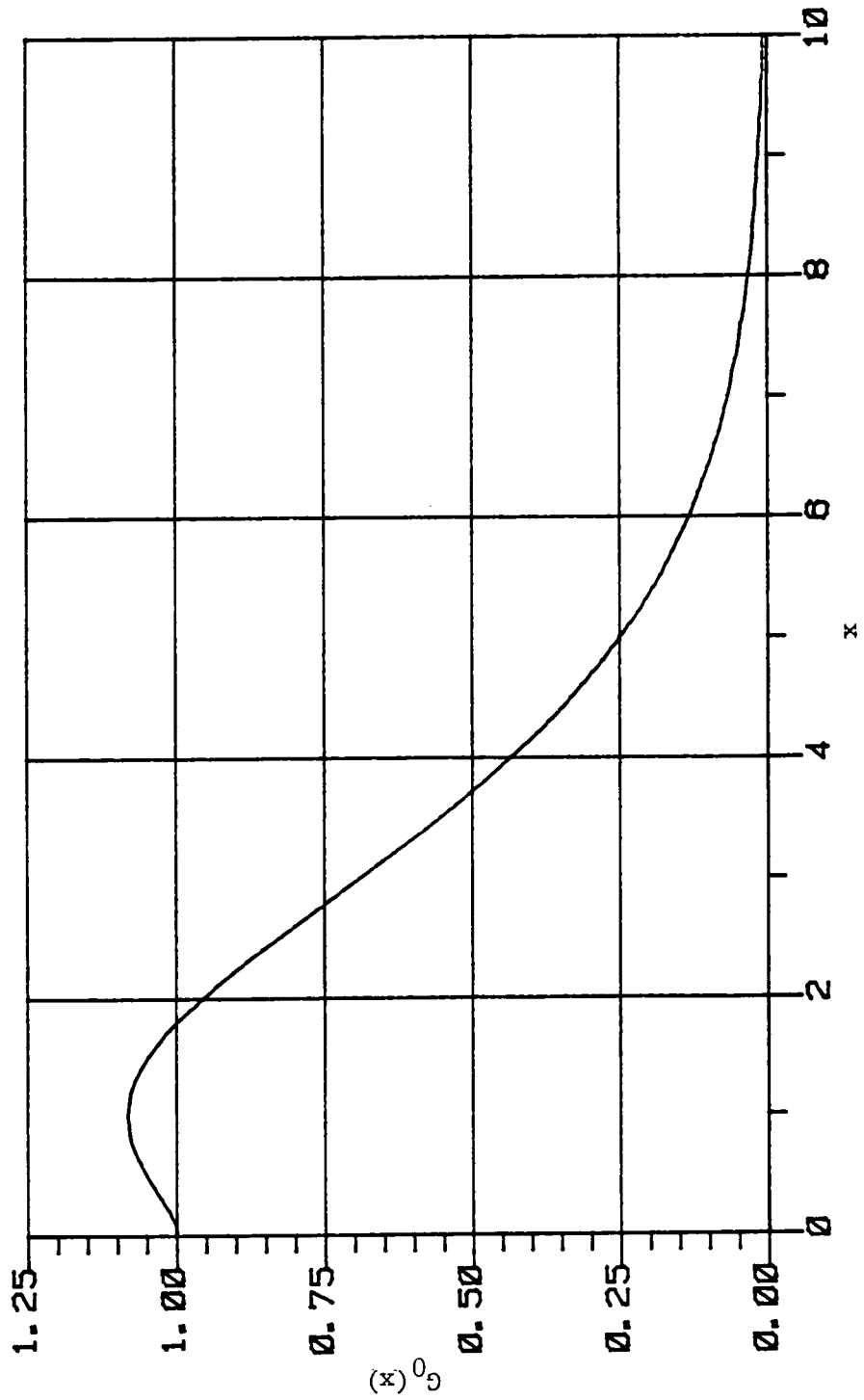

Figure 4-10. The function $G_0(x)$.

Incorporating the changes above the first and second order interruption function for a $^1\Sigma$ state perturber are formulated. The first order interruption function and its cross sectional integral given in equations (4-275) through (4-283) are modified by replacing the general definition of the coefficient B_1, equation (4-278), by the following;

$$B^{\Sigma}_{1,i} = C(J_i,g_i,\Omega_i,p_i)\ C(J_i,g_i',\Omega_i,p_i')\ X$$
$$H(J_i,J_i,2,p_i,p_i')\langle J_i 2\Omega_i 0 \mid J_i\Omega_i\rangle\langle J_2 200 \mid J_2 0\rangle \qquad (4\text{-}305)$$

similarly for $B_{1,f}$. For the second order interruption functions, the coefficients $B_i(k_1,k_2)$, equation (4-221), $B_f(k_1,k_2)$, and $B_m(k_1,k_2)$, equation (4-226), are modified according to the prescription above, yielding for $^1\Sigma$ state perturbers;

$$B^{\Sigma}_i(k_1,k_2) = C(J_i,g_i,\Omega_i,p_i)\ C(J_i'',g_i'',\Omega_i,p_i'')\ C(J_i,g_i',\Omega_i',p_i')\ X$$
$$C(J_i'',g_i'',\Omega_i',p_i'')\ H(J_i,J_i'',k_1,p_i,p_i'')\ H(J_i,J_i''k_1,p_i,p_i'')$$
$$\langle J_i k_i\Omega_i 0 \mid J_i''\Omega_i\rangle\langle J_i k_1\Omega_i',0 \mid J_i''\Omega_i',\rangle\langle J_2 k_2 00 \mid J_2''0\rangle^2 \qquad (4\text{-}306)$$

similarly for $B_f(k_1,k_2)$ and:

$$B^{\Sigma}_m(k_1,k_2) = C(J_i,g_i\Omega_i,p_i)\ C(J_i',g_i',\Omega_i,p_i')\ C(J_f',g_f',\Omega_f,p_f')$$
$$C(J_f,G_f,\Omega_f,p_f)\ H(J_i,J_i',k_1,p_i,p_i')\ H(J_f',J_f,k_1,p_f',p_f)$$
$$\langle J_i k_1\Omega_i 0 \mid J_i',\Omega_i\rangle\langle J_f,k_1\Omega_f 0 \mid J_f\Omega_f\rangle\langle J_2 k_2 00 \mid J_2',0\rangle^2$$
$$W(J_i,J_f,J_i',J_f':1,\ k_1) \qquad (4\text{-}307)$$

Thus, utilizing these modifications the formulas for $S_1(b)$, $S_2(b)$, and their cross sectional integrals for the $^1\Sigma$ state perturber can be readily obtained from those given in section IV-5. The cross sectional integrals are then used in equations (4-141) through (4-148)

for the calculation of the matrix elements of $\bar{G}$ matrix. With these matrix elements the coupled line absorption coefficient can be determined using equation (4-130).

In summary for the case of a $^1\Sigma$ state perturber the first and second order interruption function and their cross sectional integrals are as follows:

First Order:

$$S^{\Sigma}_{1,i}(b) = iD_1[C_{1,i}\sum_{\Omega_i} B^{\Sigma}_{1,i}g_0(k_\alpha)-C_{1,f}\sum_{\Omega_f} B^{\Sigma}_{1,f}g_0(k_\alpha)] \tag{4-308}$$

$$2\pi\int_b^\infty S^{\Sigma}_{1,i}(b)bdb =$$

$$i\pi b^2 S_i D_1[C_{1,i}\sum_{\Omega_i} B^{\Sigma}_{1,i}G_0(k_\alpha)-C_{1,f}\sum_{\Omega_f} B^{\Sigma}_{1,f}G_0(k_\alpha)] \tag{4-309}$$

Second Order

$$S^{\Sigma}_2(b) = \sum_n [S^{\Sigma,n}_{2,i}(b)+S^{\Sigma,n}_{2,f}(b)+S^{\Sigma,n}_{2,m}(b)] \tag{4-310}$$

$$S^{\Sigma,n}_{2,i}(b) = S_i C^n_i \sum_{J_2"} \sum_{J_i"g_i"p_i"} \sum_{\Omega_i,\Omega_{i'}} B^{\Sigma}_i(k^n_1,k^n_2)g_n(\alpha,\beta,b) \tag{4-311}$$

$$S^{\Sigma,n}_{2,m}(b) = C^n_m \sum_{J_2'} \sum_{\Omega_i,\Omega_f} B^{\Sigma}_m(k^n_1,k^n_2)g_n(\alpha,\beta,b) \tag{4-312}$$

$$2\pi\int_0^\infty S^{\Sigma}_2(b)bdb = \sum_n [2\pi\int_0^\infty S^{\Sigma,n}_{2,i}(b)bdb\ 2\pi\int_b^\infty S^{\Sigma,n}_{2,f}(b)bdb$$

$$+ 2\pi\int_b^\infty S^{\Sigma,n}_{2,m}(b)bdb]+\pi b^2\delta_{i,i'}\delta_{f,f'} \tag{4-313}$$

$$2\pi\int_b^\infty S^{\Sigma,n}_{2,i}(b)bdb =$$

$$\pi b^2 S_i C^n_i \sum_{J_2"} \sum_{J_i"g_i"p_i"} \sum_{\Omega_i,\Omega_{i'}} B^{\Sigma}_i(k^n_1,k^n_2)G_n(\alpha,\beta,b) \tag{4-314}$$

$$2\pi\int_b^\infty S_{2,m}^{\Sigma,n}(b)bdb =$$

$$\pi b^2 C_m^n \sum_{J_2'} \sum_{\Omega_i,\Omega_f} B_m^{\Sigma}(k_2^n,k_2^n)G_n(\alpha,\beta,b) \qquad (4\text{-}315)$$

The term $S_{2,f}^{\Sigma,n}(b)$ is identical to $S_{2,i}^{\Sigma,n}(b)$ with i replaced everywhere by f. The superscript n denotes the particular interaction, for example dipole-dipole, dipole-quadrupole, etc. Thus for a particular interaction the appropriate C's, g_n's and values of k_1^n and k_2^n need to be used according to those given in Chapter IV-5 for the various intermolecular potentials.

7. IMPOSING THE RESOLVED LINE APPROXIMATION ASSUMING A SIGMA STATE PERTURBER

This section focuses on the derivation of the expressions needed for a calculation of broadening paramenters of NO in the presence of $^1\Sigma$ state perturbers utilizing the resolved line approximation. From Chapter IV-1-F it was stated that for the case of the resolved line approximation the matrix $\bar{G}$ is diagonal and results in an absorption coefficient which is the sum of Lorentz line profiles. It is shown in this section that this is indeed the case and expressions for the diagonal matrix elements are derived.

Examination of equation (4-141) indicates that for the matrix $\bar{G}$ to be diagonal requires that the primed and unprimed quantum numbers involving the states of molecule 1 be equal. This translates into the following conditions on the states of molecule 1:

$$J_1' = J_i \qquad J_{f'} = J_f$$

$$p_i' = p_i \qquad p_{f'} = p_f$$

$$g_i' = g_i \qquad g_{f'} = g_f. \qquad (4\text{-}317)$$

These conditions are easily incorporated into the formula for the general interruption functions derived in Chapter IV-5. Since one of the aims of this work is the calculation of the effects of broadening of NO by CO only the $^1\Sigma$ state perturber formulation will be modified here for the resolved line approximation.

Consider the first order interruption function. From equation (4-277) and (4-278) it is readily seen that there are no changes to the terms D_1, $C_{1,i}$, or $C_{1,f}$ upon incorporating the resolved line approximation conditions. However, the $B^{\Sigma}_{1,i}$ term of equation (4-306) becomes;

$$B'^{\Sigma}_{1,i} = C^2(J_i,g_i,\Omega_i,p_i)\langle J_i 2\Omega_i 0 \mid J_i\Omega_i\rangle\langle J_2 200 \mid J_2 0\rangle \qquad (4\text{-}318)$$

similarly for $B'^{\Sigma}_{1,f}$. The prime is used to denote the quantity was derived assuming the resolved line approximation. By examining equation (4-280) one finds that k_α and k_β vanish in the resolved line approximation. Therefore, as seen from equations (4-303) and (4-304) the functions $g_0(k)$ and $G_0(k)$ become unity.

The terms appearing in the second order interruption function undergoes a little more drastic transformation under the resolved line approximation than does the first order interruption function terms. From Chapter IV-5 it is evident that the C_i and C_f terms remain unchanged. The B^{Σ} terms of the previous section are changed somewhat and are now given by;

$$B'^{\Sigma}_i(k_1,k_2) = C(J_i,g_i,\Omega_i,p_i)\ C(J_i'',g_i'',\Omega_i,p_i'')\ X$$
$$C(J_i,g_i,\Omega_i',p_i)\ C(J_i'',g_i'',\Omega_i',p_i'')\ H(J_i,J_i'',k_1,p_i,p_i'')$$
$$\langle J_i k_1 \Omega_i 0 \mid J_i''\Omega_i\rangle\langle J_i k_1 \Omega_i' 0 \mid J_i''\Omega_i'\rangle\langle J_2 k_2 00 \mid J_2''0\rangle^2 \qquad (4\text{-}319)$$

similarly for $B_f^{'\Sigma}(k_1,k_2)$, and

$$B_m^{'\Sigma}(k_1,k_2) = C^2(J_i,g_i,\Omega_i,p_i)\ C^2(J_f,g_f,\Omega_f,p_f)\ X$$

$$H(J_i,J_i,k_1,p_i,p_i)\ H(J_f,J_f,k_1,p_f,p_f)\langle J_i k_1 \Omega_i 0 \mid J_i \Omega_i\rangle$$

$$\langle J_f k_1 \Omega_f 0 \mid J_f \Omega_f\rangle\langle J_2 k_2 00 \mid J_2,0\rangle^2 W(J_i,J_f,J_i,J_f:1,k_1). \qquad (4\text{-}320)$$

The C_m terms from section IV-5 are not unsaved in the resolved line approximation, and are now given by:

$$C_m^{'\mu\mu} = \frac{8}{9}\left(\frac{\mu_1\mu_2}{h\nu}\right)^2 \frac{1}{b^4}(-1)^{J_i+J_f+1}\sqrt{(2J_i+1)(2J_f+1)} \qquad (4\text{-}321)$$

$$C_m^{'\mu Q} = \frac{8}{45}\left(\frac{\mu_1 Q_2}{h\nu}\right)^2 \frac{1}{b^6}(-1)^{J_i+J_f+1}\sqrt{(2J_i+1)(2J_f+1)} \qquad (4\text{-}322)$$

$$C_m^{'Q\mu} = \frac{8}{45}\left(\frac{\mu_2 Q_1}{h\nu}\right)^2 \frac{1}{b^6}(-1)^{J_i+J_f}\sqrt{(2J_i+1)(2J_f+1)} \qquad (4\text{-}323)$$

and

$$C_m^{'QQ} = \frac{2}{25}\left(\frac{Q_1 Q_2}{h\nu}\right)^2 \frac{1}{b^8}(-1)^{J_i+J_f}\sqrt{(2J_i+1)(2J_f+1)} \qquad (4\text{-}324)$$

By examining equation (4-217) it becomes obvious that α and β, the arguments of the g and G functions, are now identical. Thus from the properties of the g and G functions given in Chapter IV-5 it is seen that these functions become the f and F functions of Tsao and Curnutte.

The results of applying the resolved line approximation to the $^1\Sigma$ perturber interruption functions can be summarized by the following formulas for the interruption functions:

$$S_{1,i}^{'\Sigma}(b) = iD_1\left[C_{1,i}\sum_{\Omega_i} B_{1,i}^{'\Sigma} - C_{1,f}\sum_{\Omega_f} B_{1,f}^{'\Sigma}\right] \qquad (4\text{-}325)$$

$$S_{2,i}^{'\Sigma,n}(b) = S_i C_i^n \sum_{J_2''} \sum_{J_i'' g_i'' p_i''} \sum_{\Omega_i,\Omega_{i'}} B_i^{'\Sigma}(k_1^n,k_2^n) f_n(k) \qquad (4\text{-}326)$$

$$S_{2,m}^{'\Sigma,n}(b) = C_m^{'n} \sum_{J_2'} \sum_{\Omega_i,\Omega_f} B_m^{'\Sigma}(k_1^n,k_2^n) f_n(k). \qquad (4\text{-}327)$$

The term $S_{2,f}^{'\Sigma,n}(b)$ can be obtained from the term $S_{2,i}^{'\Sigma,n}(b)$ by replacing i everywhere by f. The k appearing in the function f_n of equation (4-326) is given by;

$$k = \frac{1}{v}(E_{J_i g_i p_i} + E_{J_2} - E_{J_i'' g_i'' p_i''} - E_{J_2''}) \qquad (4\text{-}328)$$

and that appering in equation (4-327) is given by;

$$k = \frac{1}{v}(E_{J_2} - E_{J_2'}). \qquad (4\text{-}329)$$

The superscript n is used to denote the various interactions. For the f_n functions the n is 1 for the dipole-dipole, 2 for the dipole-quadrupole and quadrupole-dipole, and 3 for the quadrupole-quadrupole interactions. The values of the terms k_1^n and k_2^n are those appropriate to the specific interactions according to the formulas derived in section IV-5. Therefore for the four interactions discussed here the total real interruption function is given by;

$$S_2^{'\Sigma}(b) = \sum_n [S_{2,i}^{'\Sigma,n}(b) + S_{2,f}^{'\Sigma,n}(b) + S_{2,m}^{'\Sigma,n}(b)]. \qquad (4\text{-}330)$$

The cross section integrated total interruption function is then given by;

$$\mathrm{Re}[2\pi \int_b^\infty S^{'\Sigma}(b) b db] =$$

$$\pi b^2 + \sum_n [2\pi \int_b^\infty S_2^{'\Sigma,n}(b) b db] \qquad (4\text{-}331)$$

and;

$$\mathrm{Im}[2\pi\int_b^\infty S'^{\Sigma}(b)bdb] = -2\pi i\int_b^\infty S_1'^{\Sigma}(b)bdb = -i\pi b^2 S_1'^{\Sigma}(b) \qquad (4\text{-}332)$$

where;

$$2\pi\int_b^\infty S_{2,i}'^{\Sigma;n}(b)bdb =$$

$$\pi b^2 S_i C_i'^n \sum_{J_2''} \sum_{J_i'' g_i'' p_i''} \sum_{\Omega_i,\Omega_{i'}} B_i'^{\Sigma}(k_1^n,k_2^n)F_n(k) \qquad (4\text{-}333)$$

$$2\pi\int_b^\infty S_{2,m}'^{\Sigma,n}(b)bdb =$$

$$\pi b^2 C_m'^n \sum_{J_2'} \sum_{\Omega_i,\Omega_f} B_m'^{\Sigma}(k_1^n,k_2^n)F_n(k) \qquad (4\text{-}334)$$

and:

$$2\pi\int_b^\infty S_1'^{\Sigma,n}(b)bdb = \pi b^2\ S_1'^{\Sigma,n}(b) \qquad (4\text{-}335)$$

Consider now the general form of the absorption coefficient for the coupled line spectrum in equation (4-121). Note, from equations (4-115) and (4-118), that both $\bar{w}_0$ and $\bar{w}$ are diagonal matrices. Since the $\bar{G}$ matrix is also assumed diagonal in the resolved line approximation, equation (4-121) becomes:

$$k(\omega) = C \sum_{\substack{J_i\alpha_i \\ J_f\alpha_f}} \rho'_{J_i\alpha_i}\ (-1)^{J_f-J_i+1}\ |\langle J_f\alpha_f||\mu^1||J_i\alpha_i\rangle|^2\ X$$

$$\mathrm{Re}[(\omega_{if}-\omega)-G_{if}]^{-1} \qquad (4\text{-}336)$$

where α represents the quantum numbers g and p. Using the fact that the first order interruption function is imaginary and the second order one is real a diagonal G matrix element can be written as,

$$G_{if} = (-1)^{J_f-J_i}(\gamma_{if}+i\Delta_{if}) \qquad (4\text{-}337)$$

where;

$$\gamma_{if} = F_1 \sum_{J_2} \rho'_{J_2} \, \mathrm{Re}\left(2\pi \int_{b_0}^{\infty} S'^{\Sigma}(b) b db\right) \tag{4-338}$$

and:

$$\Delta_{if} = F_1 \sum_{J_2} \rho'_{J_2} \left(-i 2\pi \int_{b_0}^{\infty} S_1'^{\Sigma}(b) b db\right) \tag{4-339}$$

The impact parameter b_0 is determined from the use of Anderson's cutoff procedure of Chapter IV-3-E. Substituting equation (4-337) into equation (4-336) yields;

$$k(\omega) = C \sum_{\substack{J_i p_i g_i \\ J_f p_f g_f}} \rho_{J_i p_i g_i} \left| \langle J_f g_f p_f \left| \mu^1 \right| J_i g_i p_i \rangle \right|^2 X$$

$$\frac{\gamma_{if}}{(\omega_{if} - \omega - \Delta_{if})^2 + \gamma_{if}^2} . \tag{4-340}$$

In the above the term "if" is understood to represent the set of quantum numbers $\{J_i g_i p_i J_f g_f p_f\}$.

Therefore, the coupled line formulation reduces to a sum over Lorentz line shapes in the resolved line approximation. The term γ_{if} is the halfwidth at half maximum (HWHM) in units of wave numbers (cm^{-1}) and Δ_{if} is the spectral line shift, also in units of wave numbers. From equations (4-338) and (4-143) the HWHM can be expressed in terms of a pressure independent broadening parameter, γ^0_{if} as;

$$\gamma_{if} = P_B \, \gamma^0_{if} \tag{4-341}$$

where;

$$\gamma^0_{if} = \frac{vd}{2\pi c k_B T} \sum_{J_2} \rho'_{J_2} \mathrm{Re}[\sigma'_{J_2}], \tag{4-342}$$

$$\mathrm{Re}[\sigma'_{J_2}] = \pi b_0^2 + 2\pi \int_{b_0}^{\infty} [1 + S_2'^{\Sigma}(b)] b db, \tag{4-343}$$

ρ'_{J_2} is given in equation (4-140), k_B is Boltzmann's constant, and P_B is the partial pressure of the perturbing species in units of atmospheres. Likewise the line shift can be written as;

$$\Delta_{if} = P_B \Delta^0_{if} \tag{4-344}$$

where;

$$\Delta^0_{if} = \frac{vd}{2\pi c k_B T} \sum_{J_2} \rho'_{J_2} \sigma_{1,J_2} \tag{4-345}$$

and;

$$\sigma_{1,J_2} = 2\pi \mathrm{Im}\left[\int_{b_0}^{\infty} S_1^{'\Sigma}(b) b db\right]. \tag{4-346}$$

Note that γ^0_{if} and Δ^0_{if} have units of cm^{-1} atm^{-1}.

8. REDUCTION OF COUPLED LINE RESULTS TO THOSE OF TSAO AND CURNUTTE

Here it will be demonstrated that the formulation given in this work reduces to that of Tsao and Curnutte under the appropriate conditions. The two conditions to be met are the assumption of the resolved line approximation and symmetric top rotational eigenstates. These are necessary since they are the primary conditions in the derivation by Tsao and Curnutte. In fact, these are the very conditions which are removed in order to obtain the coupled line spectrun given in this work.

The first condition to be considered, the symmetric top rotational eigenstates, requires that the discussion digress back to Chapters I and II. Note from Chapter III, equation (3-79), the general eigenstates of a molecule, in an intermediate Hund's case A and Hund's case B angular momentum coupling scheme, are given by:

$$\left| pnJMg\right\rangle = \sum_{\Omega} C(J,g,\Omega,p) \left| pn\Lambda S\Sigma JM-\Omega\right\rangle_R. \tag{4-347}$$

The eigenstates represented by $\left| pn\Lambda S\Sigma JM-\Omega\right\rangle_R$ are the basis set eigenstates used in the perturbative solution of the molecular Schrodinger equation. If all off diagonal Hamiltonian matrix elements are ignored these eigenstates become eigenstates of the Hamiltonian. In this case, the rotational energy eigenvalues, equations (3-23)-(3-26), become;

$$E_{J\Omega S\Sigma G} = Bv[J(J+1)+S(S+1)-\Omega^2-\Sigma^2]$$
$$+\varepsilon_v[3\Sigma^2-S(S+1)]+A_v\Lambda\Sigma-\gamma_v[S(S+1)-\Omega\Sigma]. \tag{4-348}$$

From equation (4-348) it is easily seen that in the case of vanishing off diagonal matrix elements the expansion coefficients become;

$$C(J,g,\Omega,p) = \delta_{g,\Omega}. \tag{4-349}$$

Examine now the eigenstates $\left| pn\Lambda S\Sigma JM-\Omega\right\rangle_R$. From equation (3-1) these parity eigenstates are defined by;

$$\left| pn\Lambda S\Sigma JM-\Omega\right\rangle_R = \frac{1}{\sqrt{2}}\left[\left| n\Lambda S\Sigma JM-\Omega\right\rangle_R \right.$$
$$\left. + p \left| n\Lambda S\Sigma JM\Omega\right\rangle_R\right]. \tag{4-350}$$

Utilizing equations (1-96) and (1-68) the coordinate representation of the eigenstates above is given by;

$$\langle\rho\theta\phi\psi \left| n\Lambda S\Sigma JM-\Omega\right\rangle_R =$$
$$(-1)^{J-\Omega}\left(\frac{2J+1}{8\pi^2}\right)^{1/2}\langle\rho \left| n\Lambda S\Sigma\right\rangle d^{*J}_{M,\Omega}(\theta\phi\psi) \tag{4-351}$$

Note that outside the electronic eigenfunction $\langle\rho \left| n\Lambda S\Sigma\right\rangle$ and the arbitrary phase factor $(-1)^{J-\Omega}$ the above eigenstate is a rotational

symmetric top eigenstate. Thus it has been determined that if all off diagonal matrix elements in the rotational Hamiltonian are ignored the general molecular rotational eigenstates of Chapter III meet the first condition set forth above.

Consider now the results of imposing the resolved line approximation on the form of the general interruption functions of section IV-5. Note that in the case presented here the parity states are degenerate, therefore the resolved line condition becomes:

$$J_i = J_{i'} \qquad J_f = J_{f'}$$
$$g_i = g_{i'} \qquad g_f = g_{f'} \tag{4-352}$$

Imposing this condition in conjunction with equation (4-349) yields the following form for the interruption functions;

$$S_1(b) = iD_1 \left[C_{1,i} \sum_{\Omega_i \Omega_2} \ddot{B}_{1,i} - C_{1,f} \sum_{\Omega_f,\Omega_2} \ddot{B}_{1,f}\right], \tag{4-353}$$

$$S^n_{2,i}(b) = S_i C^n_i \sum_{J_2" p_2" g_2"} \sum_{J_i" g_i" p_i"} \sum_{\substack{\Omega_i,\Omega_{i'} \\ \Omega_2,\Omega_{2'}}} \ddot{B}_i(k^n_1,k^n_2) f_n(k) \tag{4-354}$$

similarly for $S_{2,f}(b)$, and;

$$S^n_{2,m}(b) = C^{n'}_m \sum_{J_2',g_2',p_2'} \sum_{\substack{\Omega_i,\Omega_2 \\ \Omega_f,\Omega_{2'}}} \ddot{B}_m(k^n_1,k^n_2) f_n(k), \tag{4-355}$$

where;

$$\ddot{B}_{1,i} = \delta_{g_i,\Omega_i} \delta_{g_2,\Omega_2} \delta_{p_i,p_{i'}} \langle J_i 2\Omega_i 0 \mid J_i \Omega_i \rangle \langle J_2 2\Omega_2 0 \mid J_2 \Omega_2 \rangle, \tag{4-356}$$

$$B_i''(k_1,k_2) =$$

$$\delta_{g_i,\Omega_i}\,\delta_{g_i',\Omega_i}\,\delta_{g_2,\Omega_2}\,\delta_{g_2'',\Omega_2}\,\delta_{g_i\,\Omega_i'},\,\delta_{g_i''\,\Omega_i},\,\delta_{g_2,\Omega_2''}\;X$$

$$\delta_{g_2'',\Omega_2''}\;H(J_i,J_i'',k_1,p_i,p_i'')\;H(J_i,J_i'',k_1,p_i',p_i'')\;X$$

$$H(J_2,J_2'',k_2,p_2,p_2'')\;X$$

$$\langle J_i k_1 \Omega_i 0 \mid J_i''\Omega_i\rangle\langle J_i k_1 \Omega_i' 0 \mid J_i''\Omega_i'\rangle\langle J_2 k_2 \Omega_2 0 \mid J_2''\Omega_2\rangle\;X$$

$$\langle J_2 k_2 \Omega_2'' 0 \mid J_2''\Omega_2''\rangle \qquad (4\text{-}357)$$

similarly for $B_f''(k_1,k_2)$ and $B_{1,f}''$, and;

$$B_m''(k_1,k_2) = \delta_{g_i,\Omega_i}\,\delta_{g_2,\Omega_2}\delta_{g_2',\Omega_2}\;\;\delta_{g_f,\Omega_f}\delta_{g_2',\Omega_2'}\;X$$

$$\delta_{g_2,\Omega_2'}\;H(J_2',J_2,k_2,p_2',p_2)\;H(J_i,J_i,k_1,p_i,p_i')\;X$$

$$H(J_f,J_f,k_1,p_f',p_f)\langle J_i k_1 \Omega_i 0 \mid J_i\Omega_i\rangle\langle J_f k_1 \Omega_f 0 \mid J_f\Omega_f\rangle\;X$$

$$\langle J_2 k_2 \Omega_2 0 \mid J_2,\Omega_2\rangle\langle J_2 k_2 \Omega_2' 0 \mid J_2,\Omega_2'\rangle W(J_i,J_f,J_i,J_f{:}1,k_1). \qquad (4\text{-}358)$$

Performing the sums over the Kronker delta functions yields the following form for $S_1(b)$:

$$S_1(b) = iD_1[C_{1,i}B_{1,i}''-C_{1,f}B_{1,f}''] \qquad (4\text{-}359)$$

where $B_{1,i}''$, is given by:

$$B_{1,i}'' = \langle J_i 2\Omega_i 0 \mid J_i\Omega_i\rangle\langle J_2 2\Omega_2 0 \mid J_2\Omega_2\rangle\delta_{p_i,p_i'} \qquad (4\text{-}360)$$

The term $B_{1,f}''$ is identical to $B_{1,i}$ with i replaced everywhere by f.

