THEORETICAL CALCULATIONS OF POWER-BROADENED MICROWAVE LINESHAPES

By

Keith L. Peterson

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ABSTRACT

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The traditional method of analyzing high-power microwave transitions is to assume the lineshape is a sum of Lorentzians - one for each m-component pair connected by the microwave radiation. This assumption is tested by using extended Anderson Theory and infinite order energy sudden approximations to calculate relaxation cross sections. These cross sections appear in the power-broadening term of a recently derived expression for high-power lineshapes which correctly takes into account the degeneracy of the rotational levels. The theoretical lineshape obtained with the relaxation coefficients is fit to a sum of Lorentzians using a computer program developed for fitting experimental lineshapes. The goodness of fit is a measure of the validity of the sum of Lorentzians approximation. The results for the $J = 2 \leftarrow 1$ transition in OCS and the $(J,K)=(3,3)$ inversion transition of NH_3 show that in both modified

Anderson Theory and energy sudden approximations the value of T_1/T_2 obtained by fitting to a sum of Lorentzians is a good approximation to the calculated values of T_1/T_2.

The values of T_1 calculated above were based on the assumption that the population of the two levels connected by radiation remains constant. If this assumption is removed (inclusion of n-level effects) in the calculation of T_1, the same conclusions as above may be drawn. In addition, however, the T_1/T_2 ratios are brought into better agreement with experimental results. As expected, the n-level effects are more pronounced for OCS than for NH_3.

The sudden approximation has been applied to four-level double resonance experiments in NH_3. The analysis justifies several of the assumptions used previously in the analysis of these experiments. However, numerical calculations agree only qualitatively with experimental results.

The sudden approximation gives values for cross sections that are too large. This is due to neglect of internal state energy differences. Two energy corrections to the sudden approximation are discussed. Their practical application to the calculation of relaxation parameters requires a complex numerical integration, a reversion to a hard sphere cutoff procedure, or an approximation that is difficult to justify rigorously, but which enables analytical evaluation of a required integral.

A model of relaxation commonly used in NMR is transformed

to a spherical tensor basis. After introducing a correlation function for the intermolecular potential, the form of the relaxation parameters replicates that of the modified Anderson Theory. If a reasonable correlation function can be obtained the model offers an extremely simple method of calculating relaxation coefficients.

Phase conventions are established for matrix elements in a previous work on microwave lineshapes. A previous derivation of steady-state absorption by a linear rotor in a static electric field is extended to symmetric tops with inversion.

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INTRODUCTION

Spectral lines in steady-state, gas-phase microwave absorption experiments are characterized by a shape and width. Contributions to the width may come from uncertainty,(1) Doppler,(2) saturation,(3) and collision(4) broadening, as well as various experimental effects such as modulation broadening,(5) collisions of molecules with sample-cell walls,(6) and beam transit-times.(7) While it is possible that these various broadening mechanisms may act independently, they often act in concert. One example of this is the correlation of Doppler and collisional effects such that for certain conditions the spectral width is not merely the sum of the Doppler and collisional widths but instead a more complicated function of these quantities.(8-14)

Experimental conditions in microwave spectroscopy may easily be realized where only collisional and saturation effects are important in determining the lineshape. This dissertation will be concerned exclusively with these two effects. As will be seen later, the term in the lineshape expression that describes the saturation broadening is a function of the incident microwave power and various collisional relaxation cross sections. If the incident microwave power is known, measurement of the linewidth is capable of giving information about the cross sections. Thus, linewidth and/or lineshape measurements are probes of the dynamics of molecular collisions. This information can be used to gain information about intermolecular energy transfer and intermolecular potential energy surfaces. Steady-state absorption experiments are complementary to a host of other experiments which also yield information concerning collision dynamics. These include microwave-microwave(15-20) and infrared-microwave(21-26) double resonance, fluorescence,(27-30) beam maser,(31-38) molecular beam,(39) microwave transient effects,(40) and transport properties.(41,42)

On a more practical level, lineshape measurements are useful as temperature probes in gases and plasmas,(43) and in the study of planetary atmospheres. Carbon monoxide is pressure-broadened by carbon dioxide in the atmosphere of Mars,(44) while in the Jovian atmosphere methane is broadened by several gases.(45-48) Lineshapes have seen application in pollution analysis(49) and are also useful in determining optimal conditions for gas-laser operation.(50-52)

In view of the potential application of saturation-broadened and collision-broadened microwave transitions, it is desirable to have at hand a correct method of analyzing such lineshapes.