The terms $S_{2,i}^n(b)$ and $S_{2,m}(b)$ become $S_{2,m}^n(b)$ become;

$$S_{2,i}^n(b) = S_i C_i^n \sum_{J_2''p_2''} \sum_{J_i''p_i''} B_i''(k_1^n,k_2^n) f_n(k) \qquad (4\text{-}361)$$

and;

$$S_{2,m}^n(b) = C_m^{n'} \sum_{J_2',p_2'} B_m''(k_1^n,k_2^n) f_n(k) \qquad (4\text{-}362)$$

where;

$$\overset{\cdot\cdot}{B}_i(k_1,k_2) = H(J_i,J_i{\cdot\cdot},k_1,p_i,p_i{\cdot\cdot})\ H(J_i,J_i{\cdot\cdot},k_1,p_i,p_i{\cdot\cdot})\ X$$
$$H(J_2,J_2{\cdot\cdot},k_2,p_2,p_2{\cdot\cdot})\langle J_i k_1 \Omega_i 0 \mid J_i{\cdot\cdot}\Omega_i\rangle^2\langle J_2 k_2 \Omega_2 0 \mid J_2{\cdot\cdot}\Omega_2\rangle^2 \qquad (4\text{-}363)$$

and;

$$\overset{\cdot\cdot}{B}_m(k_1,k_2) = H(J_2{\cdot},J_2,k_2,p_2{\cdot},p_2)\ H(J_i,J_i,k_1,p_i,p_i{\cdot})\ X$$
$$H(J_f,J_f,k_1,p_f{\cdot},p_f)\langle J_i k_1 \Omega_i 0 \mid J_i\Omega_i\rangle\ X$$
$$\langle J_f k_1 \Omega_f 0 \mid J_f\Omega_f\rangle\langle J_2 k_2 \Omega_2 0 \mid J_2{\cdot},\Omega_2\rangle^2\ X$$
$$W(J_i,J_f,J_i,J_f{:}1,k_1). \qquad (4\text{-}364)$$

Summing over $p_i{\cdot\cdot}$ and $p_2{\cdot\cdot}$ in equation (4-361) yields;

$$S^n_{2,i}(b) = S_i C^n_i \sum_{J_2{\cdot\cdot}J_i{\cdot\cdot}} \overset{\cdot\cdot}{B}_i(k^n_1,k^n_2)\ f_n(k) \qquad (4\text{-}365)$$

where;

$$\overset{\cdot\cdot}{B}_i(k_1,k_2) = \langle J_i k_1 \Omega_i 0 \mid J_i{\cdot\cdot}\Omega_i\rangle^2\langle J_2 k_2 \Omega_2 0 \mid J_2{\cdot\cdot}\Omega_2\rangle^2 \qquad (4\text{-}366)$$

and similarly for $\overset{\cdot\cdot}{B}_f(k_1,k_2)$.

Summing over $p_2{\cdot}$ in equation (4-362) yields;

$$S^n_{2,m}(b) = C^{n'}_m \sum_{J_2{\cdot}} \overset{\cdot\cdot}{B}_m(k^n_1,k^n_2) f_n(k) \qquad (4\text{-}367)$$

where:

$$\overset{\cdot\cdot}{B}_m(k_1,k_2) = H(J_i,J_i,k_1,p_i,p_i{\cdot})\ H(J_f,J_f,k_1,p_f{\cdot},p_f)$$
$$\langle J_i k_1 \Omega_i 0 \mid J_i\Omega_i\rangle\langle J_f k_1 \Omega_f 0 \mid J_f\Omega_f\rangle\langle J_2 k_2 \Omega_2 0 \mid J_2{\cdot},\Omega_2\rangle^2$$
$$W(J_i,J_f,J_i,J_f{:}1,k_1) \qquad (4\text{-}368)$$

In order to further reduce equation (4-368) it is necessary to examine the absorption coefficient of (4-130) which for this case is given by;

$$k(\omega) \alpha \sum_{p_i p_f} \langle J_f g_f p_f \,||\, \mu^1 \,||\, J_i g_i p_i \rangle \; X$$

$$\sum_{p_i', p_f'} [i(\bar{\omega}_0 - \bar{\omega}) - \bar{G}]^{-1}_{p_i, p_f : p_i', p_f'} \langle J_i g_i p_i' \,||\, \mu^1 \,||\, J_f g_f p_f' \rangle . \tag{4-369}$$

For specific values of p_i and p_i', the dipole parity selection rule allows only specific values of p_f and p_f', therefore the sum over p_f and p_f' will be dropped. Since the dipole moment reduced matrix element is now independent of p_i, equation (4-369) can now be written as:

$$k(\omega) \alpha \sum_{p_i} | \langle J_f g_f p_f \,||\, \mu^1 \,||\, J_i g_i p_i \rangle |^2 \; X$$

$$\sum_{p_i'} [i(\bar{\omega} - \bar{\omega}_0) - \bar{G}]^{-1}_{p_i : p_i'} \tag{4-370}$$

For the case here it can easily be shown that the sum can be incorporated in the matrix itself. Therefore the matrix is now diagonal and the interruption functions must also include a sum over p_i', (or p_f', for $S_{1,f}$ and $S_{2,f}$). Notice that the additional summation is absorbed by the presence of the Kronker delta function $\delta_{p_i, p_i'}$, in the B terms with the exception of $B_m(k_1, k_2)$. Summation of the two H functions of equation (4-368) over the quantum number p_i', yields unity, therefore $\ddot{B}_m(k_1, k_2)$ becomes:

$$\ddot{B}_m(k_1, k_2) = \langle J_i k_1 \Omega_i 0 \,|\, J_i \Omega_i \rangle \langle J_f k_1 \Omega_f 0 \,|\, J_f \Omega_f \rangle \; X$$

$$\langle J_2 k_2 \Omega_2 0 \,|\, J_2, \Omega_2 \rangle^2 \; W(J_i J_f J_i J_f : 1, k_1) \tag{4-371}$$

In summary, upon imposing the conditions of symmetric top eigenstates and the resolved line approximation the following forms for the second order interruption function appear;

$$S_{2,i}^{n}(b) = C_{i}^{n} \sum_{J_{2}",J_{i}"} B_{i}^{"}(k_{1}",k_{1}")f_{n}(k) \tag{4-372}$$

similarly for $S_{2,f}^{n}$, and;

$$S_{2,m}^{n}(b) = C_{m}^{n'} \sum B_{m}^{"}(k_{1}^{n},k_{2}^{n})f_{n}(k) \tag{4-373}$$

where $B_{i}^{"}$ and $B_{m}^{"}$ are given in equations (4-366) and (4-371), respectively. The cross sectional integrals are therefore given by;

$$2\pi\int_{b}^{\infty} S_{2,i}(b)bdb = \pi b^{2} C_{i}^{n} \sum_{J_{2}",J_{i}"} B_{i}^{"}(k_{1}^{n},k_{1}^{n})F_{n}(k) \tag{4-374}$$

and;

$$2\pi\int_{b}^{\infty} S_{2,m}^{n}(b)bdb = \pi b^{2} C_{m}^{n'} \sum_{J_{2}'} B_{m}^{"}(k_{1}^{n},k_{2}^{n})F_{n}(k). \tag{4-375}$$

These are the same formulas as given by Tsao and Curnutte for the second order interruption function. Therefore the formulas for the HWHM as given in equations (4-342) and (4-343) reduce to those arrived at by Tsao and Curnutte when one uses the interruption functions above.

CHAPTER V

COMPUTATIONAL RESULTS OF PRESSURE BROADENING

EFFECTS OF CO ON NO

Presented here are the results of a computational study of the broadening effects of CO on several lines in the fundamental band of NO. The three different formulations of the broadening theory as discussed in Chapter IV are employed here. These theories are the ATC theory assuming symmetric top rotational eigenstates and the resolved line approximation, the modified ATC theory incorporating the parity (Λ doublet) eigenstates of NO, and the coupled line theory utilizing the NO parity eigenstates. All three computational efforts incorporated the four intermolecular potentials of Chapter IV. The CO rotational energies used here were calculated using the rotational constants B_e, D_e, α, and β given by Herzberg [52] as 1.93128087 cm^{-1}, $6.1214X10^{-6}cm^{-1}$, $1.750441X10^{-2}cm^{-1}$, and $-1.15X10^{-9}cm^{-1}$, respectively. The molecular electric multipole moments used here are those suggested by Stogryn and Stogryn [53]; $1.59X10^{-19}$ esu cm for the dipole moment of NO (μ_{NO}), $1.12X10^{-19}$ esu cm for the dipole moment of CO (μ_{CO}), $2.4X10^{-26}$ esu cm^2 for the quadrupole moment of NO (Q_{NO}), and $4.6X10^{-46}$ esu cm^2 for the value of the quadrupole moment of CO(Q_{CO}).

All calculations were performed on a VAX 11/785 computer using programs written in FORTRAN. Each program, with the exception of the plotting programs, was written utilizing IMPLICIT DOUBLE PRECISION real variables (8 byte words) in order to preserve precision.

1. ATC THEORY RESULTS

The ATC theory formulation of the collision halfwidths as given in section IV-8 was utilized here to calculate the halfwidths for several fundamental band NO lines broadened by CO. From Chapter IV the assumptions made are that the rotational eigenstates of NO are those of a symmetric top molecule and the resolved line approximation is valid. Therefore, the lambda doublets are treated as a single spectral line. The lines examined were the P(1.5) through the P(20.5) and the R(0.5) through the R(19.5) in both the 1/2 and 3/2 subband at 300K. Also, the halfwidths of the P(4.5), P(5.5), P(6.5), and P(20.5) lines of the 1/2 and 3/2 subband were calculated for the temperature range of 300 to 1000K. The line shifts were not calculated in this case but are presented for a few lines in the coupled spectral line case presented later. An extensive set of calculations could be made utilizing this theory since only 10 seconds of CPU time was required for each halfwidth calculated.

The results of the calculations are tabulated in Tables 5-1 and 5-2 and are plotted in Figures 5-1 through 5-5. It was found that for all three cases presented in this chapter the same halfwidths or $\bar{G}$ matrix elements were predicted for the R and P branch lines possessing the same value of $|m|$ ($m = -J$ for the P branch and $m = J+1$ for the R branch). Note from Figure 5-1 that for $2|m|$ values of 29 or less the 3/2 subband halfwidths are larger than those of the 1/2 subband with the maximum percent difference being 2.8% for a $2|m|$ value of seven. Figures 5-2 through 5-5 indicate the difference in the halfwidths for

Table 5-1. Computed Halfwidths of NO Pressure Broadened by CO.

$\gamma^0(T_0)$ $cm^{-1}atm^{-1}$, T_0 = 300K						
	ATC Theory		Resolved Line Approximation with Parity Eigenstates			
			$g = \frac{1}{2}$		$g = \frac{3}{2}$	
$2\|m\|$	$\Omega = \frac{1}{2}$	$\Omega = \frac{3}{2}$	$P_T = -1$	$P_T = +1$	$P_T = -1$	$P_T = +1$
3	.064549	--	.064831	.064830	--	--
5	.062998	.064214	.063105	.063104	.065148	.065148
7	.062069	.063850	.062127	.062129	.064311	.064311
9	.060821	.062509	.060865	.060860	.062794	.062794
11	.059289	.060806	.059323	.059328	.061014	.061014
13	.057832	.059138	.057866	.057862	.059293	.059293
15	.056695	.057779	.056723	.056726	.057901	.057901
17	.055906	.056775	.055932	.055931	.056872	.056872
19	.055346	.056018	.055368	.055369	.056098	.056098
21	.054861	.055360	.054882	.054881	.055427	.055427
23	.054321	.054674	.054340	.054342	.054732	.054732
25	.053644	.053874	.053665	.053663	.053926	.053925
27	.052789	.052918	.052810	.052812	.052965	.052966
29	.051752	.051798	.051778	.051775	.051843	.051842
31	.050545	.050528	.050572	.050575	.050568	.050569
33	.049198	.049132	.049233	.049230	.049170	.049169
35	.047745	.047646	.047782	.047786	.047678	.047680
37	.046220	.046103	.046268	.046265	.046134	.046132
39	.044664	.044538	.044713	.044717	.044564	.044565
41	.043102	.042978	.043161	.043158	.043003	.043001

Table 5-2. Temperature Dependent Halfwidth Calculation Results using the ATC Theory.

	$P(4.5)_{\frac{1}{2}}$	$P(4.5)_{\frac{3}{2}}$	$P(5.5)_{\frac{1}{2}}$	$P(5.5)_{\frac{3}{2}}$	$P(6.5)_{\frac{1}{2}}$	$P(6.5)_{\frac{3}{2}}$	$P(20.5)_{\frac{1}{2}}$	$P(20.5)_{\frac{3}{2}}$
γ^0 (300K) $cm^{-1}atm^{-1}$	.06082	.06251	.05929	.06080	.05783	.05914	.04310	.04298
γ^0 (400K) $cm^{-1}atm^{-1}$	.04997	.05109	.04904	.05003	.04795	.04883	.03819	.03802
γ^0 (500K) $cm^{-1}atm^{-1}$	.04270	.04356	.04218	.04290	.04142	.04205	.03427	.03413
γ^0 (600K) $cm^{-1}atm^{-1}$	.03742	.03814	.03717	.03774	.03667	.03715	.03104	.03094
γ^0 (700K) $cm^{-1}atm^{-1}$	.03339	.03403	.03330	.03379	.03301	.03340	.02835	.02829
γ^0 (800K) $cm^{-1}atm^{-1}$	.03021	.03079	.03023	.03067	.03007	.03041	.02610	.02608
γ^0 (900K) $cm^{-1}atm^{-1}$	.02763	.02818	.02771	.02811	.02765	.02796	.02421	.02420
γ^0 (1000K) $cm^{-1}atm^{-1}$	.02549	.02601	.02561	.02599	.02562	.02590	.02259	.02259
γ^0_{fit} (300K) $cm^{-1}atm^{-1}$	.06139	.06292	.05985	.06108	.05823	.05934	.04432	.04411
n_{fit}	.73278	.72916	.69763	.70347	.67554	.68294	.54151	.53789

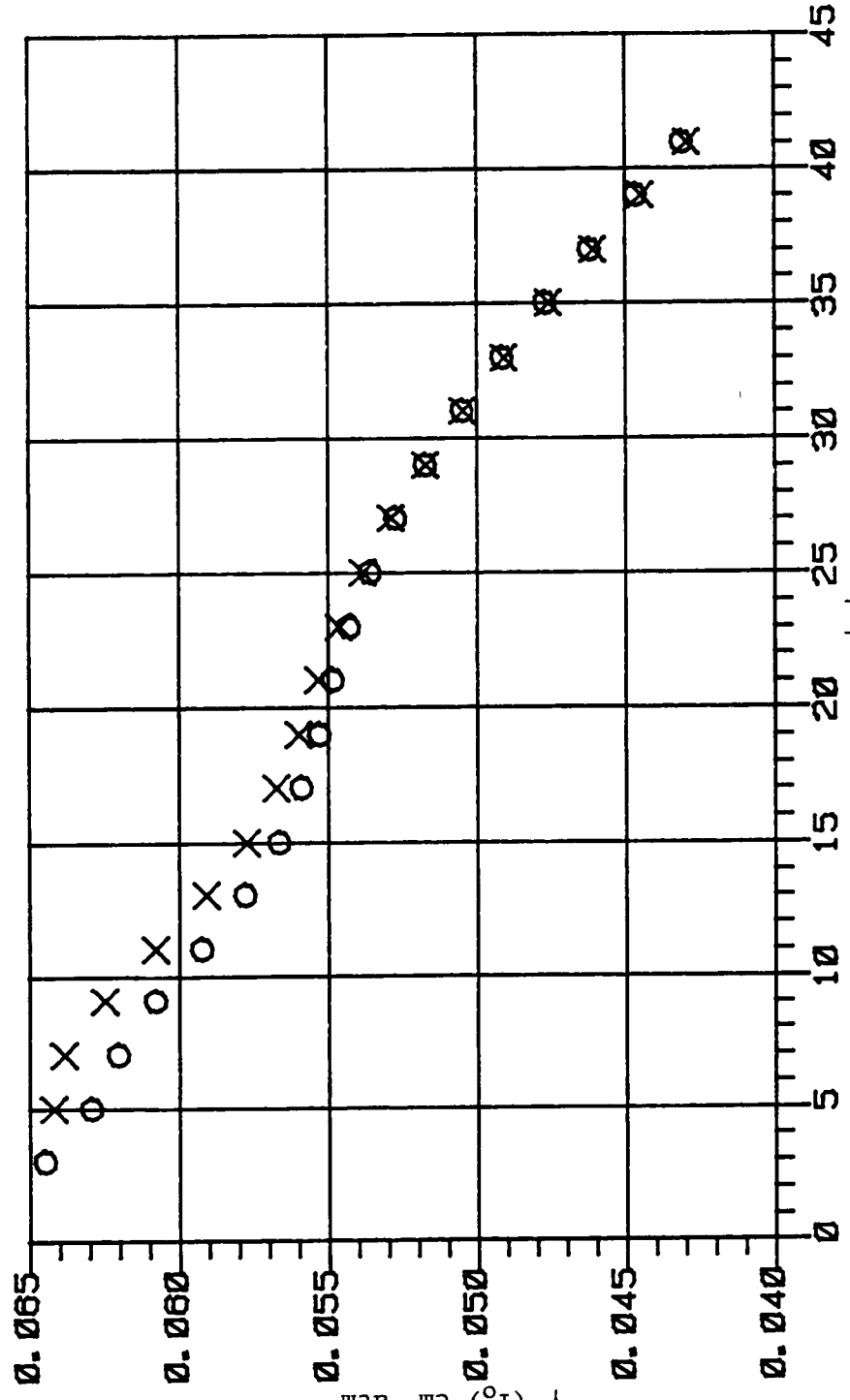

Figure 5-1. Calculated collison halfwidths of NO broadened by CO at a temperature of 300K. The symbol 0 represents spectral lines of the 1/2 subband and X represents the 3/2 subband.

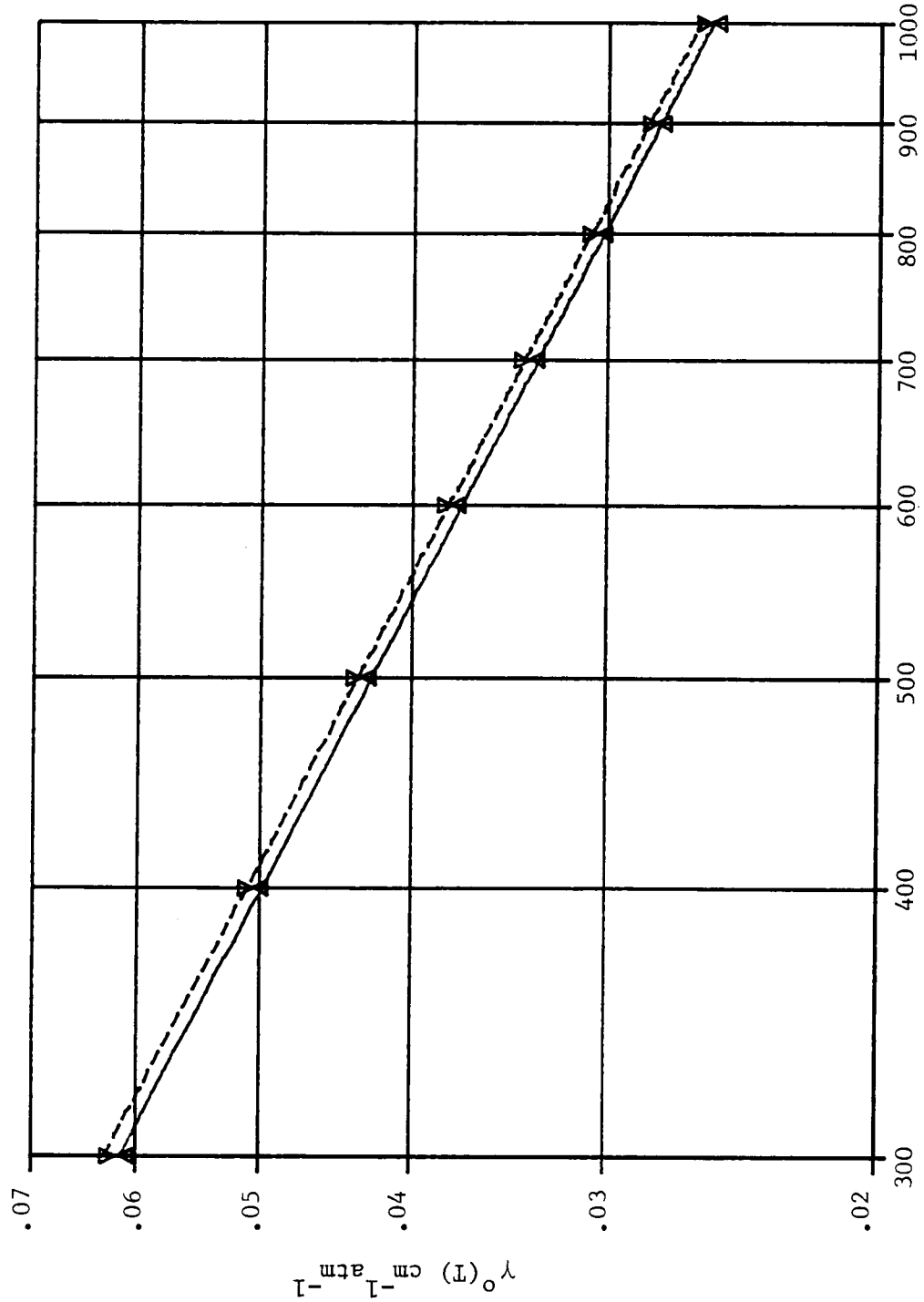

Figure 5-2. $\gamma^o(T)$ vs. T for the $P_{1/2}(4.5)$ and $P_{3/2}(4.5)$ spectral lines of NO broadened by CO. The symbols Δ and ∇ represent the half widths of the 1/2 and 3/2 subband, respectively. The curves ——— and - - - - - are the curve fits using Birnbaum's formula for the 1/2 and 3/2 subband, respectively. The fit parameters are given in Table 5-2.

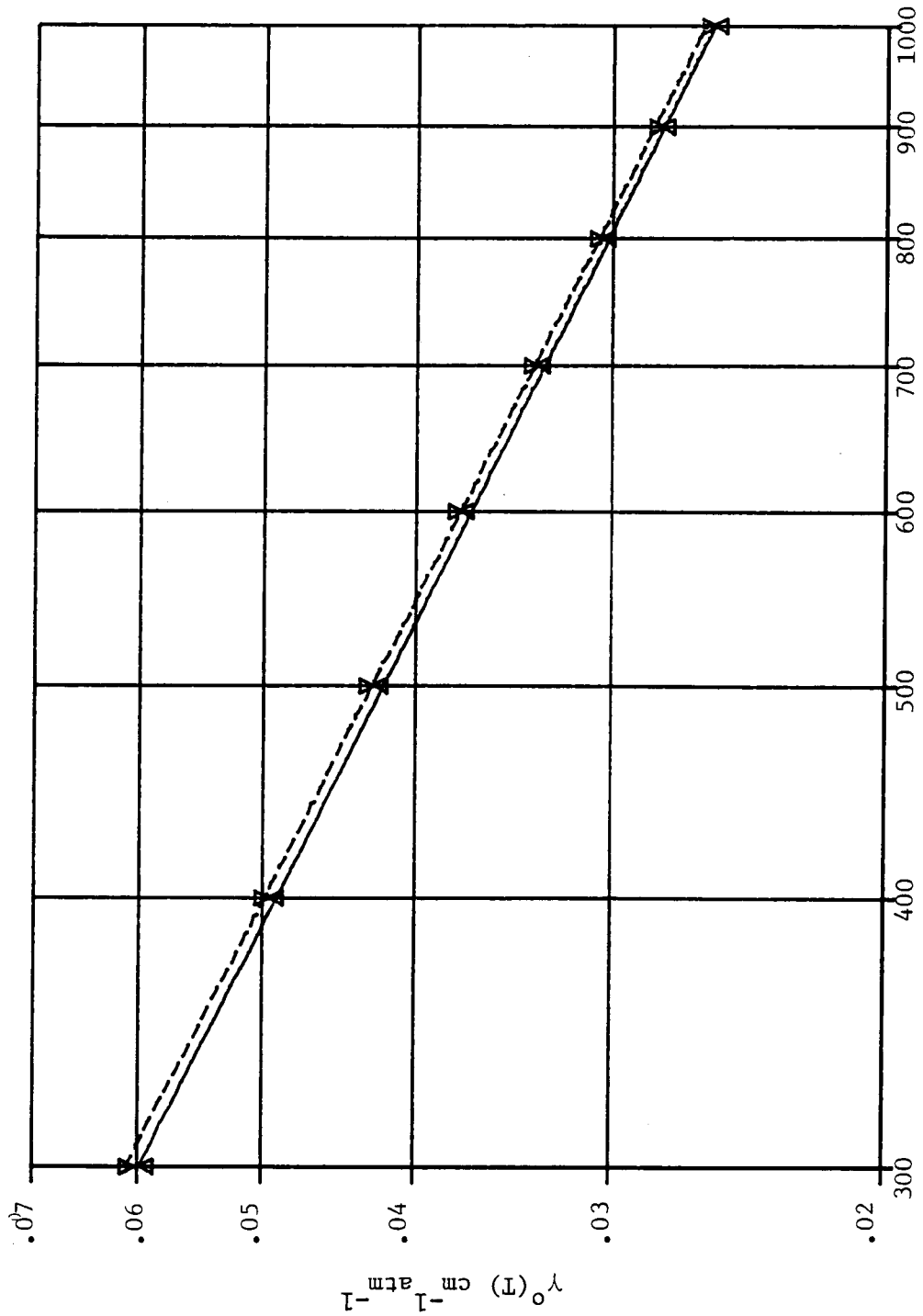

Figure 5-3. $\gamma^o(T)$ vs. T for the $P_{1/2}(5.5)$ and $P_{3/2}(5.5)$ spectral lines of NO broadened by CO. The symbols Δ and ∇ represent the half widths of the 1/2 and 3/2 subband, respectively. The curves —— and - - - - are the curve fits using Birnbaum's formula for the 1/2 and 3/2 subband, respectively. The fit parameters are given in Table 5-2.

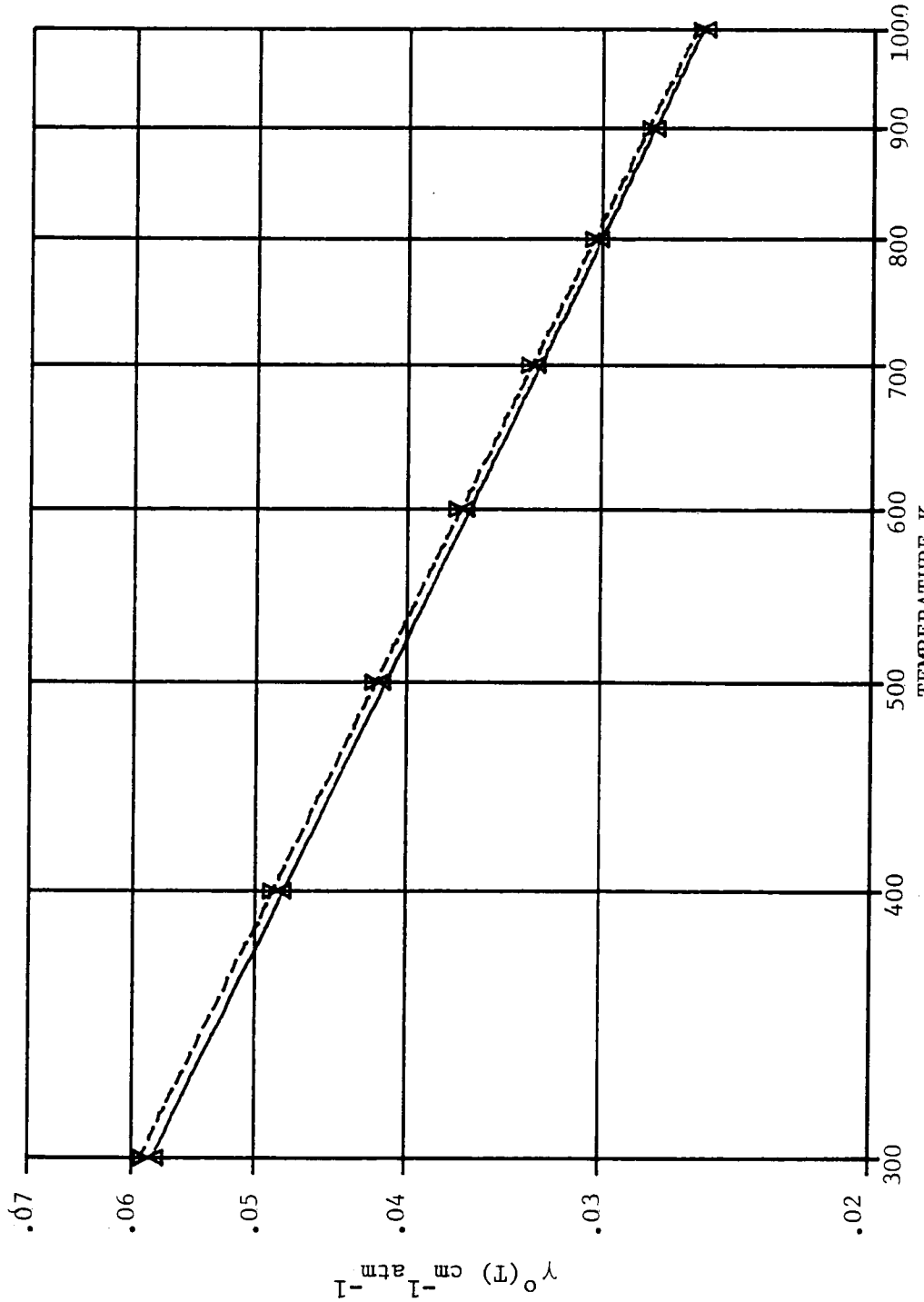

Figure 5-4. $\gamma^o(T)$ vs. T for the $P_{1/2}(6.5)$ and $P_{3/2}(6.5)$ spectral lines of NO broadened by CO. The symbols Δ and ∇ represent the half widths of the 1/2 and 3/2 subband, respectively. The curves ——— and - - - - are the curve fits using Birnbaum's formula for the 1/2 and 3/2 subband, respectively. The fit parameters are given in Table 5-2.

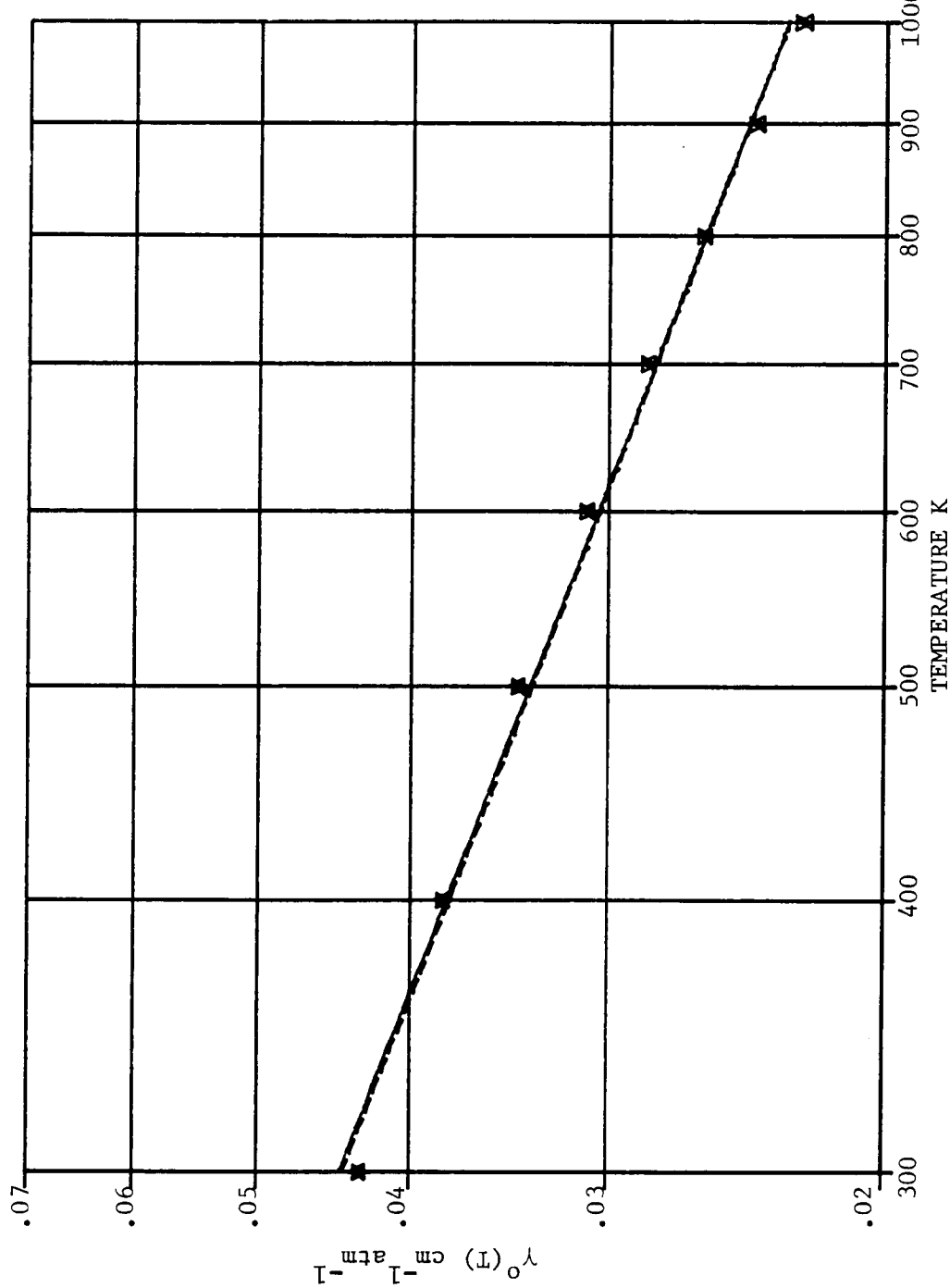

Figure 5-5. $\gamma^o(T)$ vs. T for the $P_{1/2}(20.5)$ and $P_{3/2}(20.5)$ spectral lines of NO broadened by CO. The symbols Δ and ∇ represent the half widths of the 1/2 and 3/2 subband, respectively. The curves —— and - - - - are the curve fits using Birnbaum's formula for the 1/2 and 3/2 subband, respectively. The fit parameters are given in Table 5-2.

the two subbands is relatively independent of temperature. The halfwidths calculated here for the elevated temperatures, as shown in Figures 5-2 through 5-5, have been linear least square fitted to the semiemperial formula suggested by Birnbaum; [54]

$$\gamma^0(T) = \gamma^0(T_0)(T/T_0)^{-n}. \qquad (5\text{-}1)$$

From the figures it is easily seen that as J increases the quality of the curve fit deteriorates. Listed in Table 5-2, page 153, are the elevated temperature halfwidths and the curve fit parameters $\gamma^0_{fit}(T_0)$ and n_{fit} used in curve fitting the elevated temperature half widths to equation (5-1).

2. RESULTS USING THE RESOLVED LINE APPROXIMATION WITH PARITY EIGENSTATES

The next series of halfwidth calculations are those utilizing the formulation of Chapter IV-7 where the NO parity (lambda doubling) eigenstates are incorporated into a resolved line approximation theory. Thus a halfwidth for each individual doublet component was calculated for the same lines as those considered in the ATC calculations. These halfwidths are presented in Table 5-2 where the (total) parity, P_T, of the ground state is used to denote the different doublet component halfwidths. Each doublet (both doublet components) required approximately 1.25 minutes of CPU time for their computation. From Table 5-2 it is seen that the results of incorporating the parity eigenstates is to increase the half widths only slightly. The maximum increase is for the low J values of the 3/2 subband where the maximum percent increase is 1.45% for a $2|m|$ value of five.

The calculation of the coupled line absorption coefficient was performed utilizing the expressions derived in Chapter IV-6. Since the two subband lines of NO are well separated compared to the lambda doublet component lines (see Appendix C) only the coupling effects of the doublet components were considered. Therefore the coupling matrix used here was a four-by-four matrix due to the two possible parity states for both the initial and final states of the transition. The values of the impact parameter, b_0, used as the lower limit of integration of the interruption functions were determined using Anderson's cutoff procedure. For a given value of J_2 the total diagonal interruption function was used in equation (4-151) which was then solved for b_0 using a simple Newton-Raphson algorithm. These roots were then used to calculate the cross sectional integrals of the respective diagonal interruption function from which the diagonal coupling matrix elements were determined. The off-diagonal coupling matrix elements were calculated using the average of the four b_0's obtained from the diagonal interruption functions. The line shifts were also calculated using this averaged impact parameter. The dipole moment reduced matrix elements were calculated using the results of Appendix H and using the band strength value of 122.0 $cm^{-2}atm^{-1}$ suggest by Abels and Shaw.[1] The inverse matrix appearing in the expression of the coupled line absorption-coefficient was calculated utilizing the IMSL complex double precision linear equation solver

subroutine LEQT1C. Approximately five minutes of CPU time was required for the computation of each absorption coefficient profile which consisted of approximately one hundred points.

Presented in Figure 5-6 through 5-12 are the coupled line absorption coefficients, $k_c(\omega)$ (solid curve), for several lines of NO. Although Doppler broadening contributes to the total absorption coefficient at low pressures (<250 Torr) no attenpt was made to convolve the Doppler profile with the coupled line absorption coefficient. Thus for pressures below approximatley 250 Torr the results presented here are good for comparison purposes only. Self broadening effects were also ignored in all calculation and the CO partial pressure was equated to the total pressure. The NO partial pressure was kept at 2 percent of the total pressure and was used only for the calculation of the lambda doublet integrated absorptances. The zero wavenumber point in Figures 5-6 through 5-12 corresponds to the point midway between the two doublet components. From the coupled line absorption coefficient, $k_c(\omega)$, was subtracted $k_L(\omega)$, the absorption profile obtained from the sum of two Lorentz absorption coefficient profiles utilizing the halfwidths of Table 5-2 and the line shifts calculated here. This quantity is denoted as the interference absorption profile $k_I(\omega)$ given by

$$k_I(\omega) = k_c(\omega) - k_L(\omega) \tag{5-2}$$

and is represented in Figures 5-6 through 5-12 by the broken line. Note that since the frequency integral of the absorption coefficient is independent of the broadening mechanism one has; [55]

$$\int_{\text{line}} k_c(\omega)d\omega = \int_{\text{line}} k_L(\omega)d\omega \tag{5-3}$$

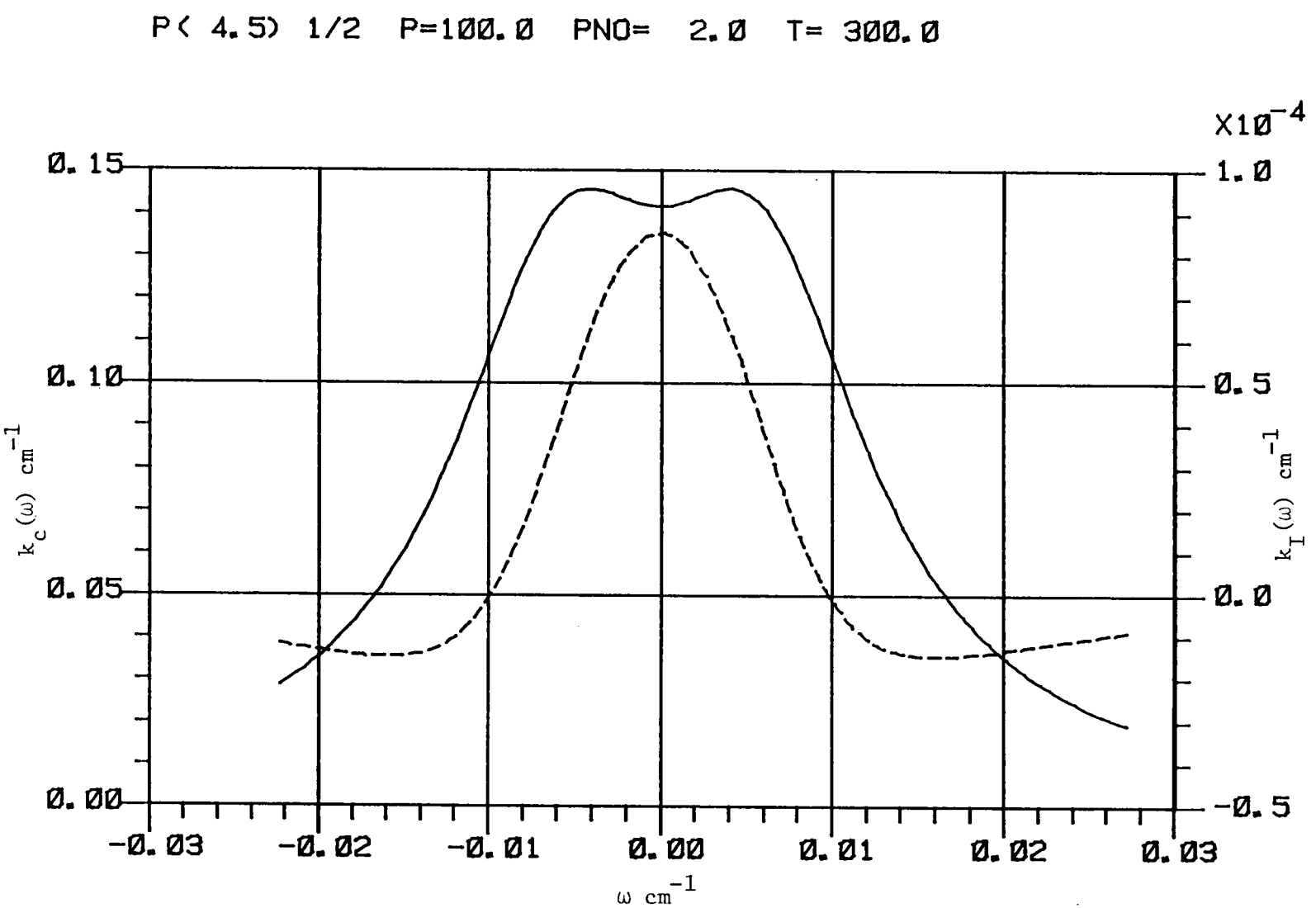

Figure 5-6. Coupled line absorption coefficient for the $P_{1/2}(4.5)$ line with P_B=100.0 Torr, P_{NO}=2.0 Torr, and T=300K. The solid curve represents $k_c(\omega)$ and the broken curve represents $k_I(\omega)$. The calculated integrated absorptances and line shifts are: $S_+=2.0578\times10^{-3}$ cm^{-2}, $S_-=2.0586\times10^{-3}$ cm^{-2}, $\Delta_+=3.6956\times10^{-5}$ cm^{-1}, and $\Delta_-=3.6194\times10^{-5}$ cm^{-1}.

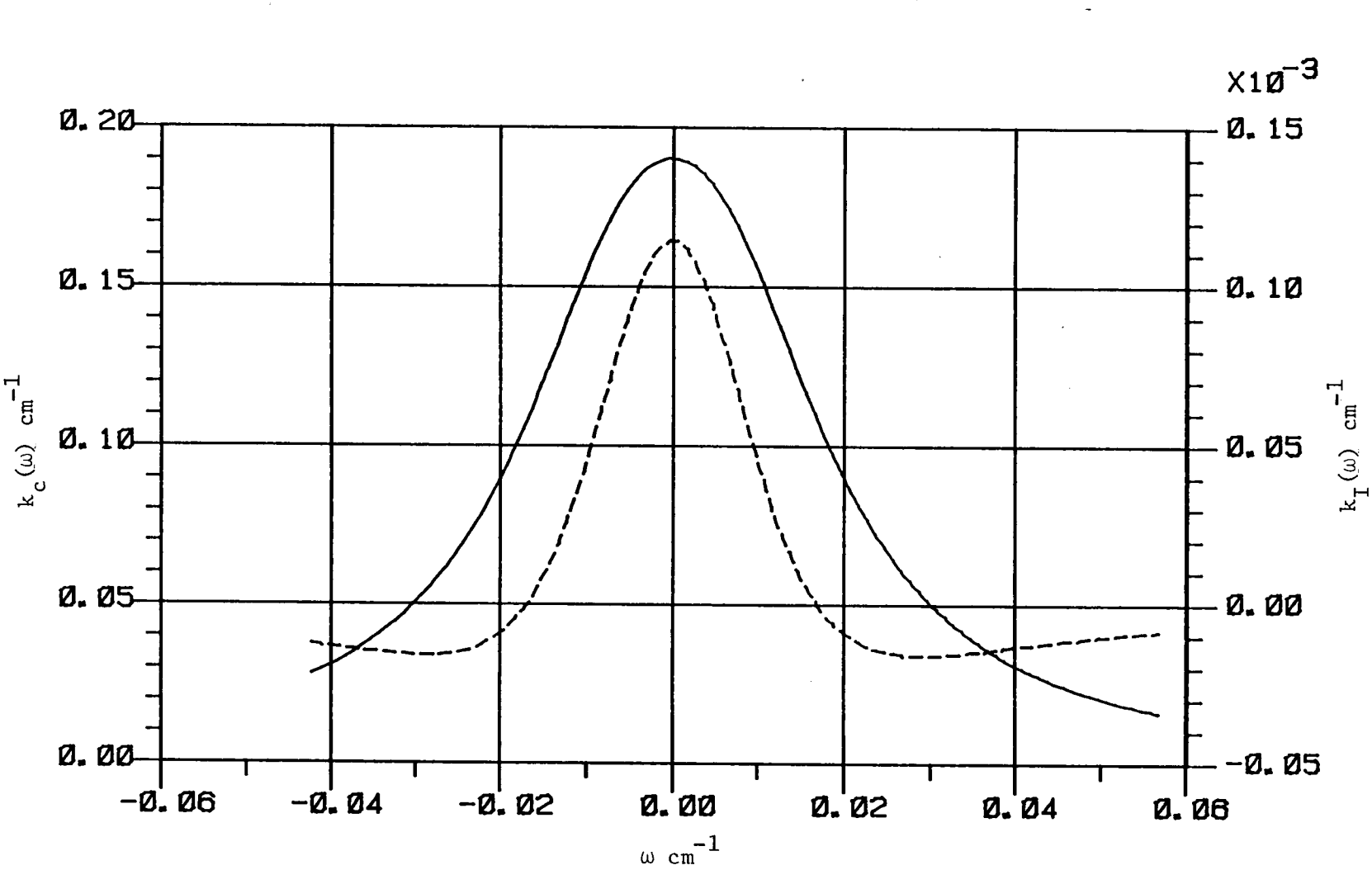

Figure 5-7. Coupled line absorption coefficient for the $P_{1/2}(4.5)$ line with P_B=200.0 Torr, P_{NO}=4.0 Torr, and T=300K. The solid curve represents $k_c(\omega)$ and the broken curve represents $k_I(\omega)$. The calculated integrated absorptances and line shifts are: $S_+=4.1156\times10^{-3}$ cm^{-2}, $S_-=4.1172\times10^{-3}$ cm^{-2}, $\Delta_+=7.3912\times10^{-5}$ cm^{-1}, and $\Delta_-=7.2388\times10^{-5}$ cm^{-1}.

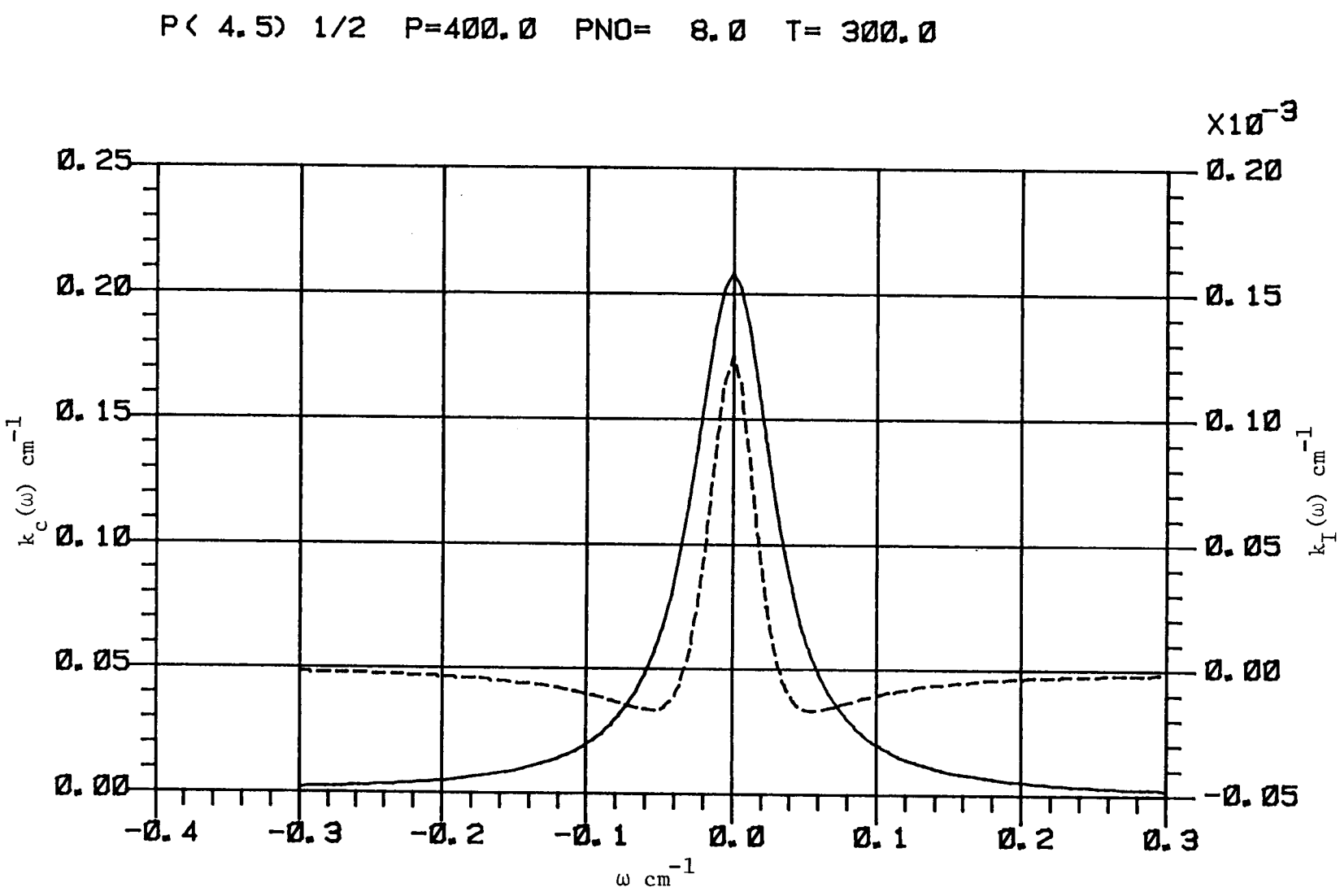

Figure 5-8. Coupled line absorption coefficient for the $P_{1/2}(4.5)$ line with P_B=400.0 Torr, P_{NO}=8.0 Torr, and T=300K. The solid curve represents $k_c(\omega)$ and the broken curve represents $k_I(\omega)$. The calculated integrated absorptances and line shifts are: $S_+=8.2312\times10^{-3}$ cm^{-2}, $S_-=8.2344\times10^{-3}$ cm^{-2}, $\Delta_+=1.4782\times10^{-4}$ cm^{-1}, and $\Delta_-=1.4477\times10^{-4}$ cm^{-1}.

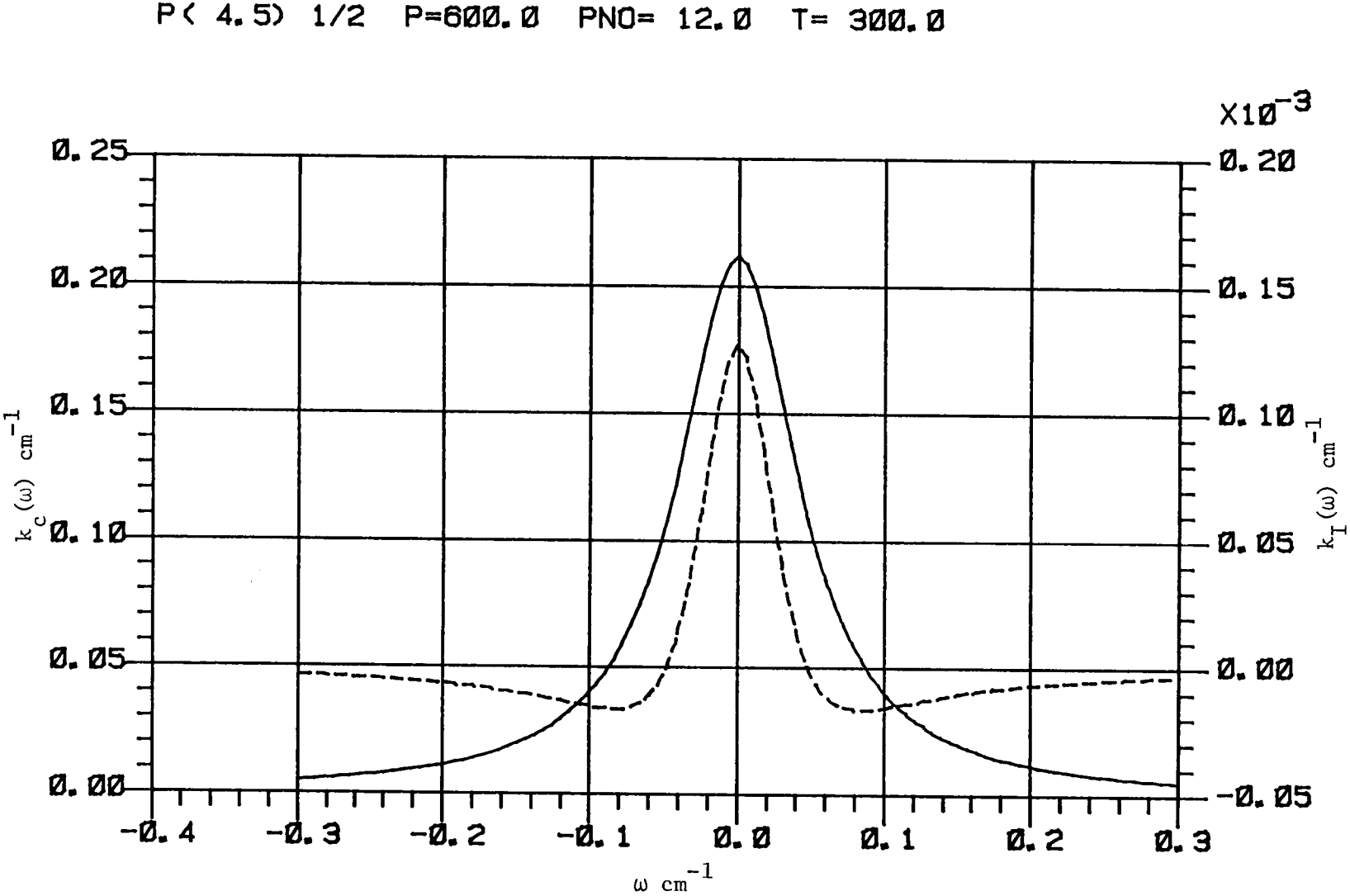

Figure 5-9. Coupled line absorption coefficient for the $P_{1/2}(4.5)$ line with P_B=600.0 Torr, P_{NO}=12.0 Torr, and T=300K. The solid curve represents $k_c(\omega)$ and the broken curve represents $k_I(\omega)$. The calculated integrated absorptances and line shifts are: $S_+=1.2347\times10^{-2}$ cm^{-2}, $S_-=1.2350\times10^{-2}$ cm^{-2}, $\Delta_+=2.2173\times10^{-4}$ cm^{-1}, and $\Delta_-=2.1716\times10^{-4}$ cm^{-1}.

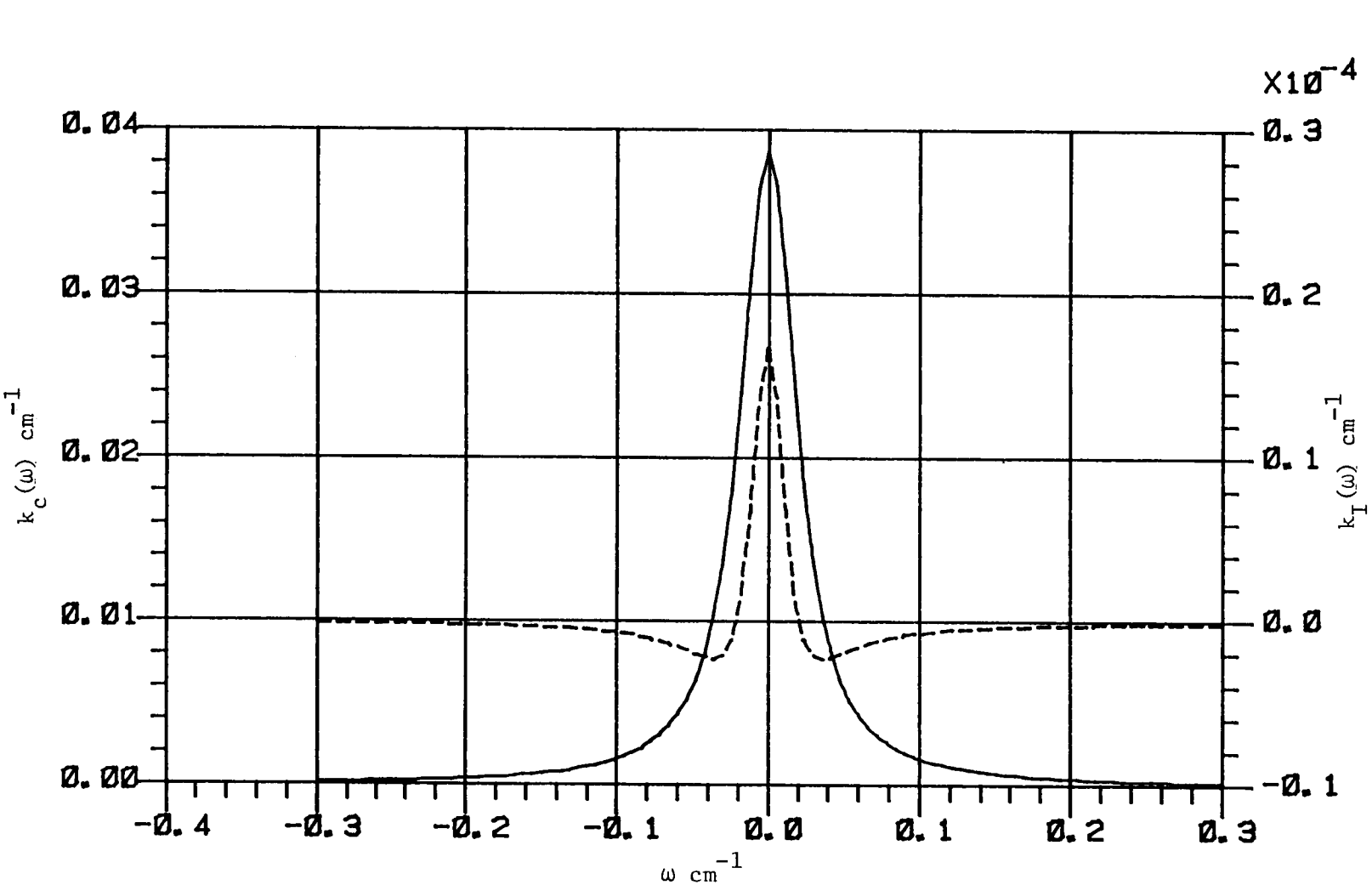

Figure 5-10. Coupled line absorption coefficient for the $P_{1/2}(4.5)$ line with P_B=600.0 Torr, P_{NO}=12.0 Torr, and T=1000K. The solid curve represents $k_c(\omega)$ and the broken curve represents $k_I(\omega)$. The calculated integrated absorptances and line shifts are: $S_+=1.3271\times10^{-3}$ cm^{-2}, $S_-=1.3273\times10^{-3}$ cm^{-2}, $\Delta_+=8.9160\times10^{-5}$ cm^{-1}, and $\Delta_-=8.9165\times10^{-5}$ cm^{-1}.