It is well known that low-power lineshapes, *i.e.*, those lineshapes where saturation effects are not important, can be analyzed in terms of a single Lorentzian whose width is proportional to a polarization relaxation cross section.(53) The inverse of this cross section is denoted T_2 in analogy with NMR relaxation. The traditional assumption for analyzing high-power lineshapes where saturation effects are important is that the lineshape can be expressed as a sum of Lorentzians - one for each m-component pair connected by the microwave radiation - each of which has its own T_1 and T_2.(54) (T_1 is a population relaxation time, again in analogy to NMR relaxation.) These assumptions are difficult to justify theoretically. Recently, an expression for power-broadened transitions has been derived which correctly accounts for the degeneracy of the rotational levels.(55) The term which describes the power-broadening contains various relaxation cross sections. The main thrust of this dissertation is the following: Procedures are developed for the theoretical calculation of the cross sections in the exact lineshape expression. The procedures involve either an extended Anderson theory or an infinite order sudden approximation. Lineshapes are computed from the theoretical cross sections and are fit to a sum of Lorentzians(54) by using a computer program developed to analyze experimental lineshapes. The goodness of fit is a measure of the validity of the sum of Lorentzians approximation. In addition to the lineshape calculations a model of relaxation commonly used in NMR is adapted to the microwave absorption case and is shown to be in qualitative agreement with the extended Anderson theory results. Also, the effect of two adiabatic corrections to the infinite order sudden approximation is developed. Finally, because of the interest in microwave-microwave double resonance experiments in collisions causing the rotational angular momentum to change by two or more units, the infinite order sudden approximation is developed for use in calculating cross sections for such collisions.

CHAPTER I

CURRENT STATUS OF POWER-BROADENED MICROWAVE LINESHAPES AND RELAXATION PARAMETERS

A. History and Summary of Steady-State Microwave Lineshapes

In any discussion of steady-state microwave lineshapes it is necessary first to distinguish a two-state approach from a two-level approach. In the absence of fields, rotation or rotation-vibration energy levels have at least a (2J + 1)-fold degeneracy, where J is the total angular momentum. This degeneracy is usually termed m-degeneracy (m = -J, -J + 1, . . . J) and is a result of the 2J + 1 possible projections of the angular momentum on a space-fixed z axis. In the sum of Lorentzians approximation, each m-component pair connected by microwave radiation is treated as a two-state system. Equations of motion for a two-state density matrix are solved in the steady-state to obtain an expression for the absorption coefficient. Degeneracy of rotational levels is accounted for by summing over the m-component pairs. In the two-level approach, the degeneracy is considered from the beginning by forming appropriate linear combinations of density matrix elements. Equations of motion for these linear combinations are solved in a manner analogous to the two-state case to obtain the absorption coefficient.

The following summary of the two-state approach follows a review by Flygare and his coworkers.(54) An incident radiation field

$$\varepsilon = E(z,t)\cos[\omega t-kz+\phi] \qquad (1)$$

induces a macroscopic polarization

$$P = P_c \cos[\omega t-kz+\phi] + P_s \sin[\omega t-kz+\phi] \qquad (2)$$

In Equations (1) and (2), z is a spatial coordinate, t is time, ω is the angular frequency of the field, k is the wave vector, ϕ is a phase, and P_c and P_s are components of the polarization. By starting with the wave equation,(56)

$$\frac{\partial^2\varepsilon}{\partial z^2} = \frac{1}{C^2}\frac{\partial^2\varepsilon}{\partial t^2} + \frac{4\pi}{C^2}\frac{\partial^2 P}{\partial t^2}, \qquad (3)$$

it is possible to deduce that the absorption coefficient α as a function of frequency can be written as

$$\alpha(\omega) = \frac{4\pi\omega}{C}\frac{P_s}{E}. \qquad (4)$$

(C is the speed of light.)