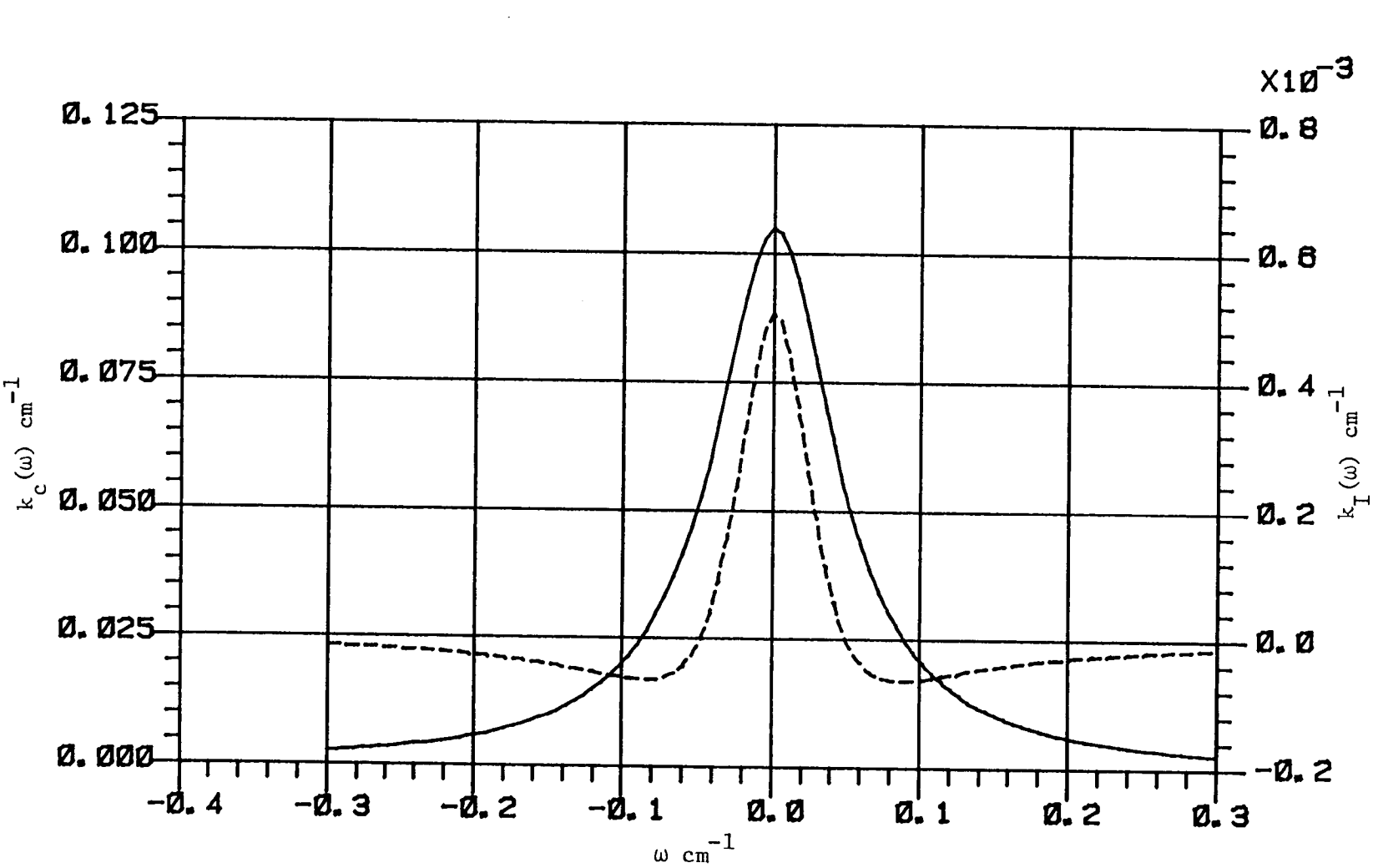

Figure 5-11. Coupled line absorption coefficient for the $P_{3/2}(4.5)$ line with P_B=600.0 Torr, P_{NO}=12.0 Torr, and T=300K. The solid curve represents $k_c(\omega)$ and the broken curve represents $k_I(\omega)$. The calculated integrated absorptances and line shifts are: $S_+=8.1931\times10^{-3}$ cm^{-2}, $S_-=8.1931\times10^{-3}$ cm^{-2}, $\Delta_+=1.2712\times10^{-3}$ cm^{-1}, and $\Delta_-=1.2712\times10^{-3}$ cm^{-1}.

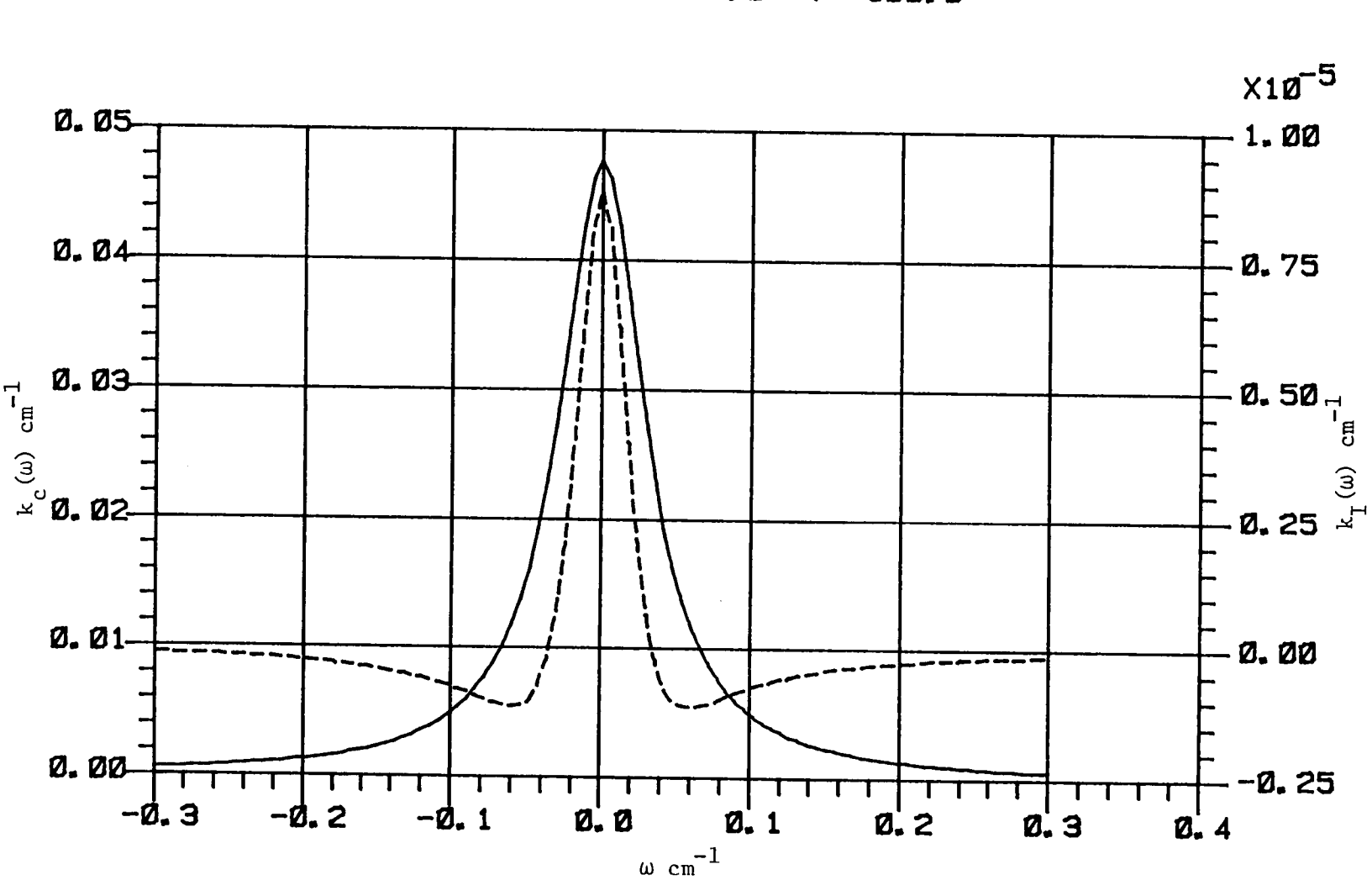

Figure 5-12. Coupled line absorption coefficient for the $P_{1/2}(20.5)$ line with P_B=600.0 Torr, P_{NO}=12.0 Torr, and T=300K. The solid curve represents $k_c(\omega)$ and the broken curve represents $k_I(\omega)$. The calculated integrated absorptances and line shifts are: $S_+=2.5812\times10^{-3}$ cm^{-2}, $S_-=2.5838\times10^{-3}$ cm^{-2}, $\Delta_+=1.5309\times10^{-5}$ cm^{-1}, and $\Delta_-=1.5309\times10^{-5}$ cm^{-1}.

and therefore;

$$\int k_I(w)dw = 0. \qquad (5\text{-}4)$$

The effects of the vanishing integral can be seen by examining Figures 5-6 through 5-12 in which coupling effects add to the absorption coefficient near the doublet and subtract from it further from the doublet.

Several characteristics of the coupling effects can be inferred are confirmed from examining Figures 5-6 through 5-12. Note from the theory of Chapter IV the coupling matrix elements possesses the same basic temperature and pressure dependence as the collision half widths. These dependencies are demonstrated in the interference absorption coefficient profiles of Figures 5-6 through 5-10. The same dependency on J quantum number is also implied from the Figures 5-9 and 5-12 where a smaller coupling effect is noted for the larger J value P branch line, .06% at doublet center for the $P_{1/2}$ (4.5) line and .02% for the $P_{1/2}$ (20.5) line. From the values of the line shifts, from Figures 5-6 through 5-12, and the halfwidths, Table 5-2, page 153, it is inferred that the line shifts are typically three orders of magnitude smaller than the line widths, and are not even noticable in the absorption coefficient profiles of Figure 5-6 through 5-12. Comparison of Figures 5-9 and 5-11 indicate a larger coupling effect contribution to the $P(4.5)_{3/2}$ line than that of the $P(4.5)_{1/2}$ line .06% at doublet center for the $P_{1/2}(4.5)$ and .5% for the $P_{3/2}(4.5)$. This is due mainly to the smaller doublet separation in the 3/2 subband line as compared to the 1/2 subband line and not due

to an intrinsically larger coupling effect in the 3/2 subband. Of the spectral lines examined in the course of this work, the coupling effects were found to contribute no more than 1.42 percent ($P_{3/2}(2.5)$ P_{NO} = 12.0 Torr P_B = 600 Torr, T = 300K) of the absorption coefficient at frequencies where the absorption coefficient is non-negligible.

CHAPTER VI

CONCLUSIONS

In conclusion, the effects of line coupling was found to be negligible in the case of the NO lambda doublets broadened by CO. By examining the CO pressure broadening halfwidths of NO, utilizing the NO parity eigenstates, it was also predicted that only a slight difference exists between the halfwidths of the lambda doublet components. When the ATC theory was used, assuming symmetric top eigenstates for the rotational eigenstates of NO, halfwidths were obtained which were reasonably close (<1.45 percent difference) to those obtained using more accurate eigenstates. The ATC theory calculations also offered a thirty-to-one reduction in computational time over the less approximate calculations using the parity eigenstates of NO. Thus for the purpose of determining NO collision broadening halfwidths the ATC theory seem to offer good results at a substantial savings in computer time.

For non-$\sum$ state diatomics which possess a weaker spin-orbit coupling potential the mixing between the subbands should be more pronounced. Thus for these type molecules, OH for example, the line coupling effects may be larger and warrant a coupled line spectral calculation. The Q branch of NO may also need to be modeled by a coupled line absorption coefficient due to its close line spacing. Because of the limited computer time available, no attempt was made here to examine the Q branch since it would require large coupling matrices due to the increased spectral line density of the Q branch.

If more accurate radiation modeling is required in the future it may become necessary to examine the effects of line coupling in the Q branch of NO and the spectral line coupling effects of other non-Σ state IR active species such as OH.

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APPENDIXES

APPENDIX A

PROPERTIES OF THE HUND'S CASE A TOTAL ANGULAR MOMENTUM EIGENSTATES UNDER PARITY

The effect of the parity operator on the eigenstates of Hund's case A total angular momentum eigenstates given in equation (1-68) and (1-95) is examined by first investigating its effects on the electron coordinates. The coordinates of an electron in the MFS in terms of the SFS coordinates is given, from section I-2, by

$$\bar{\rho}_t = R_p(\phi\theta\psi)\bar{r}_t R_p^\dagger(\phi\theta\psi) \tag{A-1}$$

where the notation is the same as that of Chapter 1. Applying the parity operator, the inverted electron vector in the MFS, $\bar{\rho}'$, is given by

$$\bar{\rho}_t' = \bar{\rho}_t = R_p(\pi - \theta, \phi + \pi, \psi)(-\bar{r}_t)R_p^\dagger(\pi - \theta, \phi + \pi, \psi) \tag{A-2}$$

where the Euler angles were changed to reflect the fact that

$$\mathcal{P}\,\bar{R}_{BA} = -\bar{R}_{BA} \tag{A-3}$$

By writing out equation (A-2) in detail and letting $\psi \to \pi - \psi$, since ψ is completely arbitrary as seen from section 1-B, the electron coordinates in the MFS behave under parity according to

$$\mathcal{P}(\xi, n, \zeta) = (\xi, -n, \zeta). \tag{A-4}$$

Thus the effect of a parity operation on the spatial electron coordinates in the SFS is equivalent to a reflection of the electron coordinates in the $\xi\zeta$ plane of the MFS. Therefore, the result of the parity operator on the total eigenstates is summarized by

$$\mathcal{P}\langle\rho, \bar{R}_{BA} \mid n\ \Lambda S\Sigma JM\text{-}\Omega\rangle_R = (\mathcal{P}\langle\bar{\rho} \mid n\Lambda S\Sigma\rangle)(\mathcal{P}\langle\bar{R}_{BA} \mid JM\text{-}\Omega\rangle_R)$$

$$= (R_{\xi\zeta}\langle\bar{\rho} \mid n\Lambda S\Sigma\rangle)(\mathcal{P}\langle R_{BA} \mid JM\text{-}\Omega\rangle_R), \qquad \text{(A-5)}$$

where $R_{\xi\zeta}$ is a reflection operator in the $\xi\zeta$ plane.

The effects of the parity operator on the rotational portion of the eigenstate is examined using the coordinate representation of the rotational eigenstates given in equation (1-67), thus

$$\mathcal{P}\langle\bar{R}_{BA} \mid JM\text{-}\Omega_R\rangle = (-1)^{J-\Omega}\,\mathcal{P}\, d^{J*}_{M,\Omega(\phi\theta\psi)}$$

$$= (-1)^{J-\Omega} \quad d^{J*}_{M,\Omega}(\phi + \pi,\ \pi - \theta,\ \pi - \psi). \qquad \text{(A-6)}$$

Applying the properties of the d matrices [11,44] equation (A-6) becomes

$$\mathcal{P}\langle\bar{R}_{BA} \mid JM - \Omega\rangle_R = (-1)^{J-\Omega}\,\langle\bar{R}_{BA} \mid JM\Omega\rangle_R \qquad \text{(A-7)}$$

The total electronic spatial eigenstates are axially symmetric and thus have a coordinate representation given by

$$\bar{\rho} \mid n\Lambda\rangle = f(\bar{\rho},\theta_s)e^{-i\Lambda\phi_s} \qquad \text{(A-8)}$$

where Λ is the quantum number of the component of total orbital electronic angular momentum about the ζ axis. The angles θ_s and ϕ_s are polar angles in the MFS which represent some or all electronic coordinates in this system for ease of demonstration. For the case of $\Lambda = 0$ the eigenstates are designated $\Sigma^{\pm}$ according to their eigenvalues under reflection, that is

$$R_{\xi\zeta}\langle\bar{\rho} \mid n\Sigma^{\pm}\rangle = \pm\langle\bar{\rho} \mid n\Sigma^{\pm}\rangle. \qquad \text{(A-9)}$$

For nonvanishing Λ a reflection in the $\xi\zeta$ plane can be represented by replacing ϕ_s by $\pi-\phi_s$, therefore

$$\mathcal{P}\langle\bar{\rho} \mid n\Lambda\rangle = f(\bar{\rho},\theta_s)e^{i\Lambda(\pi-\phi_s)} \qquad \text{(A-10)}$$

$$= \langle\bar{\rho} \mid n - \Lambda\rangle(-1)^{\Lambda} = (-1)^{\Lambda}\langle\rho \mid n - \Lambda\rangle.$$

Thus the general result of a reflection on the spatial electronic eigenstates is given by

$$R_{\xi\zeta} \langle \rho \mid n\Lambda \rangle = (-1)^{\Lambda+q} \langle \rho \mid n\Lambda \rangle \tag{A-11}$$

where

$$q = \begin{cases} 1 & \Sigma^- \text{state} \\ 0 & \text{otherwise} \end{cases} \tag{A-12}$$

Examination of the total spin eigenstates requires a close look at the result of the reflection operator on the individual electronic spin states and the overall effect on the Slater determinant. First, note a reflection in the $\xi\zeta$ plane is equivalent to a parity operation in the MFS and a rotation of the coordinates about the η axis by π, in any order. The spin like any other angular momentum is parity invariant [11] thus only the rotation about the η axis is of concern.

A rotation about the η axis by π is achieved by rotating through the Euler angle θ by π with no rotation through the other Euler angles. Thus the individual electronic spin eigenstates, $\mid SM_S\rangle$, in the rotated system are given by

$$R_S(\theta = \pi) \mid SM_S\rangle = \sum_{M'_S=-S}^{S} d^S_{M'_S, M_S}(\phi=0, \theta=\pi, \psi=0) \mid SM'_S\rangle \tag{A-13}$$

where $S = 1/2$. Expanding the above expression leads to

$$R_S \mid \alpha\rangle \equiv R_S \mid 1/2,\ 1/2\rangle = \mid 1/2,\ -1/2\rangle \equiv \mid \beta\rangle \tag{A-14a}$$

and

$$R_S \mid \beta\rangle \equiv R_S \mid 1/2,\ -1/2\rangle = -\mid 1/2,\ 1/2\rangle \equiv -\mid \alpha\rangle. \tag{A-14b}$$

The effects of the rotation of spin eigenstates on the electronic Slater determinant is two-fold. The inner shell electrons are paired and thus there is a change of sign associated with the β spin state

which is rotated to a negative α spin state. This change of sign causes a row in the Slater determinant to change sign and thus the Slater determinant itself changes sign. There is also a change of sign due to the interchange of rows since paired inner shell electrons have one electron in the α spin state and one in the β spin state which are interchanged in the rotation. Thus the rotation has no net effect on the sign of the total state due to the inner shell electrons since the change of sign due to the interchange of rows cancels the change of sign due to the negative α state.

The effects of a rotation on unpaired electrons is best considered case by case. For one unpaired electron the net electronic spin of the molecule is $1/2$ and the molecule can have spin eigenstates $|\, s = 1/2,\ \Sigma = 1/2\rangle$ or $|\, s = 1/2,\ \Sigma = 1/2\rangle$. Rotating these spin states yield simply the results of equation (A-14) since the paired inner shell electrons do not contribute to the net spin. For two unpaired electrons the net spin is one and thus can have three possible total spin eigenstates $|\, s = 1,\ \Sigma = 1\rangle$, $|\, s = 1,\ \Sigma = -1\rangle$, and $|\, s = 1,\ \Sigma = 0\rangle$. For the molecule to have net spin eigenstate $|\, s = 1,\ \Sigma = 1\rangle$ or $|\, s = 1,\ \Sigma = -1\rangle$ requires that both electrons to be in spin eigenstates α or β, respectively. Under a rotation the effects is to change the spin eigenstates of the unpaired electrons such that the produce of the spin eigenstates which appear in the Slater determinant is given by

$$R_{\xi\zeta}\,|\,\beta\beta\rangle = (-|\,\alpha\rangle)(-|\,\alpha\rangle) = |\,\alpha\alpha\rangle \qquad \text{(A-15)}$$

or

$$R_{\xi\zeta}\,|\,\alpha\alpha\rangle = |\,\beta\beta\rangle. \qquad \text{(A-16)}$$

Thus the reflection of the spin one eigenstates with $|\Sigma| = 1$ behaves according to

$$R_{\xi\zeta} |S = 1, \Sigma = \pm 1\rangle = |S = 1, \Sigma \mp 1\rangle, \tag{A-17}$$

For the spin eigenstate $|s = 1, \Sigma = 0\rangle$ one unpaired electron has spin eigenstate α and the other β, but each of the unpaired electrons have different spatial eigenstates due to the Pauli exclusion principle. Thus the effect of rotation on the $|s = 1, \Sigma = 0\rangle$ state is to change sign of the net spin eigenstate since the β electron spin state becomes a negative α state, thus

$$R_{\xi\zeta} |S = 1, \tilde{\Sigma} = 0\rangle = -|S = 1, \Sigma = 0\rangle. \tag{A-18}$$

Therefore in general the total electron spin eigenstates behave under parity as

$$R_{\xi\zeta} |S, \Sigma\rangle = (-1)^{S-\Sigma} |S - \Sigma\rangle. \tag{A-19}$$

Applying the results of the parity operator on the electron spatial eigenstates given by equation (A-11), the spin eigenstates in equation (A-19), and the rotational portion given in equation (A-7) the effect on the total angular momentum eigenstate is given by

$$|\, n\Lambda S\Sigma JM-\Omega\rangle_R = (-1)^{J+S+q} |\, n - \Lambda S - \Sigma JM\Omega\rangle_R \tag{A-20}$$

For homonuclear diatomics there is another symmetry due to the invariance of the molecular Hamiltonian when the two identical nuclei are exchanged. This operation differs from the parity operation in that the electronic coordinates are kept fixed while exchanging the

coordinates of the two nuclei. Denoting the operator responsible for this operation by R_I its effects on the rotational eigenstates is easily determined from equation (A-7), thus

$$R_I\langle R_{BA} \mid JM-\Omega\rangle_R = \langle -R_{BA} \mid JM-\Omega\rangle_R$$
$$= (-1)^{J+\Omega}\langle R_{BA} \mid JM\Omega\rangle_R. \qquad \text{(A-21)}$$

In order to consider the effects of R_I on the electronic states first examine the steps leading to equation (A-2). Note that for the case here the vector $\bar{r}$ does not change sign and the effect of the exchange of nuclei on the electronic cordinates in the MFS is given by

$$\bar{\rho}' = R_p(\pi-\theta,\phi+\pi,\psi)\bar{r}R_p^{\dagger}(\pi-\theta,\phi+\pi,\psi) \qquad \text{(A-22)}$$

From equations (A-3), (A-4), and (A-22), it is determined that under the operator R_I the electronic coordinates in the MFS transform according to

$$R_I(\xi,n,\zeta) = (-\xi,n,-\zeta). \qquad \text{(A-23)}$$

This symmetry operation is equivalent to an inversion of all electronic coordinates in the MFS and a reflection in the $\xi\zeta$ plane. The effects of the reflection have already been considered and are described by equation (A-11) and (A-19). The inversion of electronic coordinates in the MFS, called the intrinsic parity operation, either leaves the electronic eigenstates unchanged or changes its sign. The intrinsic parity of an electronic state is denoted by g or u (gerade or ungerade) depending on whether the eigenstate is even or odd with respect to intrinsic parity operator. Therefore by adding the label q_e to the electronic eigenstate one has

$$R_I \mid n\Lambda S\Sigma q_e\rangle = (-1)^{S-\Sigma+q+q_e} \mid n-\Lambda S-\Sigma q_e\rangle \qquad \text{(A-24)}$$

where q_e is zero for a gerade state, or if the molecule is heternuclear, or has a value of one for an ungerade state. Combining the electronic and rotational eigenstates, the effects of R_I on total angular momentum can be described by

$$R_I \mid n\Lambda S\Sigma q_e JM-\Omega\rangle_R = (-1)^{J+S+q+q_e} \mid n-\Lambda S-\Sigma q_e JM\Omega\rangle_R. \qquad (A-25)$$

Note that the intrinsic parity does not contribute to the total parity.

Eigenstates of parity and the operator R_I are formed from linear combinations of the states of equation (A-25). By examining equation (A-20) the parity eigenstates can easily be constructed and are given by:

$$\mid pn\Lambda S\Sigma q_e JM-\Omega\rangle_R = \frac{1}{\sqrt{2}} [\mid n\Lambda S\Sigma q_e JM-\Omega\rangle_R + p \mid n-\Lambda S-\Sigma JM\Omega\rangle_R] \qquad (A-26)$$

where

$$\mathcal{P} \mid pn\Lambda S\Sigma q_e JM-\Omega\rangle_R = p(-1)^{J+S+q} \mid pn\Lambda S\Sigma q_e JM-\Omega\rangle_R \qquad (A-27)$$

and

$$p = \pm 1. \qquad (A-28)$$

These parity eigenstates are also eigenstates of the operator R_I;

$$R_I \mid pn\Lambda S\Sigma q_e JM-\Omega\rangle_R = p(-1)^{J+S+q+q_e} \mid pn\Lambda S\Sigma q_e JM-\Omega\rangle_R \qquad (A-29)$$

APPENDIX B

THE VAN VLECK TRANSFORMATION

The Van Vleck transformation and variations of it are discussed briefly by several authors [29-32]. A discussion is given here of the Van Vleck transformation and an investigation of its effects on the eigenvalues and eigenstates are examined.

From Section III-3 the problem is seen as one of removing matrix elements which connect a diagonal block of matrix elements of interest to another block so that the eigenvalues of the diagonal block of interest can be calculated independently of another block of matrix elements. This would allow the calculation of rotational energy eigenvalues in a given vibrational ane electornic state without diagonalizing the total Hamiltonian which is virtually impossible. For the purpose of investigating the transformation let H represent the Hamiltonian, let $|m\rangle$ represent the states which lie in the diagonal block of interest, and let $|n\rangle$ represent the states outside those of interest. In order to apply the transformation, H is expressed in the form

$$H = H^{(0)} + \lambda H^{(1)} \tag{B-1}$$

where $H^{(0)}$ is diagonal and $H^{(1)}$ is responsible for all the matrix elements of H outside the diagonal blocks but may also have matrix elements inside. It is also allowable for the diagonal blocks of $H^{(0)}$ to contain more than one degenerate groups of states.

The Van Vleck transformation operator $T(\lambda)$ is given by

$$T(\lambda) = e^{is\lambda} = 1 + i\lambda S - 1/2\lambda^2 S^2 + \ldots \tag{B-2}$$

where S is Hermitian and T is unitary. The transformed Hamiltonian G is expressed as

$$G = G^{(0)} + \lambda G^{(1)} + \lambda^2 G^{(2)} + \ldots \tag{B-3}$$

and is related to the Hamiltonian H by the simularity transformation

$$T^{-1}HT = G \tag{B-4}$$

Expanding equation (B-4) and equating both sides in like powers of λ yields the following transformation equations through third order

$$G^{(0)} = H^{(0)}, \tag{B-5}$$

$$G^{(1)} = H^{(1)} + i\,(H^{(0)}S - SH^{(0)}), \tag{B-6}$$

$$G^{(2)} = i(H^{(1)}S - SH^{(1)}) + SH^{(0)}S - 1/2(H^{(0)}S^2 + S^2H^{(0)}), \tag{B-7}$$

and

$$G^{(3)} = SH^{(1)}S - 1/2(H^{(1)}S^2 + S^2H^{(1)}) + \tfrac{i}{2}(SH^{(0)}S^2 - S^2H^{(0)}S) - \tfrac{i}{6}(H^{(0)}S^3 - S^3H^{(0)}). \tag{B-8}$$

From equation (B-5) the matrix elements of $G^{(0)}$ are equal to those of $H^{(0)}$ and are therefore given by

$$\langle m \mid G^{(0)} \mid m' \rangle = E_m^0\, \delta_{mm'} \tag{B-9}$$

and

$$\langle n \mid G^{(0)} \mid n \rangle = E_n^0\, \delta_{nn'}. \tag{B-10}$$

The first order matrix elements are calculated using the transformation equation (B-6). The matrix elements of $G^{(1)}$ within the diagonal blocks are given by:

$$\langle m \mid G^{(1)} \mid m' \rangle = \langle m \mid H^{(1)} \mid m \rangle + i(E_m^0 - E_{m'}^0)\langle m \mid S \mid m' \rangle. \tag{B-11}$$

and

$$\langle n \mid G^{(1)} \mid n \rangle = \langle n \mid H^{(1)} \mid n' \rangle + i\,(E_n^0 - E_{n'}^0)\langle n \mid S \mid n' \rangle. \tag{B-12}$$

Imposing the requirement

$$\langle m \mid S \mid m' \rangle = \delta_{mm'} \langle m \mid S \mid m \rangle \tag{B-13}$$

and

$$\langle n \mid S \mid n' \rangle = \delta_{nn'} \langle n \mid S \mid n \rangle \tag{B-14}$$

on S simplifies equations (B-11) and (B-12) to

$$\langle m \mid G^{(1)} \mid m' \rangle = \langle m \mid H^{(1)} \mid m' \rangle \tag{B-15}$$

and

$$\langle n \mid G^{(1)} \mid n' \rangle = \langle n \mid H^{(1)} \mid n' \rangle. \tag{B-16}$$

The requirement on S given in equations (B-13) and (B-14) guarantees that the matrix elements inside the diagonal blocks remain unchanged. Thus the matrix elements of the transformed Hamiltonian are equal to those of the original Hamiltonian inside the diagonal blocks through first order. Requiring matrix elements of $G^{(1)}$ which connects the block of interest to other blocks to vanish yields the equation

$$\langle n \mid G^{(1)} \mid m \rangle = \langle n \mid H^{(1)} \mid m \rangle + i(E_n^0 - E_m^0)\langle n \mid S \mid m \rangle = 0 \tag{B-17}$$

Solving for the matrix elements of S yields:

$$\langle n \mid S \mid m \rangle = i \frac{\langle n \mid H^{(1)} \mid m \rangle}{E_n^0 - E_m^0} \tag{B-18}$$

Therefore by imposing the condition on S given in equations (B-13), (B-14), and (B-18) all the matrix elements of H connecting the diagonal block of interest to other blocks has been removed through first order. None of the conditions imposed on S contradict the requirement that S be Hermitian.

Matrix elements of higher order terms of G are calculated using the transformation equations (B-7) and (B-8) along with the matrix

elements of S given in equations (B-13), (B-14), (B-17) and (B-18). The matrix elements of $G^{(2)}$ inside the diagonal block of interest is given by

$$\langle m \mid G^{(2)} \mid m' \rangle = \sum_n \langle m \mid H^{(1)} \mid n \rangle \langle n \mid H^{(1)} \mid m' \rangle \qquad \text{(B-19)}$$

$$\frac{\frac{1}{2}(E_m^0 + E_{m'}^0) - E_n^0}{(E_m^0 - E_n^0)(E_{m'}^0 - E_n^0)} \quad .$$

By imposing on S the conditions

$$\langle m \mid S \mid m \rangle = \langle n \mid S \mid n \rangle = \langle m' \mid S \mid m' \rangle = \langle n' \mid S \mid n' \rangle$$

the matrix elements of $G^{(3)}$ within the diagonal block of interest are given by

$$\langle m \mid G^{(3)} \mid m' \rangle = \sum_{n\ n'} \frac{\langle m \mid H^{(1)} \mid n \rangle \langle n \mid H^{(1)} \mid n' \rangle \langle n' \mid H^{(1)} \mid m' \rangle}{(E_m^0 - E_n^0)(E_{m'}^0 - E_{n'}^0)}$$

$$- \frac{1}{2} \sum_{n\ m''} \left[\frac{\langle m \mid H^{(1)} \mid m'' \rangle \langle m'' \mid H^{(1)} \mid n \rangle \langle n \mid H^{(1)} \mid m' \rangle}{(E_{m''}^0 - E_n^0)(E_{m'}^0 - E_n^0)} \right.$$

$$\left. + \frac{\langle m \mid H^{(1)} \mid n \rangle \langle n \mid H^{(1)} \mid m'' \rangle \langle m'' \mid H^{(1)} \mid n' \rangle}{(E_m^0 - E_n^0)(E_{m''}^0 - E_n^0)} \right] \qquad \text{(B-20)}$$

The effects of the Van Vleck Transformation on the eigenvectors and energy eigenstates is examined by means of degenerate perturbation theory. Upon examination it is found that only energy terms of order four or higher contain matrix elements which connect the block of interest to other blocks. This is due to the condition imposed on the matrix elements of $G^{(1)}$ given by equation (B-17). Those matrix elements which connect the block of interest to other blocks belong to $G^{(2)}$ and $G^{(3)}$ and are therefore ignored since they contribute only in fourth order or higher to the energy.

The eigenvectors of H are calculated with the help of both the transformation and perturbation theory. According to perturbation theory the eigenstates of G may be written

$$| M\rangle = | m\rangle = \lambda | M^{(1)}\rangle + \lambda^2 | M^{(2)}\rangle + \ldots \tag{B-21}$$

where $| M\rangle$ represents the total eigenstate, $| m\rangle$, the eigenstate of $H^{(0)}$, and $| M^{(k)}\rangle$ the k^{th} approximation to the eigenstate. Through second order the total eigenstate of G is calculaed by perturbation theory to be given by

$$| M\rangle = | m\rangle + \lambda^2 \sum_n \frac{\langle n | G^{(2)} | m\rangle}{E_m^0 - E_n^0} | n\rangle \tag{B-22}$$

where the sum runs over all states except those of the diagonal block of interest. Note that the first order eigenstate vanishes which is a result of the condition imposed on $G^{(1)}$ given in equation (B-17). The eigenstates of H denoted $| N\rangle$ and those of G are not equal. The relation between the two can be seen by noting

$$\langle N' | H | N\rangle = \delta_{NN'} E_N \tag{B-23}$$

or

$$\begin{aligned} \langle N' | TT^{-1} H T T^{-1} | N\rangle &= \delta_{NN'} E_N \\ &= \langle M' | G | M\rangle = \delta_{MM'} E_M \end{aligned} \tag{B-24}$$

where

$$E_M = E_N \tag{B-25}$$

and

$$| N\rangle = T | M\rangle. \tag{B-26}$$

Expanding the eigenstates of H

$$|N\rangle = |N^{(0)}\rangle + \lambda |N^{(1)}\rangle + \lambda^2 |N^{(2)}\rangle + \ldots \tag{B-27}$$

and utilizing these in equation (B-26) with the expansion of $T(\lambda)$ yields the transformation equations for the eigenstates of H and G through second order

$$|N^{(0)}\rangle = |m\rangle, \tag{B-28}$$

$$|N^{(1)}\rangle = |M^{(1)}\rangle + iS|N^{(0)}\rangle = iS|m\rangle, \tag{B-29}$$

$$|N^{(2)}\rangle = |M^{(2)}\rangle - S^2/2|m\rangle. \tag{B-30}$$

Expanding the first order eigenstates of $|N\rangle$ in terms of the eigenstates of $|N^0\rangle$ (the $|m\rangle$ and $|n\rangle$ eigenstates of $G^{(0)} = H^{(0)}$) yields

$$|N^{(1)}\rangle = i\langle m|S|m\rangle|m\rangle - \sum_n \frac{\langle n|H^{(1)}|n\rangle}{E_n^0 - E_m^0}|n\rangle. \tag{B-31}$$

Thus through first order the normalized eigenstates of H are given by

$$|N\rangle = \frac{1}{\sqrt{3}}\left[(1+\lambda)|m\rangle - \lambda \sum_n \frac{\langle n|H^{(1)}|m\rangle}{E_n^0 - E_m^0}|n\rangle\right] \tag{B-32}$$

where

$$\langle m|S|m\rangle = \langle n|S|n\rangle \tag{B-33}$$

is set equal to one and the sum over n runs over all except the states of the block of interest.

APPENDIX C

ROTATIONAL ENERGIES AND SPECTRAL LINE POSITIONS OF THE NO FUNDAMENTAL

The following four tables contain the eigenstates and eigenvalues of the Van Vleck transformed Hamiltonian. The energies are calculated through third order for both the v = 0 and v = 1 vibrational states. Tables C-1 and C-2 take into account lambda doubling and utilize the lambda doubling and centrifugal distortion matrix elements of Chapter III. Tables C-3 and C-4 ignore the lambda doubling effects.

The parity quoted in the tables is the total parity P_T and not the "partial parity" p which are related by

$$P_T = p(-1)^{J+S}. \tag{C-1}$$

Thus in terms of the total parity the eigenstates of the transformed Hamiltonian are given by

$$| P_T n\Lambda SJM\rangle = \sum_{\Omega} C(J,g,P_T,\Omega) | P_T n\Lambda S\Sigma JM-\Omega\rangle \tag{C-2}$$

Tables C-5 and C-65 contain the spectral line assignments and positions of the NO fundamental. Table C-5 incorporates lambda doubling and the separation between the lambda doublets is included in the table. Again the parity quoted is the total parity of the ground state. The table C-6 ignores any lambda doubling.

Table C-1

Energy Eigenstates and Eigenvalues for v=0 with Lambda Doubling

J	g	PARITY	ENERGY (CM**-1)	C(J,g,P,1/2)	C(J,g,P,3/2)
0.5	1/2	-	-5.99355474D+01	1.00000000D+00	0.00000000D+00
0.5	1/2	+	-5.99236934D+01	1.00000000D+00	0.00000000D+00
1.5	1/2	+	-5.49255869D+01	9.99700712D-01	-2.44639801D-02
1.5	1/2	-	-5.49019087D+01	9.99700528D-01	-2.44714995D-02
1.5	3/2	+	6.49780622D+01	2.44639801D-02	9.99700712D-01
1.5	3/2	-	6.49780922D+01	2.44714995D-02	9.99700528D-01
2.5	1/2	-	-4.65716945D+01	9.99204278D-01	-3.98849653D-02
2.5	1/2	+	-4.65362519D+01	9.99203546D-01	-3.99033010D-02
2.5	3/2	-	7.35784798D+01	3.98849653D-02	9.99204278D-01
2.5	3/2	+	7.35785994D+01	3.99033010D-02	9.99203546D-01
3.5	1/2	+	-3.48738781D+01	9.98514127D-01	-5.44934658D-02
3.5	1/2	-	-3.48267596D+01	9.98512311D-01	-5.45267318D-02
3.5	3/2	+	8.56181485D+01	5.44934658D-02	9.98514127D-01
3.5	3/2	-	8.56184463D+01	5.45267318D-02	9.98512311D-01
4.5	1/2	-	-1.98321596D+01	9.97634930D-01	-6.87353313D-02
4.5	1/2	+	-1.97734821D+01	9.97631334D-01	-6.87875079D-02
4.5	3/2	-	1.01096171D+02	6.87353313D-02	9.97634930D-01
4.5	3/2	+	1.01096764D+02	6.87875079D-02	9.97631334D-01
5.5	1/2	+	-1.44658044D+00	9.96572515D-01	-8.27237709D-02
5.5	1/2	-	-1.37648796D+00	9.96566297D-01	-8.27986481D-02
5.5	3/2	+	1.20011406D+02	8.27237709D-02	9.96572515D-01
5.5	3/2	-	1.20012438D+02	8.27986481D-02	9.96566297D-01
6.5	1/2	-	2.02827922D+01	9.95333760D-01	-9.64920027D-02
6.5	1/2	+	2.03641301D+01	9.95323950D-01	-9.65931436D-02
6.5	3/2	-	1.42362477D+02	9.64920027D-02	9.95333760D-01
6.5	3/2	+	1.42364118D+02	9.65931436D-02	9.95323950D-01
7.5	1/2	+	4.53558584D+01	9.93926474D-01	-1.10046188D-01
7.5	1/2	-	4.54482481D+01	9.93911994D-01	-1.10176899D-01
7.5	3/2	+	1.68147776D+02	1.10046188D-01	9.93926474D-01
7.5	3/2	-	1.68150219D+02	1.10176899D-01	9.93911994D-01
8.5	1/2	-	7.37724775D+01	9.92359269D-01	-1.23381850D-01
8.5	1/2	+	7.38757028D+01	9.92338951D-01	-1.23545162D-01
8.5	3/2	-	1.97365475D+02	1.23381850D-01	9.92359269D-01
8.5	3/2	+	1.97368937D+02	1.23545162D-01	9.92338951D-01
9.5	1/2	+	1.05532459D+02	9.90641417D-01	-1.36490231D-01
9.5	1/2	-	1.05646284D+02	9.90614027D-01	-1.36688876D-01
9.5	3/2	+	2.30013533D+02	1.36490231D-01	9.90641417D-01
9.5	3/2	-	2.30018249D+02	1.36688876D-01	9.90614027D-01
10.5	1/2	-	1.40635556D+02	9.88782713D-01	-1.49361127D-01
10.5	1/2	+	1.40759723D+02	9.88746973D-01	-1.49597536D-01
10.5	3/2	-	2.66089703D+02	1.49361127D-01	9.88782713D-01

Table C-1 (Continued)

J	g	PARITY	ENERGY (CM**-1)	C(J,g,P,1/2)	C(J,g,P,3/2)
10.5	3/2	+	2.66095930D+02	1.49597536D-01	9.88746973D-01
11.5	1/2	+	1.79081451D+02	9.86793335D-01	-1.61984299D-01
11.5	1/2	-	1.79215689D+02	9.86747942D-01	-1.62260591D-01
11.5	3/2	+	3.05591548D+02	1.61984299D-01	9.86793335D-01
11.5	3/2	-	3.05599558D+02	1.62260591D-01	9.86747942D-01
12.5	1/2	-	2.20869750D+02	9.84683709D-01	-1.74350202D-01
12.5	1/2	+	2.21013773D+02	9.84627353D-01	-1.74668186D-01
12.5	3/2	-	3.48516442D+02	1.74350202D-01	9.84683709D-01
12.5	3/2	+	3.48526522D+02	1.74668186D-01	9.84627353D-01
13.5	1/2	+	2.65999976D+02	9.82464379D-01	-1.86450381D-01
13.5	1/2	-	2.66153483D+02	9.82395766D-01	-1.86811562D-01
13.5	3/2	+	3.94861588D+02	1.86450381D-01	9.82464379D-01
13.5	3/2	-	3.94874038D+02	1.86811562D-01	9.82395766D-01
14.5	1/2	-	3.14471554D+02	9.80145889D-01	-1.98277675D-01
14.5	1/2	+	3.14634234D+02	9.80063753D-01	-1.98683264D-01
14.5	3/2	-	4.44624019D+02	1.98277675D-01	9.80145889D-01
14.5	3/2	+	4.44639149D+02	1.98683264D-01	9.80063753D-01
15.5	1/2	+	3.66283805D+02	9.77738678D-01	-2.09826303D-01
15.5	1/2	-	3.66455339D+02	9.77641799D-01	-2.10277230D-01
15.5	3/2	+	4.97800613D+02	2.09826303D-01	9.77738678D-01
15.5	3/2	-	4.97818745D+02	2.10277230D-01	9.77641799D-01
16.5	1/2	-	4.21435940D+02	9.75252982D-01	-2.21091885D-01
16.5	1/2	+	4.21616000D+02	9.75140195D-01	-2.21588810D-01
16.5	3/2	-	5.54388100D+02	2.21091885D-01	9.75252982D-01
16.5	3/2	+	5.54409559D+02	2.21588810D-01	9.75140195D-01
17.5	1/2	+	4.79927050D+02	9.72698752D-01	-2.32071407D-01
17.5	1/2	-	4.80115302D+02	9.72568959D-01	-2.32614744D-01
17.5	3/2	+	6.14383064D+02	2.32071407D-01	9.72698752D-01
17.5	3/2	-	6.14408185D+02	2.32614744D-01	9.72568959D-01
18.5	1/2	-	5.41756100D+02	9.70085588D-01	-2.42763160D-01
18.5	1/2	+	5.41952208D+02	9.69937767D-01	-2.43353094D-01
18.5	3/2	-	6.77781961D+02	2.42763160D-01	9.70085588D-01
18.5	3/2	+	6.77811081D+02	2.43353094D-01	9.69937767D-01
19.5	1/2	+	6.06921924D+02	9.67422680D-01	-2.53166662D-01
19.5	1/2	-	6.07125545D+02	9.67255888D-01	-2.53803166D-01
19.5	3/2	+	7.44581116D+02	2.53166662D-01	9.67422680D-01
19.5	3/2	-	7.44614576D+02	2.53803166D-01	9.67255888D-01
20.5	1/2	-	6.75423216D+02	9.64718765D-01	-2.63282556D-01
20.5	1/2	+	6.75634009D+02	9.64532145D-01	-2.63965417D-01
20.5	3/2	-	8.14776732D+02	2.63282556D-01	9.64718765D-01
20.5	3/2	+	8.14814875D+02	2.63965417D-01	9.64532145D-01

Table C-1 (Continued)

J	g	PARITY	ENERGY (CM**-1)	C(J,g,P,1/2)	C(J,g,P,3/2)
21.5	1/2	+	7.47258528D+02	9.61982097D-01	-2.73112513D-01
21.5	1/2	-	7.47476149D+02	9.61774878D-01	-2.73841347D-01
21.5	3/2	+	8.88364898D+02	2.73112513D-01	9.61982097D-01
21.5	3/2	-	8.88408066D+02	2.73841347D-01	9.61774878D-01
22.5	1/2	-	8.22426267D+02	9.59220423D-01	-2.82659123D-01
22.5	1/2	+	8.22650373D+02	9.58991923D-01	-2.83433400D-01
22.5	3/2	-	9.65341589D+02	2.82659123D-01	9.59220423D-01
22.5	3/2	+	9.65390126D+02	2.83433400D-01	9.58991923D-01
23.5	1/2	+	9.00924687D+02	9.56440972D-01	-2.91925789D-01
23.5	1/2	-	9.01154936D+02	9.56190594D-01	-2.92744850D-01
23.5	3/2	+	1.04570267D+03	2.91925789D-01	9.56440972D-01
23.5	3/2	-	1.04575692D+03	2.92744850D-01	9.56190594D-01
24.5	1/2	-	9.82751889D+02	9.53650452D-01	-3.00916627D-01
24.5	1/2	+	9.82987941D+02	9.53377685D-01	-3.01779702D-01
24.5	3/2	-	1.12944391D+03	3.00916627D-01	9.53650452D-01
24.5	3/2	+	1.12950421D+03	3.01779702D-01	9.53377685D-01
25.5	1/2	+	1.06790582D+03	9.50855049D-01	-3.09636362D-01
25.5	1/2	-	1.06814734D+03	9.50559467D-01	-3.10542590D-01
25.5	3/2	+	1.21656097D+03	3.09636362D-01	9.50855049D-01
25.5	3/2	-	1.21662766D+03	3.10542590D-01	9.50559467D-01
26.5	1/2	-	1.15638427D+03	9.48060441D-01	-3.18090238D-01
26.5	1/2	+	1.15663092D+03	9.47741695D-01	-3.19038680D-01
26.5	3/2	-	1.30704942D+03	3.18090238D-01	9.48060441D-01
26.5	3/2	+	1.30712283D+03	3.19038680D-01	9.47741695D-01
27.5	1/2	+	1.24818486D+03	9.45271812D-01	-3.26283928D-01
27.5	1/2	-	1.24843631D+03	9.44929628D-01	-3.27273584D-01
27.5	3/2	+	1.40090470D+03	3.26283928D-01	9.45271812D-01
27.5	3/2	-	1.40098517D+03	3.27273584D-01	9.44929628D-01
28.5	1/2	-	1.34330507D+03	9.42493864D-01	-3.34223452D-01
28.5	1/2	+	1.34356099D+03	9.42128039D-01	-3.35253274D-01
28.5	3/2	-	1.49812221D+03	3.34223452D-01	9.42493864D-01
28.5	3/2	+	1.49821006D+03	3.35253274D-01	9.42128039D-01
29.5	1/2	+	1.44174219D+03	9.39730844D-01	-3.41915109D-01
29.5	1/2	-	1.44200226D+03	9.39341241D-01	-3.42984012D-01
29.5	3/2	+	1.59869721D+03	3.41915109D-01	9.39730844D-01
29.5	3/2	-	1.59879276D+03	3.42984012D-01	9.39341241D-01
30.5	1/2	-	1.54349339D+03	9.36986562D-01	-3.49365401D-01
30.5	1/2	+	1.54375729D+03	9.36573106D-01	-3.50472276D-01
30.5	3/2	-	1.70262488D+03	3.49365401D-01	9.36986562D-01
30.5	3/2	+	1.70272845D+03	3.50472276D-01	9.36573106D-01
31.5	1/2	+	1.64855564D+03	9.34264419D-01	-3.56580981D-01

Table C-1 (Continued)

J	g	PARITY	ENERGY (CM**-1)	C(J,g,P,1/2)	C(J,g,P,3/2)
31.5	1/2	-	1.64882306D+03	9.33827091D-01	-3.57724703D-01
31.5	3/2	+	1.80990030D+03	3.56580981D-01	9.34264419D-01
31.5	3/2	-	1.81001222D+03	3.57724703D-01	9.33827091D-01
32.5	1/2	-	1.75692577D+03	9.31567430D-01	-3.63568595D-01
32.5	1/2	+	1.75719639D+03	9.31106262D-01	-3.64748034D-01
32.5	3/2	-	1.92051849D+03	3.63568595D-01	9.31567430D-01
32.5	3/2	+	1.92063905D+03	3.64748034D-01	9.31106262D-01
33.5	1/2	+	1.86860045D+03	9.28898250D-01	-3.70335038D-01
33.5	1/2	-	1.86887397D+03	9.28413321D-01	-3.71549061D-01
33.5	3/2	+	2.03447432D+03	3.70335038D-01	9.28898250D-01
33.5	3/2	-	2.03460384D+03	3.71549061D-01	9.28413321D-01
34.5	1/2	-	1.98357618D+03	9.26259200D-01	-3.76887110D-01
34.5	1/2	+	1.98385230D+03	9.25750630D-01	-3.78134594D-01
34.5	3/2	-	2.15176262D+03	3.76887110D-01	9.26259200D-01
34.5	3/2	+	2.15190139D+03	3.78134594D-01	9.25750630D-01
35.5	1/2	+	2.10184930D+03	9.23652291D-01	-3.83231582D-01
35.5	1/2	-	2.10212773D+03	9.23120236D-01	-3.84511416D-01
35.5	3/2	+	2.27237809D+03	3.83231582D-01	9.23652291D-01
35.5	3/2	-	2.27252641D+03	3.84511416D-01	9.23120236D-01
36.5	1/2	-	2.22341602D+03	9.21079247D-01	-3.89375168D-01
36.5	1/2	+	2.22369645D+03	9.20523899D-01	-3.90686257D-01
36.5	3/2	-	2.39631536D+03	3.89375168D-01	9.21079247D-01
36.5	3/2	+	2.39647352D+03	3.90686257D-01	9.20523899D-01
37.5	1/2	+	2.34827235D+03	9.18541532D-01	-3.95324493D-01
37.5	1/2	-	2.34855451D+03	9.17963111D-01	-3.96665763D-01
37.5	3/2	+	2.52356894D+03	3.95324493D-01	9.18541532D-01
37.5	3/2	-	2.52373724D+03	3.96665763D-01	9.17963111D-01
38.5	1/2	-	2.47641419D+03	9.16040369D-01	-4.01086078D-01
38.5	1/2	+	2.47669779D+03	9.15439120D-01	-4.02456478D-01
38.5	3/2	-	2.65413328D+03	4.01086078D-01	9.16040369D-01
38.5	3/2	+	2.65431199D+03	4.02456478D-01	9.15439120D-01
39.5	1/2	+	2.60783725D+03	9.13576765D-01	-4.06666318D-01
39.5	1/2	-	2.60812201D+03	9.12952955D-01	-4.08064826D-01
39.5	3/2	+	2.78800270D+03	4.06666318D-01	9.13576765D-01
39.5	3/2	-	2.78819211D+03	4.08064826D-01	9.12952955D-01
40.5	1/2	-	2.74253711D+03	9.11151526D-01	-4.12071470D-01
40.5	1/2	+	2.74282275D+03	9.10505440D-01	-4.13497089D-01
40.5	3/2	-	2.92517145D+03	4.12071470D-01	9.11151526D-01
40.5	3/2	+	2.92537182D+03	4.13497089D-01	9.10505440D-01
41.5	1/2	+	2.88050918D+03	9.08765281D-01	-4.17307638D-01
41.5	1/2	-	2.88079544D+03	9.08097220D-01	-4.18759404D-01

Table C-1 (Continued)

J	g	PARITY	ENERGY (CM**-1)	C(J,g,P,1/2)	C(J,g,P,3/2)
41.5	3/2	+	3.06563367D+03	4.17307638D-01	9.08765281D-01
41.5	3/2	-	3.06584528D+03	4.18759404D-01	9.08097220D-01

Table C-2

Energy Eigenstates and Eigenvalues for v=1 with Lambda Doubling

J	g	PARITY	ENERGY (CM**-1)	C(J,g,P,1/2)	C(J,g,P,3/2)
0.5	1/2	-	-5.98313816D+01	1.00000000D+00	0.00000000D+00
0.5	1/2	+	-5.98195270D+01	1.00000000D+00	0.00000000D+00
1.5	1/2	+	-5.48727557D+01	9.99705856D-01	-2.42528494D-02
1.5	1/2	-	-5.48490761D+01	9.99705674D-01	-2.42603639D-02
1.5	3/2	+	6.48189349D+01	2.42528494D-02	9.99705856D-01
1.5	3/2	-	6.48189646D+01	2.42603639D-02	9.99705674D-01
2.5	1/2	-	-4.66044287D+01	9.99217920D-01	-3.95417334D-02
2.5	1/2	+	-4.65689833D+01	9.99217195D-01	-3.95600583D-02
2.5	3/2	-	7.33292234D+01	3.95417334D-02	9.99217920D-01
2.5	3/2	+	7.33293420D+01	3.95600583D-02	9.99217195D-01
3.5	1/2	+	-3.50264200D+01	9.98539507D-01	-5.40264019D-02
3.5	1/2	-	-3.49792968D+01	9.98537708D-01	-5.40596518D-02
3.5	3/2	+	8.52427246D+01	5.40264019D-02	9.98539507D-01
3.5	3/2	-	8.52430200D+01	5.40596518D-02	9.98537708D-01
4.5	1/2	-	-2.01387675D+01	9.97675139D-01	-6.81492277D-02
4.5	1/2	+	-2.00800824D+01	9.97671575D-01	-6.82013863D-02
4.5	3/2	-	1.00558554D+02	6.81492277D-02	9.97675139D-01
4.5	3/2	+	1.00559142D+02	6.82013863D-02	9.97671575D-01
5.5	1/2	+	-1.94153271D+00	9.96630454D-01	-8.20227872D-02
5.5	1/2	-	-1.87142850D+00	9.96624290D-01	-8.20976508D-02
5.5	3/2	+	1.19275587D+02	8.20227872D-02	9.96630454D-01
5.5	3/2	-	1.19276611D+02	8.20976508D-02	9.96624290D-01
6.5	1/2	-	1.95651936D+01	9.95412114D-01	-9.56803183D-02
6.5	1/2	+	1.96465485D+01	9.95402387D-01	-9.57814600D-02
6.5	3/2	-	1.41392465D+02	9.56803183D-02	9.95412114D-01
6.5	3/2	+	1.41394092D+02	9.57814600D-02	9.95402387D-01
7.5	1/2	+	4.43812842D+01	9.94027685D-01	-1.09128193D-01
7.5	1/2	-	4.44736973D+01	9.94013323D-01	-1.09258933D-01
7.5	3/2	+	1.66907602D+02	1.09128193D-01	9.94027685D-01
7.5	3/2	-	1.66910026D+02	1.09258933D-01	9.94013323D-01
8.5	1/2	-	7.25065682D+01	9.92485513D-01	-1.22362191D-01
8.5	1/2	+	7.26098248D+01	9.92465356D-01	-1.22525577D-01
8.5	3/2	-	1.95819193D+02	1.22362191D-01	9.92485513D-01
8.5	3/2	+	1.95822628D+02	1.22525577D-01	9.92465356D-01
9.5	1/2	+	1.03940823D+02	9.90794598D-01	-1.35373799D-01
9.5	1/2	-	1.04054687D+02	9.90767417D-01	-1.35572587D-01
9.5	3/2	+	2.28125223D+02	1.35373799D-01	9.90794598D-01
9.5	3/2	-	2.28129904D+02	1.35572587D-01	9.90767417D-01
10.5	1/2	-	1.38683764D+02	9.88964449D-01	-1.48153024D-01
10.5	1/2	+	1.38807983D+02	9.88928970D-01	-1.48389667D-01
10.5	3/2	-	2.63823472D+02	1.48153024D-01	9.88964449D-01

Table C-2 (Continued)

J	g	PARITY	ENERGY (CM**-1)	C(J,g,P,1/2)	C(J,g,P,3/2)
10.5	3/2	+	2.63829654D+02	1.48389667D-01	9.88928970D-01
11.5	1/2	+	1.76735039D+02	9.87004961D-01	-1.60689787D-01
11.5	1/2	-	1.76869340D+02	9.86959881D-01	-1.60966433D-01
11.5	3/2	+	3.02911529D+02	1.60689787D-01	9.87004961D-01
11.5	3/2	-	3.02919483D+02	1.60966433D-01	9.86959881D-01
12.5	1/2	-	2.18094215D+02	9.84926276D-01	-1.72974655D-01
12.5	1/2	+	2.18238315D+02	9.84870289D-01	-1.73293145D-01
12.5	3/2	-	3.45386798D+02	1.72974655D-01	9.84926276D-01
12.5	3/2	+	3.45396810D+02	1.73293145D-01	9.84870289D-01
13.5	1/2	+	2.62760775D+02	9.82738665D-01	-1.84999234D-01
13.5	1/2	-	2.62914373D+02	9.82670474D-01	-1.85361104D-01
13.5	3/2	+	3.91246509D+02	1.84999234D-01	9.82738665D-01
13.5	3/2	-	3.91258877D+02	1.85361104D-01	9.82670474D-01
14.5	1/2	-	3.10734104D+02	9.80452411D-01	-1.96756370D-01
14.5	1/2	+	3.10896890D+02	9.80370748D-01	-1.97162867D-01
14.5	3/2	-	4.40487724D+02	1.96756370D-01	9.80452411D-01
14.5	3/2	+	4.40502758D+02	1.97162867D-01	9.80370748D-01
15.5	1/2	+	3.62013482D+02	9.78077706D-01	-2.08240247D-01
15.5	1/2	-	3.62185138D+02	9.77981344D-01	-2.08692335D-01
15.5	3/2	+	4.93107348D+02	2.08240247D-01	9.78077706D-01
15.5	3/2	-	4.93125367D+02	2.08692335D-01	9.77981344D-01
16.5	1/2	-	4.16598079D+02	9.75624556D-01	-2.19446406D-01
16.5	1/2	+	4.16778277D+02	9.75512323D-01	-2.19944783D-01
16.5	3/2	-	5.49102135D+02	2.19446406D-01	9.75624556D-01
16.5	3/2	+	5.49123466D+02	2.19944783D-01	9.75512323D-01
17.5	1/2	+	4.74486945D+02	9.73102704D-01	-2.30371717D-01
17.5	1/2	-	4.74675353D+02	9.72973492D-01	-2.30916832D-01
17.5	3/2	+	6.08468699D+02	2.30371717D-01	9.73102704D-01
17.5	3/2	-	6.08493675D+02	2.30916832D-01	9.72973492D-01
18.5	1/2	-	5.35679006D+02	9.70521558D-01	-2.41014327D-01
18.5	1/2	+	5.35875286D+02	9.70374334D-01	-2.41606397D-01
18.5	3/2	-	6.71203516D+02	2.41014327D-01	9.70521558D-01
18.5	3/2	+	6.71232475D+02	2.41606397D-01	9.70374334D-01
19.5	1/2	+	6.00173053D+02	9.67890141D-01	-2.51373577D-01
19.5	1/2	-	6.00376864D+02	9.67723950D-01	-2.52012612D-01
19.5	3/2	+	7.37302935D+02	2.51373577D-01	9.67890141D-01
19.5	3/2	-	7.37336216D+02	2.52012612D-01	9.67723950D-01
20.5	1/2	-	6.67967742D+02	9.65217043D-01	-2.61449918D-01
20.5	1/2	+	6.68178742D+02	9.65031013D-01	-2.62135735D-01
20.5	3/2	-	8.06763179D+02	2.61449918D-01	9.65217043D-01
20.5	3/2	+	8.06801127D+02	2.62135735D-01	9.65031013D-01