It is assumed that the radiation interacts only with the dipole moments of the molecules. Then, for a sample of dipoles the polarization is a macroscopic dipole moment and can be written as

$$P = N\mathrm{tr}(\mu\rho) \qquad (5)$$

where N is the number of dipoles, μ is the dipole moment, and ρ is the density matrix.(57) The symbol tr(x) denotes the trace of the matrix x. From Equations (2), (4) and (5) it is seen that if ρ can be determined, P, $\alpha(\omega)$ and therefore, the lineshape can be obtained.

The equation of motion for the density matrix is

$$i\hbar \frac{\partial\rho}{\partial t} = [H,\rho] = H\rho - \rho H \qquad (6)$$

where $H = H_o - \mu E \ \cos[\omega t - kz + \phi]$. For rigid rotors H_o supports the rotational levels of an unperturbed molecule. In writing H, the effect of collisions has been ignored. As in all previous two-state approaches, collisional effects will be added phenomenologically. When the two-level approach is considered, collisions will be treated more rigorously. Diagonal elements of the density matrix, ρ_{ii}, are proportional to the population of state i. To see the meaning of the off-diagonal elements consider a two-state system with states i and f. The polarization of this system is

$$P \sim \mathrm{tr}(\mu\rho) = \mathrm{tr}\left\{\begin{pmatrix} 0 & \mu_{if} \\ \mu_{fi} & 0 \end{pmatrix}\begin{pmatrix} \rho_{ii} & \rho_{if} \\ \rho_{fi} & \rho_{ff} \end{pmatrix}\right\}$$

$$= \mu_{if}\rho_{fi} + \mu_{fi}\rho_{if} \;. \tag{7}$$

(The assumption has been made that the diagonal matrix elements of μ are zero.) That is, the off-diagonal density matrix elements are related to the polarization. If Equation (6) is written out in detail the following equations for density matrix elements in the interaction representation(58) result.

$$i\hbar \frac{\partial\rho_{fi}}{\partial t} = E\mu_{fi}(\rho_{ff}-\rho_{ii}) - \hbar\Delta\omega\rho_{fi} \tag{8}$$

$$i\hbar \frac{\partial\rho_{ii}}{\partial t} = -E\mu_{fi}\rho_{if} + E\rho_{fi}\mu_{if} \tag{9}$$

(The interaction representation is simply a device which allows the operators to carry the time-dependence of H_o.) The rotating wave approximation, which assumes that the experimental apparatus has a limited ability to follow rapid time variation, has also been made. In Equation (8) $\Delta\omega$ is the difference between the frequency of the applied radiation and the resonant frequency of the spectral transition i → f. Equations (8) and (9) and the corresponding equations for ρ_{ff} and ρ_{if} are equivalent to the following set of equations

$$\frac{dP_c}{dt} + \Delta\omega P_s = 0 \qquad (10)$$

$$\frac{dP_s}{dt} - \Delta\omega P_c + \frac{\mu_{if}^2 E\Delta N}{2} = 0 \qquad (11)$$

$$\frac{d(\Delta N)}{dt} - 2EP_s = 0 \qquad (12)$$

where ΔN is the population difference between states i and f.