Table C-2 (Continued)

J	g	PARITY	ENERGY (CM**-1)	C(J,g,P,1/2)	C(J,g,P,3/2)
21.5	1/2	+	7.39061586D+02	9.62510391D-01	-2.71244809D-01
21.5	1/2	-	7.39279431D+02	9.62303737D-01	-2.71977055D-01
21.5	3/2	+	8.79580356D+02	2.71244809D-01	9.62510391D-01
21.5	3/2	-	8.79623314D+02	2.71977055D-01	9.62303737D-01
22.5	1/2	-	8.13452954D+02	9.59777826D-01	-2.80760617D-01
22.5	1/2	+	8.13677300D+02	9.59549847D-01	-2.81538790D-01
22.5	3/2	-	9.55750458D+02	2.80760617D-01	9.59777826D-01
22.5	3/2	+	9.55798770D+02	2.81538790D-01	9.59549847D-01
23.5	1/2	+	8.91140063D+02	9.57026489D-01	-2.90000515D-01
23.5	1/2	-	8.91370567D+02	9.56776573D-01	-2.90823982D-01
23.5	3/2	+	1.03526937D+03	2.90000515D-01	9.57026489D-01
23.5	3/2	-	1.03532338D+03	2.90823982D-01	9.56776573D-01
24.5	1/2	-	9.72120977D+02	9.54263017D-01	-2.98968384D-01
24.5	1/2	+	9.72357298D+02	9.53990636D-01	-2.99836399D-01
24.5	3/2	-	1.11813286D+03	2.98968384D-01	9.54263017D-01
24.5	3/2	+	1.11819291D+03	2.99836399D-01	9.53990636D-01
25.5	1/2	+	1.05639361D+03	9.51493543D-01	-3.07668713D-01
25.5	1/2	-	1.05663541D+03	9.51198253D-01	-3.08580433D-01
25.5	3/2	+	1.20433661D+03	3.07668713D-01	9.51493543D-01
25.5	3/2	-	1.20440304D+03	3.08580433D-01	9.51198253D-01
26.5	1/2	-	1.14395571D+03	9.48723708D-01	-3.16106510D-01
26.5	1/2	+	1.14420265D+03	9.48405141D-01	-3.17061016D-01
26.5	3/2	-	1.29387619D+03	3.16106510D-01	9.48723708D-01
26.5	3/2	+	1.29394933D+03	3.17061016D-01	9.48405141D-01
27.5	1/2	+	1.23480487D+03	9.45958667D-01	-3.24287218D-01
27.5	1/2	-	1.23505662D+03	9.45616533D-01	-3.25283525D-01
27.5	3/2	+	1.38674707D+03	3.24287218D-01	9.45958667D-01
27.5	3/2	-	1.38682725D+03	3.25283525D-01	9.45616533D-01
28.5	1/2	-	1.32893853D+03	9.43203111D-01	-3.32216633D-01
28.5	1/2	+	1.32919476D+03	9.42837190D-01	-3.33253706D-01
28.5	3/2	-	1.48294463D+03	3.32216633D-01	9.43203111D-01
28.5	3/2	+	1.48303218D+03	3.33253706D-01	9.42837190D-01
29.5	1/2	+	1.42635396D+03	9.40461282D-01	-3.39900834D-01
29.5	1/2	-	1.42661435D+03	9.40071422D-01	-3.40977598D-01
29.5	3/2	+	1.58246413D+03	3.39900834D-01	9.40461282D-01
29.5	3/2	-	1.58255938D+03	3.40977598D-01	9.40071422D-01
30.5	1/2	-	1.52704828D+03	9.37736997D-01	-3.47346115D-01
30.5	1/2	+	1.52731250D+03	9.37323106D-01	-3.48461469D-01
30.5	3/2	-	1.68530077D+03	3.47346115D-01	9.37736997D-01
30.5	3/2	+	1.68540404D+03	3.48461469D-01	9.37323106D-01
31.5	1/2	+	1.63101844D+03	9.35033671D-01	-3.54558929D-01

Table C-2 (Continued)

J	g	PARITY	ENERGY (CM**-1)	C(J,g,P,1/2)	C(J,g,P,3/2)
31.5	1/2	-	1.63128619D+03	9.34595714D-01	-3.55711754D-01
31.5	3/2	+	1.79144962D+03	3.54558929D-01	9.35033671D-01
31.5	3/2	-	1.79156123D+03	3.55711754D-01	9.34595714D-01
32.5	1/2	-	1.73826124D+03	9.32354339D-01	-3.61545829D-01
32.5	1/2	+	1.73853219D+03	9.31892333D-01	-3.62734999D-01
32.5	3/2	-	1.90090568D+03	3.61545829D-01	9.32354339D-01
32.5	3/2	+	1.90102594D+03	3.62734999D-01	9.31892333D-01
33.5	1/2	+	1.84877331D+03	9.29701681D-01	-3.68313431D-01
33.5	1/2	-	1.84904715D+03	9.29215692D-01	-3.69537816D-01
33.5	3/2	+	2.01366384D+03	3.68313431D-01	9.29701681D-01
33.5	3/2	-	2.01379306D+03	3.69537816D-01	9.29215692D-01
34.5	1/2	-	1.96255112D+03	9.27078049D-01	-3.74868365D-01
34.5	1/2	+	1.96282756D+03	9.26568184D-01	-3.76126840D-01
34.5	3/2	-	2.12971891D+03	3.74868365D-01	9.27078049D-01
34.5	3/2	+	2.12985738D+03	3.76126840D-01	9.26568184D-01
35.5	1/2	+	2.07959099D+03	9.24485486D-01	-3.81217242D-01
35.5	1/2	-	2.07986973D+03	9.23951892D-01	-3.82508695D-01
35.5	3/2	+	2.24906558D+03	3.81217242D-01	9.24485486D-01
35.5	3/2	-	2.24921361D+03	3.82508695D-01	9.23951892D-01
36.5	1/2	-	2.19988908D+03	9.21925755D-01	-3.87366624D-01
36.5	1/2	+	2.20016982D+03	9.21368611D-01	-3.88689957D-01
36.5	3/2	-	2.37169846D+03	3.87366624D-01	9.21925755D-01
36.5	3/2	+	2.37185634D+03	3.88689957D-01	9.21368611D-01
37.5	1/2	+	2.32344139D+03	9.19400358D-01	-3.93322999D-01
37.5	1/2	-	2.32372384D+03	9.18819873D-01	-3.94677135D-01
37.5	3/2	+	2.49761207D+03	3.93322999D-01	9.19400358D-01
37.5	3/2	-	2.49778010D+03	3.94677135D-01	9.18819873D-01
38.5	1/2	-	2.45024377D+03	9.16910558D-01	-3.99092757D-01
38.5	1/2	+	2.45052765D+03	9.16306969D-01	-4.00476639D-01
38.5	3/2	-	2.62680083D+03	3.99092757D-01	9.16910558D-01
38.5	3/2	+	2.62697928D+03	4.00476639D-01	9.16306969D-01
39.5	1/2	+	2.58029191D+03	9.14457402D-01	-4.04682172D-01
39.5	1/2	-	2.58057693D+03	9.13830967D-01	-4.06094771D-01
39.5	3/2	+	2.75925904D+03	4.04682172D-01	9.14457402D-01
39.5	3/2	-	2.75944820D+03	4.06094771D-01	9.13830967D-01
40.5	1/2	-	2.71358135D+03	9.12041738D-01	-4.10097389D-01
40.5	1/2	+	2.71386724D+03	9.11392736D-01	-4.11537703D-01
40.5	3/2	-	2.89498094D+03	4.10097389D-01	9.12041738D-01
40.5	3/2	+	2.89518109D+03	4.11537703D-01	9.11392736D-01
41.5	1/2	+	2.85010748D+03	9.09664235D-01	-4.15344410D-01
41.5	1/2	-	2.85039397D+03	9.08992961D-01	-4.16811464D-01

Table C-2 (Continued)

J	g	PARITY	ENERGY (CM**-1)	C(J,g,P,1/2)	C(J,g,P,3/2)
41.5	3/2	+	3.03396064D+03	4.15344410D-01	9.09664235D-01
41.5	3/2	-	3.03417205D+03	4.16811464D-01	9.08992961D-01

Table C-3

Energy Eigenstates and Eigenvalues for v=0 without Lambda Doubling

J	g	ENERGY (CM**-1)	C(J,g,1/2)	C(J,g,3/2)
0.5	1/2	-5.98179034D+01	1.00000000D+00	0.00000000D+00
1.5	1/2	-5.48022097D+01	9.99699012D-01	-2.45333351D-02
1.5	3/2	6.49785352D+01	2.45333351D-02	9.99699012D-01
2.5	1/2	-4.64427315D+01	9.99199649D-01	-4.00007659D-02
2.5	3/2	7.35797591D+01	4.00007659D-02	9.99199649D-01
3.5	1/2	-3.47394880D+01	9.98505288D-01	-5.46551937D-02
3.5	3/2	8.56205790D+01	5.46551937D-02	9.98505288D-01
4.5	1/2	-1.96925115D+01	9.97620567D-01	-6.89434794D-02
4.5	3/2	1.01100108D+02	6.89434794D-02	9.97620567D-01
5.5	1/2	-1.30185201D+00	9.96551302D-01	-8.29789319D-02
5.5	3/2	1.20017213D+02	8.29789319D-02	9.96551302D-01
6.5	1/2	2.04324163D+01	9.95304374D-01	-9.67946480D-02
6.5	3/2	1.42370525D+02	9.67946480D-02	9.95304374D-01
7.5	1/2	4.55101880D+01	9.93887615D-01	-1.10396594D-01
7.5	3/2	1.68158441D+02	1.10396594D-01	9.93887615D-01
8.5	1/2	7.39313186D+01	9.92309676D-01	-1.23780075D-01
8.5	3/2	1.97379137D+02	1.23780075D-01	9.92309676D-01
9.5	1/2	1.05695616D+02	9.90579882D-01	-1.36936106D-01
9.5	3/2	2.30030574D+02	1.36936106D-01	9.90579882D-01
10.5	1/2	1.40802830D+02	9.88708095D-01	-1.49854270D-01
10.5	3/2	2.66110507D+02	1.49854270D-01	9.88708095D-01
11.5	1/2	1.79252645D+02	9.86704571D-01	-1.62524118D-01
11.5	3/2	3.05616498D+02	1.62524118D-01	9.86704571D-01
12.5	1/2	2.21044670D+02	9.84579821D-01	-1.74935919D-01
12.5	3/2	3.48545920D+02	1.74935919D-01	9.84579821D-01
13.5	1/2	2.66178428D+02	9.82344482D-01	-1.87081048D-01
13.5	3/2	3.94895972D+02	1.87081048D-01	9.82344482D-01
14.5	1/2	3.14653348D+02	9.80009196D-01	-1.98952194D-01
14.5	3/2	4.44663686D+02	1.98952194D-01	9.80009196D-01
15.5	1/2	3.66468757D+02	9.77584501D-01	-2.10543449D-01
15.5	3/2	4.97845933D+02	2.10543449D-01	9.77584501D-01
16.5	1/2	4.21623871D+02	9.75080732D-01	-2.21850324D-01
16.5	3/2	5.54439438D+02	2.21850324D-01	9.75080732D-01
17.5	1/2	4.80117785D+02	9.72507940D-01	-2.32869718D-01
17.5	3/2	6.14440781D+02	2.32869718D-01	9.72507940D-01
18.5	1/2	5.41949473D+02	9.69875822D-01	-2.43599857D-01
18.5	3/2	6.77846410D+02	2.43599857D-01	9.69875822D-01
19.5	1/2	6.07117772D+02	9.67193659D-01	-2.54040206D-01
19.5	3/2	7.44652644D+02	2.54040206D-01	9.67193659D-01
20.5	1/2	6.75621385D+02	9.64470277D-01	-2.64191379D-01
20.5	3/2	8.14855681D+02	2.64191379D-01	9.64470277D-01

Table C-3 (Continued)

J	g	ENERGY (CM**-1)	C(J,g,1/2)	C(J,g,3/2)
21.5	1/2	7.47458872D+02	9.61714013D-01	-2.74055027D-01
21.5	3/2	8.88451600D+02	2.74055027D-01	9.61714013D-01
22.5	1/2	8.22628644D+02	9.58932689D-01	-2.83633738D-01
22.5	3/2	9.65436370D+02	2.83633738D-01	9.58932689D-01
23.5	1/2	9.01128964D+02	9.56133606D-01	-2.92930925D-01
23.5	3/2	1.04580585D+03	2.92930925D-01	9.56133606D-01
24.5	1/2	9.82957941D+02	9.53323535D-01	-3.01950721D-01
24.5	3/2	1.12955581D+03	3.01950721D-01	9.53323535D-01
25.5	1/2	1.06811353D+03	9.50508720D-01	-3.10697880D-01
25.5	3/2	1.21668188D+03	3.10697880D-01	9.50508720D-01
26.5	1/2	1.15659352D+03	9.47694892D-01	-3.19177682D-01
26.5	3/2	1.30717964D+03	3.19177682D-01	9.47694892D-01
27.5	1/2	1.24839555D+03	9.44887276D-01	-3.27395840D-01
27.5	3/2	1.40104453D+03	3.27395840D-01	9.44887276D-01
28.5	1/2	1.34351709D+03	9.42090616D-01	-3.35358423D-01
28.5	3/2	1.49827193D+03	3.35358423D-01	9.42090616D-01
29.5	1/2	1.44195546D+03	9.39309191D-01	-3.43071777D-01
29.5	3/2	1.59885710D+03	3.43071777D-01	9.39309191D-01
30.5	1/2	1.54370782D+03	9.36546840D-01	-3.50542461D-01
30.5	3/2	1.70279521D+03	3.50542461D-01	9.36546840D-01
31.5	1/2	1.64877115D+03	9.33806988D-01	-3.57777179D-01
31.5	3/2	1.81008135D+03	3.57777179D-01	9.33806988D-01
32.5	1/2	1.75714228D+03	9.31092667D-01	-3.64782736D-01
32.5	3/2	1.92071050D+03	3.64782736D-01	9.31092667D-01
33.5	1/2	1.86881789D+03	9.28406549D-01	-3.71565982D-01
33.5	3/2	2.03467757D+03	3.71565982D-01	9.28406549D-01
34.5	1/2	1.98379448D+03	9.25750965D-01	-3.78133773D-01
34.5	3/2	2.15197735D+03	3.78133773D-01	9.25750965D-01
35.5	1/2	2.10206841D+03	9.23127933D-01	-3.84492938D-01
35.5	3/2	2.27260455D+03	3.84492938D-01	9.23127933D-01
36.5	1/2	2.22363587D+03	9.20539183D-01	-3.90650243D-01
36.5	3/2	2.39655379D+03	3.90650243D-01	9.20539183D-01
37.5	1/2	2.34849290D+03	9.17986182D-01	-3.96612368D-01
37.5	3/2	2.52381959D+03	3.96612368D-01	9.17986182D-01
38.5	1/2	2.47663538D+03	9.15470152D-01	-4.02385887D-01
38.5	3/2	2.65439637D+03	4.02385887D-01	9.15470152D-01
39.5	1/2	2.60805904D+03	9.12992097D-01	-4.07977244D-01
39.5	3/2	2.78827847D+03	4.07977244D-01	9.12992097D-01
40.5	1/2	2.74275945D+03	9.10552820D-01	-4.13392744D-01
40.5	3/2	2.92546013D+03	4.13392744D-01	9.10552820D-01
41.5	1/2	2.88073204D+03	9.08152945D-01	-4.18638541D-01

Table C-3 (Continued)

J	g	ENERGY (CM**-1)	C(J,g,1/2)	C(J,g,3/2)
41.5	3/2	3.06593547D+03	4.18638541D-01	9.08152945D-01

Table C-4

Energy Eigenstates and Eigenvalues for v=1 without Lambda Doubling

J	g	ENERGY (CM**-1)	C(J,g,1/2)	C(J,g,3/2)
0.5	1/2	-5.97128470D+01	1.00000000D+00	0.00000000D+00
1.5	1/2	-5.47484835D+01	9.99704169D-01	-2.43223056D-02
1.5	3/2	6.48194062D+01	2.43223056D-02	9.99704169D-01
2.5	1/2	-4.64745634D+01	9.99213324D-01	-3.96577053D-02
2.5	3/2	7.33304981D+01	3.96577053D-02	9.99213324D-01
3.5	1/2	-3.48911176D+01	9.98530730D-01	-5.41883777D-02
3.5	3/2	8.52451463D+01	5.41883777D-02	9.98530730D-01
4.5	1/2	-1.99981941D+01	9.97660876D-01	-6.83577129D-02
4.5	3/2	1.00562476D+02	6.83577129D-02	9.97660876D-01
5.5	1/2	-1.79586303D+00	9.96609385D-01	-8.22783908D-02
5.5	3/2	1.19281373D+02	8.22783908D-02	9.96609385D-01
6.5	1/2	1.97157775D+01	9.95382922D-01	-9.59835321D-02
6.5	3/2	1.41400483D+02	9.59835321D-02	9.95382922D-01
7.5	1/2	4.45365950D+01	9.93989074D-01	-1.09479317D-01
7.5	3/2	1.66918228D+02	1.09479317D-01	9.93989074D-01
8.5	1/2	7.26664144D+01	9.92436225D-01	-1.22761309D-01
8.5	3/2	1.95832807D+02	1.22761309D-01	9.92436225D-01
9.5	1/2	1.04105010D+02	9.90733424D-01	-1.35820772D-01
9.5	3/2	2.28142205D+02	1.35820772D-01	9.90733424D-01
10.5	1/2	1.38852098D+02	9.88890248D-01	-1.48647497D-01
10.5	3/2	2.63844206D+02	1.48647497D-01	9.88890248D-01
11.5	1/2	1.76907323D+02	9.86916663D-01	-1.61231201D-01
11.5	3/2	3.02936397D+02	1.61231201D-01	9.86916663D-01
12.5	1/2	2.18270257D+02	9.84822898D-01	-1.73562262D-01
12.5	3/2	3.45416183D+02	1.73562262D-01	9.84822898D-01
13.5	1/2	2.62940383D+02	9.82619315D-01	-1.85632115D-01
13.5	3/2	3.91280788D+02	1.85632115D-01	9.82619315D-01
14.5	1/2	3.10917090D+02	9.80316291D-01	-1.97433458D-01
14.5	3/2	4.40527273D+02	1.97433458D-01	9.80316291D-01
15.5	1/2	3.62199662D+02	9.77924115D-01	-2.08960344D-01
15.5	3/2	4.93152539D+02	2.08960344D-01	9.77924115D-01
16.5	1/2	4.16787275D+02	9.75452893D-01	-2.20208205D-01
16.5	3/2	5.49153335D+02	2.20208205D-01	9.75452893D-01
17.5	1/2	4.74678983D+02	9.72912465D-01	-2.31173821D-01
17.5	3/2	6.08526267D+02	2.31173821D-01	9.72912465D-01
18.5	1/2	5.35873719D+02	9.70312336D-01	-2.41855269D-01
18.5	3/2	6.71267809D+02	2.41855269D-01	9.70312336D-01
19.5	1/2	6.00370280D+02	9.67661619D-01	-2.52251839D-01
19.5	3/2	7.37374300D+02	2.52251839D-01	9.67661619D-01
20.5	1/2	6.68167329D+02	9.64968994D-01	-2.62363946D-01
20.5	3/2	8.06841959D+02	2.62363946D-01	9.64968994D-01

Table C-4 (Continued)

J	g	ENERGY (CM**-1)	C(J,g,1/2)	C(J,g,3/2)
21.5	1/2	7.39263386D+02	9.62242669D-01	-2.72193031D-01
21.5	3/2	8.79666885D+02	2.72193031D-01	9.62242669D-01
22.5	1/2	8.13656826D+02	9.59490362D-01	-2.81741452D-01
22.5	3/2	9.55845065D+02	2.81741452D-01	9.59490362D-01
23.5	1/2	8.91345873D+02	9.56719284D-01	-2.91012391D-01
23.5	3/2	1.03537237D+03	2.91012391D-01	9.56719284D-01
24.5	1/2	9.72328599D+02	9.53936137D-01	-3.00009744D-01
24.5	3/2	1.11824458D+03	3.00009744D-01	9.53936137D-01
25.5	1/2	1.05660292D+03	9.51147114D-01	-3.08738024D-01
25.5	3/2	1.20445735D+03	3.08738024D-01	9.51147114D-01
26.5	1/2	1.14416660D+03	9.48357905D-01	-3.17202276D-01
26.5	3/2	1.29400625D+03	3.17202276D-01	9.48357905D-01
27.5	1/2	1.23501723D+03	9.45573713D-01	-3.25407980D-01
27.5	3/2	1.38688675D+03	3.25407980D-01	9.45573713D-01
28.5	1/2	1.32915227D+03	9.42799267D-01	-3.33360978D-01
28.5	3/2	1.48309420D+03	3.33360978D-01	9.42799267D-01
29.5	1/2	1.42656898D+03	9.40038846D-01	-3.41067396D-01
29.5	3/2	1.58262389D+03	3.41067396D-01	9.40038846D-01
30.5	1/2	1.52726449D+03	9.37296294D-01	-3.48533581D-01
30.5	3/2	1.68547099D+03	3.48533581D-01	9.37296294D-01
31.5	1/2	1.63123576D+03	9.34575051D-01	-3.55766037D-01
31.5	3/2	1.79163057D+03	3.55766037D-01	9.34575051D-01
32.5	1/2	1.73847959D+03	9.31878173D-01	-3.62771376D-01
32.5	3/2	1.90109763D+03	3.62771376D-01	9.31878173D-01
33.5	1/2	1.84899262D+03	9.29208354D-01	-3.69556267D-01
33.5	3/2	2.01386704D+03	3.69556267D-01	9.29208354D-01
34.5	1/2	1.96277133D+03	9.26567959D-01	-3.76127395D-01
34.5	3/2	2.12993361D+03	3.76127395D-01	9.26567959D-01
35.5	1/2	2.07981203D+03	9.23959041D-01	-3.82491427D-01
35.5	3/2	2.24929204D+03	3.82491427D-01	9.23959041D-01
36.5	1/2	2.20011089D+03	9.21383366D-01	-3.88654980D-01
36.5	3/2	2.37193693D+03	3.88654980D-01	9.21383366D-01
37.5	1/2	2.32366392D+03	9.18842440D-01	-3.94624594D-01
37.5	3/2	2.49786279D+03	3.94624594D-01	9.18842440D-01
38.5	1/2	2.45046697D+03	9.16337528D-01	-4.00406712D-01
38.5	3/2	2.62706402D+03	4.00406712D-01	9.16337528D-01
39.5	1/2	2.58051573D+03	9.13869674D-01	-4.06007658D-01
39.5	3/2	2.75953496D+03	4.06007658D-01	9.13869674D-01
40.5	1/2	2.71380575D+03	9.11439725D-01	-4.11433625D-01
40.5	3/2	2.89526980D+03	4.11433625D-01	9.11439725D-01
41.5	1/2	2.85033242D+03	9.09048344D-01	-4.16690662D-01

Table C-4 (Continued)

J	g	ENERGY (CM**-1)	C(J,g,1/2)	C(J,g,3/2)
41.5	3/2	3.03426268D+03	4.16690662D-01	9.09048344D-01

Table C-5

Spectral Line Positions with Lambda Doubling

PARITY	ASSIGNMENT	SUBBAND	POSITION (CM**-1)	SEPARATION (CM**-1)
-	P(1.5)	1/2	1871.05471	1.182D-02
+	P(1.5)	1/2	1871.06654	
+	P(2.5)	1/2	1867.65951	1.176D-02
-	P(2.5)	1/2	1867.67127	
+	P(2.5)	3/2	1867.21270	8.982D-05
-	P(2.5)	3/2	1867.21279	
-	P(3.5)	1/2	1864.23011	1.167D-02
+	P(3.5)	1/2	1864.24178	
-	P(3.5)	3/2	1863.68323	1.792D-04
+	P(3.5)	3/2	1863.68340	
+	P(4.5)	1/2	1860.76652	1.155D-02
-	P(4.5)	1/2	1860.77807	
+	P(4.5)	3/2	1860.11859	2.975D-04
-	P(4.5)	3/2	1860.11888	
-	P(5.5)	1/2	1857.26874	1.141D-02
+	P(5.5)	1/2	1857.28014	
-	P(5.5)	3/2	1856.51903	4.437D-04
+	P(5.5)	3/2	1856.51948	
+	P(6.5)	1/2	1853.73677	1.123D-02
-	P(6.5)	1/2	1853.74801	
+	P(6.5)	3/2	1852.88482	6.167D-04
-	P(6.5)	3/2	1852.88544	
-	P(7.5)	1/2	1850.17063	1.103D-02
+	P(7.5)	1/2	1850.18167	
-	P(7.5)	3/2	1849.21620	8.151D-04
+	P(7.5)	3/2	1849.21702	
+	P(8.5)	1/2	1846.57032	1.081D-02
-	P(8.5)	1/2	1846.58114	
+	P(8.5)	3/2	1845.51342	1.037D-03
-	P(8.5)	3/2	1845.51446	
-	P(9.5)	1/2	1842.93587	1.057D-02
+	P(9.5)	1/2	1842.94644	
-	P(9.5)	3/2	1841.77671	1.281D-03
+	P(9.5)	3/2	1841.77799	
+	P(10.5)	1/2	1839.26729	1.030D-02
-	P(10.5)	1/2	1839.27760	
+	P(10.5)	3/2	1838.00630	1.545D-03
-	P(10.5)	3/2	1838.00785	
-	P(11.5)	1/2	1835.56462	1.002D-02
+	P(11.5)	1/2	1835.57464	

Table C-5 (Continued)

PARITY	ASSIGNMENT	SUBBAND	POSITION (CM**-1)	SEPARATION (CM**-1)
-	P(11.5)	3/2	1834.20243	1.828D-03
+	P(11.5)	3/2	1834.20425	
+	P(12.5)	1/2	1831.82790	9.721D-03
-	P(12.5)	1/2	1831.83762	
+	P(12.5)	3/2	1830.36529	2.126D-03
-	P(12.5)	3/2	1830.36742	
-	P(13.5)	1/2	1828.05716	9.408D-03
+	P(13.5)	1/2	1828.06657	
-	P(13.5)	3/2	1826.49510	2.438D-03
+	P(13.5)	3/2	1826.49754	
+	P(14.5)	1/2	1824.25247	9.083D-03
-	P(14.5)	1/2	1824.26155	
+	P(14.5)	3/2	1822.59206	2.763D-03
-	P(14.5)	3/2	1822.59482	
-	P(15.5)	1/2	1820.41388	8.747D-03
+	P(15.5)	1/2	1820.42263	
-	P(15.5)	3/2	1818.65634	3.098D-03
+	P(15.5)	3/2	1818.65944	
+	P(16.5)	1/2	1816.54147	8.404D-03
-	P(16.5)	1/2	1816.54987	
+	P(16.5)	3/2	1814.68814	3.441D-03
-	P(16.5)	3/2	1814.69158	
-	P(17.5)	1/2	1812.63530	8.054D-03
+	P(17.5)	1/2	1812.64336	
-	P(17.5)	3/2	1810.68761	3.790D-03
+	P(17.5)	3/2	1810.69140	
+	P(18.5)	1/2	1808.69548	7.699D-03
-	P(18.5)	1/2	1808.70317	
+	P(18.5)	3/2	1806.65492	4.144D-03
-	P(18.5)	3/2	1806.65907	
-	P(19.5)	1/2	1804.72207	7.341D-03
+	P(19.5)	1/2	1804.72941	
-	P(19.5)	3/2	1802.59023	4.502D-03
+	P(19.5)	3/2	1802.59473	
+	P(20.5)	1/2	1800.71519	6.981D-03
-	P(20.5)	1/2	1800.72217	
+	P(20.5)	3/2	1798.49367	4.861D-03
-	P(20.5)	3/2	1798.49853	
-	P(21.5)	1/2	1796.67492	6.621D-03
+	P(21.5)	1/2	1796.68154	

Table C-5 (Continued)

PARITY	ASSIGNMENT	SUBBAND	POSITION (CM**-1)	SEPARATION (CM**-1)
-	P(21.5)	3/2	1794.36539	5.221D-03
+	P(21.5)	3/2	1794.37061	
+	P(22.5)	1/2	1792.60139	6.261D-03
-	P(22.5)	1/2	1792.60765	
+	P(22.5)	3/2	1790.20552	5.580D-03
-	P(22.5)	3/2	1790.21110	
-	P(23.5)	1/2	1788.49469	5.903D-03
+	P(23.5)	1/2	1788.50060	
-	P(23.5)	3/2	1786.01418	5.937D-03
+	P(23.5)	3/2	1786.02012	
+	P(24.5)	1/2	1784.35496	5.548D-03
-	P(24.5)	1/2	1784.36050	
+	P(24.5)	3/2	1781.79149	6.291D-03
-	P(24.5)	3/2	1781.79778	
-	P(25.5)	1/2	1780.18229	5.197D-03
+	P(25.5)	1/2	1780.18749	
-	P(25.5)	3/2	1777.53758	6.642D-03
+	P(25.5)	3/2	1777.54422	
+	P(26.5)	1/2	1775.97682	4.849D-03
-	P(26.5)	1/2	1775.98167	
+	P(26.5)	3/2	1773.25254	6.989D-03
-	P(26.5)	3/2	1773.25953	
-	P(27.5)	1/2	1771.73867	4.507D-03
+	P(27.5)	1/2	1771.74318	
-	P(27.5)	3/2	1768.93649	7.331D-03
+	P(27.5)	3/2	1768.94382	
+	P(28.5)	1/2	1767.46796	4.169D-03
-	P(28.5)	1/2	1767.47213	
+	P(28.5)	3/2	1764.58953	7.668D-03
-	P(28.5)	3/2	1764.59719	
-	P(29.5)	1/2	1763.16483	3.838D-03
+	P(29.5)	1/2	1763.16866	
-	P(29.5)	3/2	1760.21175	7.999D-03
+	P(29.5)	3/2	1760.21975	
+	P(30.5)	1/2	1758.82939	3.512D-03
-	P(30.5)	1/2	1758.83290	
+	P(30.5)	3/2	1755.80326	8.324D-03
-	P(30.5)	3/2	1755.81159	
-	P(31.5)	1/2	1754.46178	3.193D-03
+	P(31.5)	1/2	1754.46497	

Table C-5 (Continued)

PARITY	ASSIGNMENT	SUBBAND	POSITION (CM**-1)	SEPARATION (CM**-1)
-	P(31.5)	3/2	1751.36415	
				8.643D-03
+	P(31.5)	3/2	1751.37279	
+	P(32.5)	1/2	1750.06212	
				2.880D-03
-	P(32.5)	1/2	1750.06500	
+	P(32.5)	3/2	1746.89451	
				8.955D-03
-	P(32.5)	3/2	1746.90347	
-	P(33.5)	1/2	1745.63055	
				2.574D-03
+	P(33.5)	1/2	1745.63312	
-	P(33.5)	3/2	1742.39443	
				9.260D-03
+	P(33.5)	3/2	1742.40369	
+	P(34.5)	1/2	1741.16719	
				2.275D-03
-	P(34.5)	1/2	1741.16946	
+	P(34.5)	3/2	1737.86400	
				9.559D-03
-	P(34.5)	3/2	1737.87356	
-	P(35.5)	1/2	1736.67216	
				1.983D-03
+	P(35.5)	1/2	1736.67415	
-	P(35.5)	3/2	1733.30330	
				9.850D-03
+	P(35.5)	3/2	1733.31315	
+	P(36.5)	1/2	1732.14561	
				1.697D-03
-	P(36.5)	1/2	1732.14730	
+	P(36.5)	3/2	1728.71242	
				1.014D-02
-	P(36.5)	3/2	1728.72255	
-	P(37.5)	1/2	1727.58764	
				1.418D-03
+	P(37.5)	1/2	1727.58906	
-	P(37.5)	3/2	1724.09143	
				1.041D-02
+	P(37.5)	3/2	1724.10185	
+	P(38.5)	1/2	1722.99839	
				1.146D-03
-	P(38.5)	1/2	1722.99953	
+	P(38.5)	3/2	1719.44044	
				1.068D-02
-	P(38.5)	3/2	1719.45112	
-	P(39.5)	1/2	1718.37797	
				8.811D-04
+	P(39.5)	1/2	1718.37885	
-	P(39.5)	3/2	1714.75950	
				1.095D-02
+	P(39.5)	3/2	1714.77045	
+	P(40.5)	1/2	1713.72651	
				6.224D-04
-	P(40.5)	1/2	1713.72713	
+	P(40.5)	3/2	1710.04871	
				1.121D-02
-	P(40.5)	3/2	1710.05992	
+	Q(0.5)	1/2	1876.06464	
				2.371D-02
-	Q(0.5)	1/2	1876.08835	

Table C-5 (Continued)

PARITY	ASSIGNMENT	SUBBAND	POSITION (CM**-1)	SEPARATION (CM**-1)
-	Q(1.5)	1/2	1876.00148	4.736D-02
+	Q(1.5)	1/2	1876.04884	
-	Q(1.5)	3/2	1875.81317	5.967D-05
+	Q(1.5)	3/2	1875.81323	
+	Q(2.5)	1/2	1875.90415	7.089D-02
-	Q(2.5)	1/2	1875.97504	
+	Q(2.5)	3/2	1875.72295	2.381D-04
-	Q(2.5)	3/2	1875.72319	
-	Q(3.5)	1/2	1875.77267	9.424D-02
+	Q(3.5)	1/2	1875.86691	
-	Q(3.5)	3/2	1875.59661	5.932D-04
+	Q(3.5)	3/2	1875.59720	
+	Q(4.5)	1/2	1875.60704	1.174D-01
-	Q(4.5)	1/2	1875.72441	
+	Q(4.5)	3/2	1875.43412	1.181D-03
-	Q(4.5)	3/2	1875.43530	
-	Q(5.5)	1/2	1875.40729	1.402D-01
+	Q(5.5)	1/2	1875.54748	
-	Q(5.5)	3/2	1875.23548	2.056D-03
+	Q(5.5)	3/2	1875.23753	
+	Q(6.5)	1/2	1875.17339	1.627D-01
-	Q(6.5)	1/2	1875.33609	
+	Q(6.5)	3/2	1875.00068	3.268D-03
-	Q(6.5)	3/2	1875.00395	
-	Q(7.5)	1/2	1874.90537	1.848D-01
+	Q(7.5)	1/2	1875.09017	
-	Q(7.5)	3/2	1874.72971	4.867D-03
+	Q(7.5)	3/2	1874.73458	
+	Q(8.5)	1/2	1874.60320	2.065D-01
-	Q(8.5)	1/2	1874.80968	
+	Q(8.5)	3/2	1874.42259	6.897D-03
-	Q(8.5)	3/2	1874.42948	
-	Q(9.5)	1/2	1874.26687	2.277D-01
+	Q(9.5)	1/2	1874.49456	
-	Q(9.5)	3/2	1874.07930	9.398D-03
+	Q(9.5)	3/2	1874.08870	
+	Q(10.5)	1/2	1873.89637	2.484D-01
-	Q(10.5)	1/2	1874.14476	
+	Q(10.5)	3/2	1873.69987	1.241D-02
-	Q(10.5)	3/2	1873.71228	

Table C-5 (Continued)

PARITY	ASSIGNMENT	SUBBAND	POSITION (CM**-1)	SEPARATION (CM**-1)
-	Q(11.5)	1/2	1873.49168	2.685D-01
+	Q(11.5)	1/2	1873.76022	
-	Q(11.5)	3/2	1873.28430	1.596D-02
+	Q(11.5)	3/2	1873.30027	
+	Q(12.5)	1/2	1873.05277	2.881D-01
-	Q(12.5)	1/2	1873.34089	
+	Q(12.5)	3/2	1872.83261	2.009D-02
-	Q(12.5)	3/2	1872.85270	
-	Q(13.5)	1/2	1872.57962	3.071D-01
+	Q(13.5)	1/2	1872.88673	
-	Q(13.5)	3/2	1872.34480	2.482D-02
+	Q(13.5)	3/2	1872.36962	
+	Q(14.5)	1/2	1872.07220	3.255D-01
-	Q(14.5)	1/2	1872.39767	
+	Q(14.5)	3/2	1871.82090	3.016D-02
-	Q(14.5)	3/2	1871.85107	
-	Q(15.5)	1/2	1871.53047	3.432D-01
+	Q(15.5)	1/2	1871.87366	
-	Q(15.5)	3/2	1871.26093	3.615D-02
+	Q(15.5)	3/2	1871.29708	
+	Q(16.5)	1/2	1870.95441	3.603D-01
-	Q(16.5)	1/2	1871.31467	
+	Q(16.5)	3/2	1870.66491	4.279D-02
-	Q(16.5)	3/2	1870.70770	
-	Q(17.5)	1/2	1870.34397	3.767D-01
+	Q(17.5)	1/2	1870.72063	
-	Q(17.5)	3/2	1870.03284	5.010D-02
+	Q(17.5)	3/2	1870.08294	
+	Q(18.5)	1/2	1869.69913	3.924D-01
-	Q(18.5)	1/2	1870.09152	
+	Q(18.5)	3/2	1869.36477	5.808D-02
-	Q(18.5)	3/2	1869.42284	
-	Q(19.5)	1/2	1869.01984	4.074D-01
+	Q(19.5)	1/2	1869.42727	
-	Q(19.5)	3/2	1868.66069	6.674D-02
+	Q(19.5)	3/2	1868.72743	
+	Q(20.5)	1/2	1868.30606	4.218D-01
-	Q(20.5)	1/2	1868.72786	
+	Q(20.5)	3/2	1867.92063	7.609D-02
-	Q(20.5)	3/2	1867.99673	

Table C-5 (Continued)

PARITY	ASSIGNMENT	SUBBAND	POSITION (CM**-1)	SEPARATION (CM**-1)
-	Q(21.5)	1/2	1867.55777	4.355D-01
+	Q(21.5)	1/2	1867.99323	
-	Q(21.5)	3/2	1867.14462	8.613D-02
+	Q(21.5)	3/2	1867.23075	
+	Q(22.5)	1/2	1866.77491	4.485D-01
-	Q(22.5)	1/2	1867.22336	
+	Q(22.5)	3/2	1866.33266	9.685D-02
-	Q(22.5)	3/2	1866.42951	
-	Q(23.5)	1/2	1865.95746	4.608D-01
+	Q(23.5)	1/2	1866.41821	
-	Q(23.5)	3/2	1865.48478	1.083D-01
+	Q(23.5)	3/2	1865.59303	
+	Q(24.5)	1/2	1865.10537	4.724D-01
-	Q(24.5)	1/2	1865.57774	
+	Q(24.5)	3/2	1864.60098	1.203D-01
-	Q(24.5)	3/2	1864.72132	
-	Q(25.5)	1/2	1864.21860	4.833D-01
+	Q(25.5)	1/2	1864.70192	
-	Q(25.5)	3/2	1863.68128	1.331D-01
+	Q(25.5)	3/2	1863.81439	
+	Q(26.5)	1/2	1863.29712	4.936D-01
-	Q(26.5)	1/2	1863.79071	
+	Q(26.5)	3/2	1862.72570	1.465D-01
-	Q(26.5)	3/2	1862.87224	
-	Q(27.5)	1/2	1862.34089	5.032D-01
+	Q(27.5)	1/2	1862.84409	
-	Q(27.5)	3/2	1861.73423	1.606D-01
+	Q(27.5)	3/2	1861.89488	
+	Q(28.5)	1/2	1861.34987	5.122D-01
-	Q(28.5)	1/2	1861.86202	
+	Q(28.5)	3/2	1860.70690	1.754D-01
-	Q(28.5)	3/2	1860.88230	
-	Q(29.5)	1/2	1860.32403	5.205D-01
+	Q(29.5)	1/2	1860.84449	
-	Q(29.5)	3/2	1859.64370	1.908D-01
+	Q(29.5)	3/2	1859.83451	
+	Q(30.5)	1/2	1859.26332	5.281D-01
-	Q(30.5)	1/2	1859.79144	
+	Q(30.5)	3/2	1858.54465	2.068D-01
-	Q(30.5)	3/2	1858.75149	

Table C-5 (Continued)

PARITY	ASSIGNMENT	SUBBAND	POSITION (CM**-1)	SEPARATION (CM**-1)
-	Q(31.5)	1/2	1858.16772	
				5.352D-01
+	Q(31.5)	1/2	1858.70287	
-	Q(31.5)	3/2	1857.40973	
				2.235D-01
+	Q(31.5)	3/2	1857.63325	
+	Q(32.5)	1/2	1857.03718	
				5.416D-01
-	Q(32.5)	1/2	1857.57875	
+	Q(32.5)	3/2	1856.23896	
				2.408D-01
-	Q(32.5)	3/2	1856.47978	
-	Q(33.5)	1/2	1855.87167	
				5.474D-01
+	Q(33.5)	1/2	1856.41904	
-	Q(33.5)	3/2	1855.03233	
				2.587D-01
+	Q(33.5)	3/2	1855.29107	
+	Q(34.5)	1/2	1854.67115	
				5.526D-01
-	Q(34.5)	1/2	1855.22371	
+	Q(34.5)	3/2	1853.78985	
				2.772D-01
-	Q(34.5)	3/2	1854.06709	
-	Q(35.5)	1/2	1853.43560	
				5.572D-01
+	Q(35.5)	1/2	1853.99275	
-	Q(35.5)	3/2	1852.51149	
				2.964D-01
+	Q(35.5)	3/2	1852.80785	
+	Q(36.5)	1/2	1852.16496	
				5.612D-01
-	Q(36.5)	1/2	1852.72613	
+	Q(36.5)	3/2	1851.19727	
				3.161D-01
-	Q(36.5)	3/2	1851.51332	
-	Q(37.5)	1/2	1850.85921	
				5.646D-01
+	Q(37.5)	1/2	1851.42382	
-	Q(37.5)	3/2	1849.84716	
				3.363D-01
+	Q(37.5)	3/2	1850.18349	
+	Q(38.5)	1/2	1849.51831	
				5.675D-01
-	Q(38.5)	1/2	1850.08579	
+	Q(38.5)	3/2	1848.46116	
				3.572D-01
-	Q(38.5)	3/2	1848.81833	
-	Q(39.5)	1/2	1848.14223	
				5.698D-01
+	Q(39.5)	1/2	1848.71201	
-	Q(39.5)	3/2	1847.03926	
				3.786D-01
+	Q(39.5)	3/2	1847.41783	
+	Q(40.5)	1/2	1846.73093	
				5.715D-01
-	Q(40.5)	1/2	1847.30247	
+	Q(40.5)	3/2	1845.58144	
				4.005D-01
-	Q(40.5)	3/2	1845.98196	

Table C-5 (Continued)

PARITY	ASSIGNMENT	SUBBAND	POSITION (CM**-1)	SEPARATION (CM**-1)
+	R(0.5)	1/2	1881.04695	1.183D-02
-	R(0.5)	1/2	1881.03512	
-	R(1.5)	1/2	1884.30526	1.177D-02
+	R(1.5)	1/2	1884.29349	
-	R(1.5)	3/2	1884.32358	8.860D-05
+	R(1.5)	3/2	1884.32349	
+	R(2.5)	1/2	1887.52929	1.168D-02
-	R(2.5)	1/2	1887.51760	
+	R(2.5)	3/2	1887.63675	1.758D-04
-	R(2.5)	3/2	1887.63657	
-	R(3.5)	1/2	1890.71901	1.157D-02
+	R(3.5)	1/2	1890.70744	
-	R(3.5)	3/2	1890.91303	2.904D-04
+	R(3.5)	3/2	1890.91274	
+	R(4.5)	1/2	1893.87438	1.143D-02
-	R(4.5)	1/2	1893.86296	
+	R(4.5)	3/2	1894.15218	4.309D-04
-	R(4.5)	3/2	1894.15175	
-	R(5.5)	1/2	1896.99537	1.126D-02
+	R(5.5)	1/2	1896.98410	
-	R(5.5)	3/2	1897.35398	5.959D-04
+	R(5.5)	3/2	1897.35339	
+	R(6.5)	1/2	1900.08190	1.108D-02
-	R(6.5)	1/2	1900.07082	
+	R(6.5)	3/2	1900.51824	7.837D-04
-	R(6.5)	3/2	1900.51745	
-	R(7.5)	1/2	1903.13391	1.087D-02
+	R(7.5)	1/2	1903.12304	
-	R(7.5)	3/2	1903.64474	9.925D-04
+	R(7.5)	3/2	1903.64375	
+	R(8.5)	1/2	1906.15131	1.064D-02
-	R(8.5)	1/2	1906.14068	
+	R(8.5)	3/2	1906.73330	1.221D-03
-	R(8.5)	3/2	1906.73208	
-	R(9.5)	1/2	1909.13403	1.039D-02
+	R(9.5)	1/2	1909.12363	
-	R(9.5)	3/2	1909.78374	1.466D-03
+	R(9.5)	3/2	1909.78227	
+	R(10.5)	1/2	1912.08195	1.013D-02
-	R(10.5)	1/2	1912.07181	

Table C-5 (Continued)

PARITY	ASSIGNMENT	SUBBAND	POSITION (CM**-1)	SEPARATION (CM**-1)
+	R(10.5)	3/2	1912.79588	1.727D-03
-	R(10.5)	3/2	1912.79416	
-	R(11.5)	1/2	1914.99496	9.861D-03
+	R(11.5)	1/2	1914.98509	
-	R(11.5)	3/2	1915.76958	2.001D-03
+	R(11.5)	3/2	1915.76758	
+	R(12.5)	1/2	1917.87293	9.575D-03
-	R(12.5)	1/2	1917.86335	
+	R(12.5)	3/2	1918.70468	2.287D-03
-	R(12.5)	3/2	1918.70240	
-	R(13.5)	1/2	1920.71574	9.279D-03
+	R(13.5)	1/2	1920.70646	
-	R(13.5)	3/2	1921.60105	2.584D-03
+	R(13.5)	3/2	1921.59847	
+	R(14.5)	1/2	1923.52323	8.975D-03
-	R(14.5)	1/2	1923.51426	
+	R(14.5)	3/2	1924.45855	2.888D-03
-	R(14.5)	3/2	1924.45566	
-	R(15.5)	1/2	1926.29527	8.665D-03
+	R(15.5)	1/2	1926.28660	
-	R(15.5)	3/2	1927.27705	3.200D-03
+	R(15.5)	3/2	1927.27385	
+	R(16.5)	1/2	1929.03168	8.348D-03
-	R(16.5)	1/2	1929.02334	
+	R(16.5)	3/2	1930.05645	3.517D-03
-	R(16.5)	3/2	1930.05293	
-	R(17.5)	1/2	1931.73231	8.028D-03
+	R(17.5)	1/2	1931.72429	
-	R(17.5)	3/2	1932.79662	3.838D-03
+	R(17.5)	3/2	1932.79278	
+	R(18.5)	1/2	1934.39699	7.704D-03
-	R(18.5)	1/2	1934.38928	
+	R(18.5)	3/2	1935.49747	4.162D-03
-	R(18.5)	3/2	1935.49330	
-	R(19.5)	1/2	1937.02553	7.379D-03
+	R(19.5)	1/2	1937.01815	
-	R(19.5)	3/2	1938.15888	4.488D-03
+	R(19.5)	3/2	1938.15439	
+	R(20.5)	1/2	1939.61775	7.052D-03
-	R(20.5)	1/2	1939.61070	

Table C-5 (Continued)

PARITY	ASSIGNMENT	SUBBAND	POSITION (CM**-1)	SEPARATION (CM**-1)
+	R(20.5)	3/2	1940.78077	4.815D-03
-	R(20.5)	3/2	1940.77595	
-	R(21.5)	1/2	1942.17348	6.725D-03
+	R(21.5)	1/2	1942.16676	
-	R(21.5)	3/2	1943.36303	5.143D-03
+	R(21.5)	3/2	1943.35789	
+	R(22.5)	1/2	1944.69252	6.398D-03
-	R(22.5)	1/2	1944.68613	
+	R(22.5)	3/2	1945.90558	5.470D-03
-	R(22.5)	3/2	1945.90011	
-	R(23.5)	1/2	1947.17469	6.072D-03
+	R(23.5)	1/2	1947.16862	
-	R(23.5)	3/2	1948.40832	5.797D-03
+	R(23.5)	3/2	1948.40252	
+	R(24.5)	1/2	1949.61980	5.747D-03
-	R(24.5)	1/2	1949.61405	
+	R(24.5)	3/2	1950.87115	6.122D-03
-	R(24.5)	3/2	1950.86503	
-	R(25.5)	1/2	1952.02764	5.424D-03
+	R(25.5)	1/2	1952.02222	
-	R(25.5)	3/2	1953.29400	6.446D-03
+	R(25.5)	3/2	1953.28755	
+	R(26.5)	1/2	1954.39803	5.103D-03
-	R(26.5)	1/2	1954.39293	
+	R(26.5)	3/2	1955.67676	6.768D-03
-	R(26.5)	3/2	1955.66999	
-	R(27.5)	1/2	1956.73078	4.784D-03
+	R(27.5)	1/2	1956.72600	
-	R(27.5)	3/2	1958.01934	7.088D-03
+	R(27.5)	3/2	1958.01225	
+	R(28.5)	1/2	1959.02569	4.467D-03
-	R(28.5)	1/2	1959.02123	
+	R(28.5)	3/2	1960.32166	7.405D-03
-	R(28.5)	3/2	1960.31425	
-	R(29.5)	1/2	1961.28257	4.153D-03
+	R(29.5)	1/2	1961.27842	
-	R(29.5)	3/2	1962.58361	7.720D-03
+	R(29.5)	3/2	1962.57589	
+	R(30.5)	1/2	1963.50123	3.841D-03
-	R(30.5)	1/2	1963.49738	

Table C-5 (Continued)

PARITY	ASSIGNMENT	SUBBAND	POSITION (CM**-1)	SEPARATION (CM**-1)
+	R(30.5)	3/2	1964.80511	8.033D-03
-	R(30.5)	3/2	1964.79707	
-	R(31.5)	1/2	1965.68146	3.531D-03
+	R(31.5)	1/2	1965.67793	
-	R(31.5)	3/2	1966.98605	8.343D-03
+	R(31.5)	3/2	1966.97771	
+	R(32.5)	1/2	1967.82309	3.224D-03
-	R(32.5)	1/2	1967.81987	
+	R(32.5)	3/2	1969.12634	8.651D-03
-	R(32.5)	3/2	1969.11769	
-	R(33.5)	1/2	1969.92592	2.919D-03
+	R(33.5)	1/2	1969.92300	
-	R(33.5)	3/2	1971.22587	8.956D-03
+	R(33.5)	3/2	1971.21692	
+	R(34.5)	1/2	1971.98976	2.616D-03
-	R(34.5)	1/2	1971.98715	
+	R(34.5)	3/2	1973.28455	9.259D-03
-	R(34.5)	3/2	1973.27529	
-	R(35.5)	1/2	1974.01442	2.316D-03
+	R(35.5)	1/2	1974.01211	
-	R(35.5)	3/2	1975.30226	9.560D-03
+	R(35.5)	3/2	1975.29270	
+	R(36.5)	1/2	1975.99972	2.018D-03
-	R(36.5)	1/2	1975.99770	
+	R(36.5)	3/2	1977.27891	9.859D-03
-	R(36.5)	3/2	1977.26905	
-	R(37.5)	1/2	1977.94547	1.721D-03
+	R(37.5)	1/2	1977.94375	
-	R(37.5)	3/2	1979.21437	1.016D-02
+	R(37.5)	3/2	1979.20421	
+	R(38.5)	1/2	1979.85148	1.427D-03
-	R(38.5)	1/2	1979.85005	
+	R(38.5)	3/2	1981.10854	1.045D-02
-	R(38.5)	3/2	1981.09809	
-	R(39.5)	1/2	1981.71756	1.134D-03
+	R(39.5)	1/2	1981.71643	
-	R(39.5)	3/2	1982.96131	1.074D-02
+	R(39.5)	3/2	1982.95056	
+	R(40.5)	1/2	1983.54355	8.426D-04
-	R(40.5)	1/2	1983.54270	

Table C-5 (Continued)

PARITY	ASSIGNMENT	SUBBAND	POSITION (CM**-1)	SEPARATION (CM**-1)
+	R(40.5)	3/2	1984.77255	1.104D-02
-	R(40.5)	3/2	1984.76152	

Table C-6

Spectral Line Positions without Lambda Doubling

ASSIGNMENT	SUBBAND	POSITION (CM**-1)
P(1.5)	1/2	1871.06169
P(2.5)	1/2	1867.66658
P(2.5)	3/2	1867.21198
P(3.5)	1/2	1864.23725
P(3.5)	3/2	1863.68225
P(4.5)	1/2	1860.77372
P(4.5)	3/2	1860.11737
P(5.5)	1/2	1857.27599
P(5.5)	3/2	1856.51759
P(6.5)	1/2	1853.74405
P(6.5)	3/2	1852.88318
P(7.5)	1/2	1850.17792
P(7.5)	3/2	1849.21437
P(8.5)	1/2	1846.57761
P(8.5)	3/2	1845.51142
P(9.5)	1/2	1842.94313
P(9.5)	3/2	1841.77456
P(10.5)	1/2	1839.27451
P(10.5)	3/2	1838.00403
P(11.5)	1/2	1835.57178
P(11.5)	3/2	1834.20004
P(12.5)	1/2	1831.83498
P(12.5)	3/2	1830.36281
P(13.5)	1/2	1828.06416
P(13.5)	3/2	1826.49254
P(14.5)	1/2	1824.25937
P(14.5)	3/2	1822.58943
P(15.5)	1/2	1820.42066
P(15.5)	3/2	1818.65367
P(16.5)	1/2	1816.54812
P(16.5)	3/2	1814.68543
P(17.5)	1/2	1812.64182
P(17.5)	3/2	1810.68488
P(18.5)	1/2	1808.70184
P(18.5)	3/2	1806.65219
P(19.5)	1/2	1804.72828
P(19.5)	3/2	1802.58749
P(20.5)	1/2	1800.72122
P(20.5)	3/2	1798.49095
P(21.5)	1/2	1796.68079

Table C-6 (Continued)

ASSIGNMENT	SUBBAND	POSITION (CM**-1)
P(21.5)	3/2	1794.36269
P(22.5)	1/2	1792.60707
P(22.5)	3/2	1790.20284
P(23.5)	1/2	1788.50019
P(23.5)	3/2	1786.01154
P(24.5)	1/2	1784.36026
P(24.5)	3/2	1781.78890
P(25.5)	1/2	1780.18740
P(25.5)	3/2	1777.53503
P(26.5)	1/2	1775.98173
P(26.5)	3/2	1773.25005
P(27.5)	1/2	1771.74338
P(27.5)	3/2	1768.93405
P(28.5)	1/2	1767.47247
P(28.5)	3/2	1764.58715
P(29.5)	1/2	1763.16913
P(29.5)	3/2	1760.20944
P(30.5)	1/2	1758.83349
P(30.5)	3/2	1755.80101
P(31.5)	1/2	1754.46567
P(31.5)	3/2	1751.36197
P(32.5)	1/2	1750.06581
P(32.5)	3/2	1746.89240
P(33.5)	1/2	1745.63404
P(33.5)	3/2	1742.39239
P(34.5)	1/2	1741.17047
P(34.5)	3/2	1737.86202
P(35.5)	1/2	1736.67525
P(35.5)	3/2	1733.30140
P(36.5)	1/2	1732.14849
P(36.5)	3/2	1728.71058
P(37.5)	1/2	1727.59032
P(37.5)	3/2	1724.08967
P(38.5)	1/2	1723.00087
P(38.5)	3/2	1719.43875
P(39.5)	1/2	1718.38026
P(39.5)	3/2	1714.75788
P(40.5)	1/2	1713.72861
P(40.5)	3/2	1710.04716
Q(0.5)	1/2	1876.07739

Table C-6 (Continued)

ASSIGNMENT	SUBBAND	POSITION (CM**-1)
Q(1.5)	1/2	1876.02606
Q(1.5)	3/2	1875.81320
Q(2.5)	1/2	1875.94050
Q(2.5)	3/2	1875.72307
Q(3.5)	1/2	1875.82070
Q(3.5)	3/2	1875.59690
Q(4.5)	1/2	1875.66665
Q(4.5)	3/2	1875.43470
Q(5.5)	1/2	1875.47832
Q(5.5)	3/2	1875.23649
Q(6.5)	1/2	1875.25569
Q(6.5)	3/2	1875.00229
Q(7.5)	1/2	1874.99874
Q(7.5)	3/2	1874.73212
Q(8.5)	1/2	1874.70743
Q(8.5)	3/2	1874.42600
Q(9.5)	1/2	1874.38172
Q(9.5)	3/2	1874.08396
Q(10.5)	1/2	1874.02160
Q(10.5)	3/2	1873.70603
Q(11.5)	1/2	1873.62701
Q(11.5)	3/2	1873.29223
Q(12.5)	1/2	1873.19792
Q(12.5)	3/2	1872.84259
Q(13.5)	1/2	1872.73429
Q(13.5)	3/2	1872.35715
Q(14.5)	1/2	1872.23607
Q(14.5)	3/2	1871.83592
Q(15.5)	1/2	1871.70323
Q(15.5)	3/2	1871.27894
Q(16.5)	1/2	1871.13573
Q(16.5)	3/2	1870.68623
Q(17.5)	1/2	1870.53353
Q(17.5)	3/2	1870.05782
Q(18.5)	1/2	1869.89658
Q(18.5)	3/2	1869.39373
Q(19.5)	1/2	1869.22484
Q(19.5)	3/2	1868.69399
Q(20.5)	1/2	1868.51827
Q(20.5)	3/2	1867.95861

Table C-6 (Continued)

ASSIGNMENT	SUBBAND	POSITION (CM**-1)
Q(21.5)	1/2	1867.77684
Q(21.5)	3/2	1867.18762
Q(22.5)	1/2	1867.00051
Q(22.5)	3/2	1866.38102
Q(23.5)	1/2	1866.18924
Q(23.5)	3/2	1865.53885
Q(24.5)	1/2	1865.34299
Q(24.5)	3/2	1864.66111
Q(25.5)	1/2	1864.46172
Q(25.5)	3/2	1863.74780
Q(26.5)	1/2	1863.54541
Q(26.5)	3/2	1862.79895
Q(27.5)	1/2	1862.59402
Q(27.5)	3/2	1861.81455
Q(28.5)	1/2	1861.60751
Q(28.5)	3/2	1860.79461
Q(29.5)	1/2	1860.58585
Q(29.5)	3/2	1859.73913
Q(30.5)	1/2	1859.52900
Q(30.5)	3/2	1858.64811
Q(31.5)	1/2	1858.43695
Q(31.5)	3/2	1857.52155
Q(32.5)	1/2	1857.30964
Q(32.5)	3/2	1856.35945
Q(33.5)	1/2	1856.14706
Q(33.5)	3/2	1855.16180
Q(34.5)	1/2	1854.94918
Q(34.5)	3/2	1853.92860
Q(35.5)	1/2	1853.71595
Q(35.5)	3/2	1852.65982
Q(36.5)	1/2	1852.44735
Q(36.5)	3/2	1851.35547
Q(37.5)	1/2	1851.14335
Q(37.5)	3/2	1850.01553
Q(38.5)	1/2	1849.80392
Q(38.5)	3/2	1848.63998
Q(39.5)	1/2	1848.42903
Q(39.5)	3/2	1847.22881
Q(40.5)	1/2	1847.01863
Q(40.5)	3/2	1845.78200

Table C-6 (Continued)

ASSIGNMENT	SUBBAND	POSITION (CM**-1)
R(0.5)	1/2	1881.04175
R(1.5)	1/2	1884.29998
R(1.5)	3/2	1884.32429
R(2.5)	1/2	1887.52394
R(2.5)	3/2	1887.63772
R(3.5)	1/2	1890.71362
R(3.5)	3/2	1890.91423
R(4.5)	1/2	1893.86898
R(4.5)	3/2	1894.15359
R(5.5)	1/2	1896.98996
R(5.5)	3/2	1897.35560
R(6.5)	1/2	1900.07651
R(6.5)	3/2	1900.52003
R(7.5)	1/2	1903.12856
R(7.5)	3/2	1903.64670
R(8.5)	1/2	1906.14602
R(8.5)	3/2	1906.73540
R(9.5)	1/2	1909.12881
R(9.5)	3/2	1909.78596
R(10.5)	1/2	1912.07682
R(10.5)	3/2	1912.79822
R(11.5)	1/2	1914.98994
R(11.5)	3/2	1915.77201
R(12.5)	1/2	1917.86804
R(12.5)	3/2	1918.70720
R(13.5)	1/2	1920.71099
R(13.5)	3/2	1921.60363
R(14.5)	1/2	1923.51864
R(14.5)	3/2	1924.46118
R(15.5)	1/2	1926.29085
R(15.5)	3/2	1927.27973
R(16.5)	1/2	1929.02744
R(16.5)	3/2	1930.05916
R(17.5)	1/2	1931.72826
R(17.5)	3/2	1932.79936
R(18.5)	1/2	1934.39314
R(18.5)	3/2	1935.50022
R(19.5)	1/2	1937.02189
R(19.5)	3/2	1938.16164
R(20.5)	1/2	1939.61433

Table C-6 (Continued)

ASSIGNMENT	SUBBAND	POSITION (CM**-1)
R(20.5)	3/2	1940.78353
R(21.5)	1/2	1942.17028
R(21.5)	3/2	1943.36580
R(22.5)	1/2	1944.68956
R(22.5)	3/2	1945.90833
R(23.5)	1/2	1947.17197
R(23.5)	3/2	1948.41106
R(24.5)	1/2	1949.61731
R(24.5)	3/2	1950.87388
R(25.5)	1/2	1952.02540
R(25.5)	3/2	1953.29670
R(26.5)	1/2	1954.39605
R(26.5)	3/2	1955.67944
R(27.5)	1/2	1956.72905
R(27.5)	3/2	1958.02200
R(28.5)	1/2	1959.02422
R(28.5)	3/2	1960.32429
R(29.5)	1/2	1961.28136
R(29.5)	3/2	1962.58622
R(30.5)	1/2	1963.50027
R(30.5)	3/2	1964.80769
R(31.5)	1/2	1965.68078
R(31.5)	3/2	1966.98861
R(32.5)	1/2	1967.82267
R(32.5)	3/2	1969.12887
R(33.5)	1/2	1969.92577
R(33.5)	3/2	1971.22837
R(34.5)	1/2	1971.98988
R(34.5)	3/2	1973.28702
R(35.5)	1/2	1974.01481
R(35.5)	3/2	1975.30471
R(36.5)	1/2	1976.00038
R(36.5)	3/2	1977.28133
R(37.5)	1/2	1977.94640
R(37.5)	3/2	1979.21677
R(38.5)	1/2	1979.85268
R(38.5)	3/2	1981.11092
R(39.5)	1/2	1981.71905
R(39.5)	3/2	1982.96366
R(40.5)	1/2	1983.54530

Table C-6 (Continued)

ASSIGNMENT	SUBBAND	POSITION (CM**-1)
R(40.5)	3/2	1984.77488

APPENDIX D

TIME DEVELOPMENT OPERATORS

The purpose of this appendix is to demonstrate the equivalence of two time development operators (TDO) for a general time dependent Hamiltonian given by:

$$H(t) = H_0(t) + H_1(t) \tag{D-1}$$

where $H_1(t)$ vanishes at $t = 0$.

The first form of the TDO considered is that involving the total Hamiltonian, which is given by the time ordered product TDO

$$U(t) = \left(e^{-i/\hbar \int_0^t H(t')dt'}\right)_+. \tag{D-2}$$

The second form of the TDO is that obtained from the use of time dependent perturbation theory.

Consider the approach taken by using time dependent perturbation theory. Suppose that at $t = 0$ the system is in a state $|\psi(0)\rangle$ which solves the equation

$$H(t=0)\,|\psi(0)\rangle = H_0(t=0)\,|\psi(0)\rangle = i\hbar \frac{\partial}{\partial t}|\psi(t=0)\rangle. \tag{D-3}$$

At some later time, t, the system is in a state $|\psi(t)\rangle$ which solves;

$$H(t)\,|\psi(t)\rangle = (H_0(t) + H_1(t))\,|\psi(t)\rangle = i\hbar \frac{\partial}{\partial t}|\psi(t)\rangle. \tag{D-4}$$

Define the interaction representation state $|\psi^I(t)\rangle$ by

$$|\psi^I(t)\rangle \equiv U_0^{-1}(t)\,|\psi(t)\rangle \tag{D-5}$$

where

$$U_0(t) = \left(e^{-i/\hbar \int_0^t H_0(t')dt'}\right)_+. \tag{D-6}$$

From equation (D-5)

$$| \psi(t)\rangle = U_0(t) | \psi^I(t)\rangle. \tag{D-7}$$

Inserting the above expression in equation (D-4) yields:

$$i\hbar \frac{\partial}{\partial t} | \psi(t)^I\rangle = H_1'(t) | \psi(t)^I\rangle \tag{D-8}$$

where $H_1'(t)$ is the interaction $H_1(t)$ in the interaction representation defined by

$$H_1'(t) = U_0^{-1}(t) H_1(t) U_0(t). \tag{D-9}$$

Solving equation D-8 iteratively for $| \psi(t)\rangle$ using the boundary condition

$$H_1(t=0) = 0 \tag{D-10}$$

yields a solution;

$$| \psi(t)^I\rangle = U_1(t) | \psi(0)^I\rangle \tag{D-11}$$

where

$$U_1(t) = (e^{-i/\hbar \int_0^t H'(t)dt'})_+ \tag{D-12}$$

Equations (D-11) and (D-5) combine to give an expression for the state $| \psi(t)\rangle$:

$$| \psi(t) = U_0(t) | \psi^I(t)\rangle = U_0(t)U_1(t) | \psi(t=0)\rangle \tag{D-13}$$

or

$$| \psi(t)\rangle = W(t) | \psi(t=0)\rangle. \tag{D-14}$$

The task is now to demonstrate that W(t) and U(t) are equivalent. First examine the differential equation solved by each:

$$\frac{d}{dt} U(t) = -i\hbar H(t) U(t) \tag{D-15}$$

and

$$\frac{d}{dt} W(t) = \frac{d}{dt} U_0(t)U_1(t)$$

$$= - i\hbar H_0(t)U_0(t) - i\hbar U_0(t)H_1'(t)U_1(t)$$

$$= - i\hbar H(t)W(t). \qquad \text{(D-16)}$$

Also note that each obeys the same boundary condition

$$W(t=0) = 1 = U(t=0). \qquad \text{(D-17)}$$

Since the two operators obey the same boundary condition and each solves the same first order differential equation they are equivalent.

APPENDIX E

COLLISION AVERAGED TIME DEVELOPED DIPOLE MOMENT

The relationship given by equation (3-58)

$$U_m^{-1}(-\tau)\bar{\mu}U_m(-\tau)_{AVE} = U_m(\tau)\bar{\mu}U_m(\tau)_{AVE} \tag{E-1}$$

is proven by first examining the following dipole moment operator;

$$U_m^{-1}(t''\to t')\bar{\mu}U_m(t''\to t'). \tag{E-2}$$

From the definition of the TDO's appearing above, equation (E-2) is equivalent to

$$U_m(t'')U_m^{-1}(t''+\tau)\bar{\mu}U_m(t''+\tau)U_m^{-1}(\tau'') \tag{E-3}$$

or

$$U_m^{-1}(t''\to t''+\tau)\bar{\mu}U_m(t''\to t''+\tau) \tag{E-4}$$

where $\tau = t' - t''$. Upon averaging over random collisions the time developed dipole moment becomes independent of initial times and the collision averaged quantity appearing in equation (E-3) can be written

$$U^{-1}(\tau)\bar{\mu}U_m(\tau)_{AVE} = U^{-1}(t''\to t''+\tau)\bar{\mu}U_m(t''\to t''+\tau)_{AVE}. \tag{E-5}$$

Now consider equation (E-5) with τ replaced by $-\tau$;

$$U_m^{-1}(-\tau)\bar{\mu}U_m(-\tau)_{AVE} = U_m^{-1}(t''\to t''-\tau)\bar{\mu}U_m(t''\to t''-\tau)_{AVE}. \tag{E-6}$$

For the sake of convenience, with no loss in accuracy, consider only the right most TDO in equation (E-6). Using the definition of $U(t''\to t''-\tau)$, from equation (3-54) and (3-55), and the definition of a general TDO one has:

$$U(t''\to t''-\tau) = \left(e^{-i/\hbar\int_0^{t''-\tau}H(t')dt'}\right)_+ e^{i/\hbar\int_0^{t''}H(t')dt'}\Big)_-. \tag{E-7}$$

Averaging the above equation over collisions it becomes independent of initial time t" therefore by replacing t" by t"+τ equation (E-8) becomes

$$U(t"\to t"-\tau)_{AVE} = U_m(t"+\tau\to t")_{AVE}$$

$$=(e^{-i/h\int_0^{t'} H(t')dt'})_+(e^{i/h\int_0^{t"+\tau} H(t')dt'})_{-AVE}. \quad (E-8)$$

Note that the right hand side is equal to the following:

$$U^{\dagger}(\tau)_{AVE} = U^{\dagger}(t"\to t"+\tau)_{AVE} = [(e^{i/h\int_0^{t"+\tau} H(t')dt'})_+ X \quad (E-9)$$

$$(e^{-i/h\int_0^{t"} H(t')dt'})_-]^{-1}_{AVE}$$

therefore

$$U_m^{-1}(-\tau)\bar{\mu}U_m(-\tau)_{AVE} = U_m(\tau)\bar{\mu}U^{-1}(\tau)._{AVE} \quad (E-10)$$

APPENDIX F

EQUIVALENT REPRESENTATIONS OF THE FUNCTION F(τ)

The function F(τ), given by

$$F(\tau) = e^{-iwt}\mathrm{Tr}[\rho_0\bar{\mu}\cdot\bar{\lambda}U^{-1}(t)\bar{\mu}\cdot\bar{\lambda}U(t)]_{AVE} \tag{F-1}$$

appears in various forms throughout the derivations of the ATC and coupled line theories. This appendix demonstrates that the various forms are equivalent.

The trace of equation (F-1) can be expanded by writing the dot products in terms of its spherical tensors components:

$$\mathrm{Tr}[\rho_0\bar{\mu}\cdot\bar{\lambda}U^{-1}(t)\bar{\mu}\cdot\bar{\lambda}U(t)]_{AVE}$$

$$\sum_{q,q'}(-1)^{q+q'}\lambda^1_{-q}\lambda^1_{-q'}\mathrm{Tr}[\rho_0\mu^1_q\mu^1_{q'}(t)]_{AVE}. \tag{F-2}$$

The operator $\mu^1_q(t)$ above is given by

$$\mu^1_q(t) = U^{-1}(t)\mu^1_q U(t)_{AVE} \tag{F-3}$$

where it is assumed the collision averaging process removes all directionality weighting effects in the TDO. This in effect gives $\bar{\mu}(t)$ the same directionality as $\bar{R}$. Equation (F-2) can now be expanded in terms of the states of total angular momentum and any other state denoted by a quantum number α. Upon expansion equation (F-2) becomes

$$\mathrm{Tr}[\rho_0\bar{\mu}\cdot\bar{\lambda}\bar{\mu}(t)\cdot\bar{\lambda}]_{AVE} = \sum_{q\ q'}(-1)^{q+q'}\lambda^1_{-q}\ \lambda^1_{-q'}\,X$$

$$\sum_{\substack{J_i,J_f\\ \alpha_i,\alpha_f}}\ \sum_{M_i,M_f}\rho_{J_iM_i}\langle J_i\alpha_iM_i\mid\mu^1_q\mid J_fM_f\alpha_f\rangle\langle J_fM_f\alpha_f\mid\mu^1{}_{q'}\mid J_iM_i\alpha_i\rangle. \tag{F-4}$$

Utilizing the Wigner-Eckart theorem the matrix elements can be expressed in terms of the reduced matrix elements and the produce of Clebsch-Gordon coefficients; [11]

$$\mathrm{Tr}[\ \ ] = \sum_{\substack{\alpha_i\alpha_f \\ J_iJ_f}} \rho_{\alpha_iJ_i} \langle J_i\alpha_i \,||\, \mu^1 \,||\, J_f\alpha_f\rangle\langle J_f\alpha_f \,||\, \mu^1(t) \,||\, J_i\alpha_i\rangle \times$$

$$\sum_{\substack{q\ q' \\ M_iM_f}} (-1)^{q+q'} \lambda^1_{-q}\ \lambda^1_{-q'}\ \frac{\langle 1J_fqM_f \,|\, J_iM_i\rangle\langle 1J_iq'M_i \,|\, J_fM_f\rangle}{\sqrt{(2J_i+1)(2J_f+1)}} \qquad \text{(F-5)}$$

Employing the properties of the Clebsch-Gordon coefficients, summation of the M quantum numbers leads to: [49]

$$\mathrm{Tr}[\ \ ] = \sum_{\substack{J_i,J_f \\ \alpha_i,\alpha_f}} (-1)^{J_f-J_i}\ \rho_{J_i\alpha_i}\ \langle J_i\alpha_i \,||\, \mu^1 \,||\, J_f\alpha_f\rangle \times$$

$$\langle J_f\alpha_f \,||\, \mu^1(t) \,|\, J_i\alpha_i\rangle \times$$

$$\sum_{q\ q'} (-1)^q\ \lambda^1_{-q}\ \lambda^1_{-q'}\ \delta_{q,q'}\ \frac{2J_i+1}{3}\ . \qquad \text{(F-6)}$$

Since the polarization vector is of unity magnitude the double sum over q and q' is unity (equal to the dot product), therefore;

$$\mathrm{Tr}[\ \ ] = \frac{1}{3} \sum_{\substack{\alpha_i\alpha_f \\ J_iJ_f}} (-1)^{J_f-J_i}\ \rho_{J_i\alpha_i}\ \langle J_i\alpha_i \,||\, \mu^1 \,||\, J_f\alpha_f\rangle \times$$

$$\langle J_f\alpha_f \,||\, \mu^1(t) \,||\, J_i\alpha_i\rangle. \qquad \text{(F-7)}$$

Consider now the trace given by

$$\mathrm{Tr}[\rho_0\bar{\mu}\cdot\bar{\mu}(t)]. \qquad \text{(F-8)}$$

Expanding, as before, in terms of sperical tensors and total angular momentum eigenstates the trace becomes

$$\mathrm{Tr}[\rho_0\bar{\mu}\cdot\bar{\mu}(t)] = \sum_q (-1)^q \sum_{\substack{J_i\alpha_i M_i \\ J_f\alpha_f M_f}} \rho_{J_i\alpha_i} X$$

$$\langle J_i\alpha_i M_i \mid \mu^1_q \mid J_f\alpha_f M_f\rangle\langle J_f\alpha_f M_f \mid \mu^1_{-q}(t) \mid J_i M_i\alpha_i\rangle. \qquad \text{(F-9)}$$

Again, applying the Wigner-Eckart theorem

$$\mathrm{Tr}[\rho_0\bar{\mu}\cdot\bar{\mu}(t)] = \sum_{\substack{J_i\alpha_i \\ J_f\alpha_f}} \rho_{J_i\alpha_i}\langle J_i\alpha_i \,||\, \mu^1 \,||\, J_f\alpha_f\rangle$$

$$\langle J_f\alpha_f \,||\, \mu^1(t) \,||\, J_i\alpha_i\rangle X$$

$$\sum_{qM_iM_f} \frac{\langle 1J_f qM_f \mid J_iM_i\rangle\langle 1J_i{-q}M_i \mid J_fM_f\rangle}{\sqrt{(2J_i+1)(2J_f+1)}} \qquad \text{(F-10)}$$

Performing the sum over M_i, M_f, and q yields:

$$\mathrm{Tr}[\rho_0\bar{\mu}\cdot\bar{\mu}(t)] = \sum_{\substack{J_iJ_f \\ \alpha_i\alpha_f}} \rho_{J_i\alpha_i} (-1)^{J_f-J_i} \langle J_i\alpha_i \,||\, \mu^1 \,||\, J_f\alpha_f\rangle X$$

$$\langle J_f\alpha_f \,||\, \mu^1(t) \,||\, J_i\alpha_i\rangle. \qquad \text{(F-11)}$$

Therefore, in summary, by examining equation (F-1), (F-7), and (F-11), the various forms of $F(\tau)$ are given by

$$F(t) = e^{-iwt}\mathrm{Tr}[\rho_0\bar{\mu}\cdot\bar{\lambda}\bar{\mu}(t)\cdot\bar{\lambda}]_{AVE}$$

$$= \frac{1}{3} e^{-iwt}\mathrm{Tr}[\rho_0\bar{\mu}\cdot\bar{\mu}(t)]_{AVE}$$

$$= \frac{1}{3} e^{-iwt} \sum_{\substack{J_iJ_f \\ \alpha_i\alpha_f}} \rho_{J_i\alpha_i}(-1)^{J_f-J_i}\langle J_i\alpha_i \,||\, \mu^1 \,||\, J_f\alpha_f\rangle X$$

$$\langle J_f\alpha_f \,||\, \mu^1(t) \,||\, J_i\alpha_i\rangle. \qquad \text{(F-12)}$$

APPENDIX G

COLLISION OPERATOR B(σ)

This appendix derives an expression for the collision operator B(σ) which arises out of the derivation of the dipole moment matrix element differential equation.

The operator $T_\sigma(t\to t+\Delta)$ appearing in equation (4-103) is given by

$$T_\sigma(t\to t+\Delta) = (e^{-i/\hbar\int_t^{t+\Delta} U_0^{-1}(t')H_c(t')U_0(t')dt'})+. \qquad (G-1)$$

Now making a change integration variable the above equation becomes

$$T_\sigma(t\to t+\Delta) = (e^{-i/\hbar\int_0^{\Delta} U_0^{-1}(t+t')H_c(t+t')U_0(t+t')dt'})+. \qquad (G-2)$$

Expanding the time order product: TDO;

$$T_\sigma(t\to t+\Delta) = 1 + \sum_{n=1}^{\infty}\frac{1}{(i\hbar)}n\int_0^{\Delta} dt'\int_0^{t'} dt''\ldots U_0^{-1}(t+t')\,H_{c,\sigma}(t'+t)\,X$$

$$U_0(t'+t)\,U_0^{-1}(t+t'')H_{c,\sigma}(t+t'')U_0(t''+t)\ldots . \qquad (G-3)$$

The TDO $U_0(t)$ is given simply by

$$U_0(t) = e^{-iH_0t/\hbar} \qquad (G-4)$$

therefore

$$U_0^{-1}(t''+t)U_0(t''+t) = U_0^{-1}(t)U_0(t) \qquad (G-5)$$

and equation (G-3) becomes:

$$T_\sigma(t\to t+\Delta) = 1 + U_0(t)\sum_{n=1}^{\infty}\frac{1}{(i\hbar)^n}\int_0^{t} dt'\int_0^{t'} dt''\,U_0^{-1}(t')\,H_{c,\sigma}(t+t')X$$

$$U_0(t')\,U_0^{-1}(t'')\,H_c(t+t'')U_0(t'')\ldots \qquad (G-6)$$

The above equation can then be rewritten in terms of a TDO;

$$T_\sigma(t\to t+\Delta) = U_0^{-1}(t)\,(e^{-i/\hbar\int_0^\Delta U^{-1}(t')H_c(t'+t)U_0(t')dt'})]_+U_0(t). \qquad (G\text{-}7)$$

Multiplying on the left by $U_0(t)$ and right by $U_0^{-1}(t)$ yields the combination of TDO's that appear in equation (3-101).

$$U_0(t)T(t\to t+\Delta)U_0^{-1}(t) = (e^{-i/\hbar\int_0^\Delta U_0^{-1}(t')H_c(t+t')U_0(t')dt'})+. \qquad (G\text{-}8)$$

The definition of Δ, from section III-8, is a time interval sufficiently long to allow at most one collision of type σ. If the quantity of equation (G-8) is collision averaged, the averaging process averages over all initial starting times in Δ and thus the averaged quantity is independent of t. Thus t can be set equal to zero in equation (G-8). Since the impact approximation assumes the time between collision is much larger than the duration of the collision the limits of integration in equation (G-8) is extended from minus infinity to infinity. Thus the collision operator of section IV-3A is given by:

$$B(\sigma) \equiv (e^{-i/\hbar\int_{-\infty}^{\infty} U_0^{-1}(t')H_c(t')U_0(t')dt'})_+. \qquad (G\text{-}9)$$

APPENDIX H

LINE STRENGTH AND THE DIPOLE MOMENT REDUCED MATRIX ELEMENT

The purpose of this appendix is to show the relation between the dipole moment reduced matrix element and the line strength. Consider the dipole moment matrix element given by:

$$\langle nJMgpv \mid \mu_q^1 \mid nJ'm'g'p'v' \rangle \tag{H-1}$$

By expanding the states as given in Chapter III the above matrix element can be expressed by:

$$\langle nJMgpv \mid \mu_q^1 \mid nJ'M'g'p'v' \rangle =$$

$$\frac{1}{2} \sum_{\Omega,\Omega'} C(J,g,p,\Omega)\ C(J',g',p',\Omega')\ X$$

$$[{}_R\langle JM-\Omega n\Lambda S\Sigma v \mid \mu_q^1 \mid J'M'-\Omega' n\Lambda' S\Sigma' v' \rangle_R$$

$$+p_i p_{f_R} \langle JM\Omega n-\Lambda S-\Sigma v \mid \mu_q^1 \mid J'M'\Omega' n-\Lambda' S-\Sigma' v']_R \tag{H-2}$$

Note that unity can be inserted in the last matrix element above in the form of $P^\dagger P$ and properties of the parity opeation on the molecular state used to obtain:

$$\langle nJMgpv \mid \mu_q^1 \mid nJ'M'g'p'v' \rangle =$$

$$\sum_{\Omega,\Omega'} C(J,g,p,\Omega)\ C(J',g',p',\Omega')\ X$$

$$\langle nJM-\Omega n\Lambda SSv \mid \mu_q^1 \mid J'M'-\Omega' n\Lambda' S\Sigma' v' \rangle (1+pp'(-1)^{J+J'}) \tag{H-3}$$

Now consider the specific case of q=0. Utilizing the expressions given in Chapter I for the eigenfunctions the last matrix element is found to be given by;

$$\langle nJM\text{-}\Omega\Lambda S\Sigma v \mid \mu_0^1 \mid J'M'\text{-}\Omega'n\Lambda'S\Sigma'v'\rangle =$$

$$\langle v \mid \mu \mid v'\rangle(-1)^{J+J'-2\Omega}\left(\frac{2J+1}{2J'+1}\right)^{1/2}\langle 1\ J0M \mid J'M\rangle$$

$$\langle J0\Omega \mid J\Omega\rangle\ \delta_{m,m'}\delta_{\Omega,\Omega'} \qquad \text{(H-4)}$$

Now utilizing the Wigner-Eckert theorem the dipole moment of equation (H-1) becomes:

$$\langle nJMgpv \mid \mu_0^1 \mid nJ'M'g'p'v'\rangle = \frac{\langle nJgpv \mid\mid \mu^1 \mid\mid nJ'g'p'v'\rangle}{\sqrt{2J+1}}(-1)^{J-J'}\ X$$

$$\left(\frac{2J+1}{2J'+1}\right)^{1/2}\langle 1J0M \mid J'M\rangle\delta_{M,M'}. \qquad \text{(H-5)}$$

By equating equations (H-5) and (H-4)

$$\langle nJgpv \mid\mid \mu^1 \mid\mid nJ'g'p'v'\rangle = \langle v \mid \mu \mid v'\rangle(-1)^{1+J-J'}\sum_{\Omega\Omega'} C(J,g,p,\Omega)\ X$$

$$C(J',g',p',\Omega')\ \frac{1}{2}\left[1 + p_i p_f(-1)^{J+J'}\right]\langle J1\Omega0 \mid J'\Omega\rangle\ X$$

$$\sqrt{2J+1} \qquad \text{(H-6)}$$

In order to relate the reduced dipole moment to the line strength consider the absorption coefficient in equation (4-340). This expression can be put in the customary form;

$$k(\omega) = \sum_i \frac{S_i\gamma_i}{\pi[(\omega-\omega_{0_i})+\gamma_i^2]} \qquad \text{(H-7)}$$

or for a single spectral line;

$$k(\omega) = \frac{S_i\gamma_i}{\pi[(\omega-\omega_0)^2+\gamma_i^2]} \qquad \text{(H-8)}$$

where S_i is the integrated absorptance (cm^{-2}), and γ_i is the HWHM (cm^{-1}). The integrated absorptance can be expressed in terms of a pressure independent line strength $S_i^0(cm^{-2}atm^{-1})$ by

$$S = S_i^0 P_a \tag{H-9}$$

where P_a is the pressure of the absorbing species in atmospheres. The frequency integral of the absorption coefficient over the spectral line is equal to the integrated absorptance;

$$S = \int_{\text{line}} k(\omega)dw. \tag{H-10}$$

Therefore from equation (4-122), and integrating from $-\infty$ to ∞;

$$S = C\rho_{J_i g_i p_i} \left| \langle nJ_i g_i p_i v_i \right|\left| \mu^1 \right|\left| nJ_f g_f p_f v_f, \rangle^2 \pi$$

$$= \frac{P_a 8\pi^3 \omega d}{3\hbar c k_B T} \rho_{J_i g_i p_i v_i} \left| \langle nJ_i g_i p_i v_i \right|\left| \mu^1 \right|\left| nJ_f g_f p_f v_f \rangle \right|^2 \tag{H-11}$$

or;

$$S^0 = \frac{8\pi^3 \omega d}{3\hbar c k_B T} \rho_{J_i g_i p_i v_i} \left| \langle nJ_i g_i p_i v_i \right|\left| \mu^1 \right|\left| nJ_f g_f p_f v_f \rangle \right|^2. \tag{H-12}$$

Substituting equation (H-6) into equation (H-12) yields;

$$S^0 = \frac{8\pi^3 \omega d}{3\hbar c k_B T} \rho_{J_i g_i p_i v_i} \left| \langle v \mid \mu \mid v' \rangle \right|^2 (2J+1) \times$$

$$\left[\sum_{\Omega\Omega'} C(J_i, g_i, p_i, \Omega)\, C(J_f, g_f, p_f, \Omega')\right]^2 \times$$

$$\frac{1}{2}\left[1+p_i p_f (-1)^{J_i+J_f}\right] \left| \langle J_i 1\Omega 0 \mid J_f \Omega \rangle \right|^2. \tag{H-13}$$

Using simple harmonic oscillator vibrational eigenstates and the dipole moment function of equation (4-48), the vibrational matrix element for the fundamental band becomes:

$$\left| \langle v_i \mid \mu \mid v_f \rangle \right|^2 = \frac{B_e R_e^2}{\omega_e} (v_i+1). \tag{H-14}$$

Therefore the line strength can be expressed as:

$$S^0 = S_{BS} = \frac{\omega_o}{\omega_e}\frac{T_o}{T}\rho_{J_i p_i g_i v_i}\ (v_i+1)\ f(J_i,\Omega) \qquad \text{(H-15)}$$

where the band strength S_{BS} is given by

$$S_{BS} = \frac{8\pi^3 dB_e R_e}{3\hbar ckT_o}\mu'^2(R_e). \quad (cm^{-2}atm^{-1}) \qquad \text{(H-16)}$$

The temperature T_o is some reference temperature, usually 273.15K or 300K, and $f(J,\Omega)$ is the Honl London factor given by:

$$f(J_i,\Omega) = \begin{cases} \dfrac{J_i^2-\Omega^2}{J_i} & \text{P-branch } J_f=J_i-1 \\ \dfrac{\Omega(2J_i+1)}{J_i(J_i+1)} & \text{Q-branch } J_f = J_i \\ \dfrac{(J_i+1)^2-\Omega^2}{J_i+1} & \text{R-branch } J_f = J_i + 1 \end{cases} \qquad \text{(H-17)}$$

Note that equation (H-15) is the Herman Wallis approximation.[56]

VITA

William Joe Phillips was born in Murray Kentucky on June 7, 1952. He attended Benton Elementary School and graduated in 1970 from Benton High School in Benton, Kentucky. In that same year he enrolled at Murray State University where he received a Bachelor of Science degree in 1974 with a major in Physics and Mathematics. Upon graduation from Murray State University he accepted a teaching assistantship at the University of Kentucky where he was awarded a Master of Science degree with a major in Physics in 1976.

In the fall of 1977 he started as a student at The University of Tennessee Space Institute working toward the Doctor of Philosophy degree. He was employed by Sverdrup Technology Inc. in April 1981 as a research engineer, where he is presently employed. Continuing as a part time student he was awarded the Doctor of Philosophy, with a major in physics, in 1986.

He is married to Julie Phillips of Benton, Kentucky, and has three sons, Joel, Marshall, and Will.