It is traditional to introduce the effects of collisions by phenomenologically adding relaxation times so that Equations (10) - (12) become

$$\frac{dP_c}{dt} + \Delta\omega P_s + \frac{P_c}{T_2} = 0 \ , \qquad (13)$$

$$\frac{dP_s}{dt} - \Delta\omega P_c + \frac{\mu_{if}^2 E\Delta N}{2} + \frac{P_s}{T_2} = 0 \ , \qquad (14)$$

$$\frac{d\Delta N}{dt} - 2EP_s + \left(\frac{\Delta N - \Delta N_o}{T_1}\right) = 0 \ . \qquad (15)$$

A single relaxation time, T_2, has been attributed to both P_c and P_s, while a different relaxation time, T_1, has been attributed to the population difference. The presence of $-\Delta N_o$ in Equation (15) is a statement that the perturbed population difference decays to an equilibrium population difference, ΔN_o.

Equations (13) - (15) can be solved in the steady-state by setting the time derivatives equal to zero. This results in an expression for P_s:

$$P_s \sim \frac{\mu_{if}^2 E(1/T_2)}{(\Delta\omega)^2 + (\frac{1}{T_2})^2 + \mu_{if}^2 E^2 (\frac{T_1}{T_2})} \qquad (16)$$

P_s is related to the absorption coefficient $\alpha(\omega)$ by Equation (4) so that Equation (16) is essentially the lineshape in the two-state model. The sum of Lorentzian's approximation consists of using Equation (16) for each m-component pair connected by radiation.

If the saturation term in the denominator of Equation (16) $\mu_{if}^2 E^2 (\frac{T_1}{T_2})$ goes to zero (low-power conditions), the resulting expression is essentially that derived by VanVleck and Weisskopf.(59) If the assumption is made that both the polarization and the population difference relax to equilibrium values at the same rate, <u>i.e.</u>, $T_1 = T_2$, Equation (16) becomes the expression of Karplus and

Schwinger,(60) and Snyder and Richards.(61) Townes(62) was the first to suggest that two different relaxation times be used and this approach has been used extensively by Flygare and his coworkers in their analysis of microwave transient effect experiments.(54)

It is possible to be more rigorous in defining the effects of collisions. Within the impact approximation the equation of motion for the density matrix including collisions may be written as(63)

$$i\hbar \frac{\partial \rho_{fi}}{\partial t} = E\mu_{fi}(\rho_{ff}-\rho_{ii}) - \hbar\Delta\omega\rho_{fi} - i\hbar \sum_{f'i'} \Lambda_{fif'i'}\rho_{f'i'} \qquad (17)$$

$$i\hbar \frac{\partial \rho_{ii}}{\partial t} = -E\mu_{fi}\rho_{if} + E\mu_{if}\rho_{fi} - i\hbar \sum_{k} \Lambda_{iikk}\rho_{kk} \qquad (18)$$

For the present it is sufficient to describe the Λ as thermally averaged products of scattering matrices. The impact approximation states that a collision is an instantaneous event compared to the time between collisions. If the impact approximation is not valid the Λ are thermally averaged products of both on-shell and off-shell t matrix elements. More precise discussions of the impact approximation are available.(64) It will always be assumed in this dissertation that the impact approximation is valid. It is very difficult to establish rigorous limits of validity for this approximation and it is almost impossible with present day methods to calculate the Λ when this approximation is not valid. Experimentally, it is known that the low-power lineshape is Lorentzian when the impact approximation is expected to be valid. All high-power lineshapes considered in this dissertation are obtained under conditions where the corresponding low-power lineshape is essentially Lorentzian.

The Λ will be considered in great detail later as they form the principal topic of this work. For the moment it is sufficient to recognize that a two-state approximation applied to the Λ in Equations (17) and (18) (that is, restricting the summation indices f',i' and k to i and f) allows the relaxation times T_1 and T_2 to be expressed as

$$\frac{1}{T_1} = \frac{1}{2}(\Lambda_{iiii} + \Lambda_{ffff} - \Lambda_{ffii} - \Lambda_{iiff}) \qquad (19)$$

and

$$\frac{1}{T_2} = \mathrm{Re}(\Lambda_{fifi}) \qquad (20)$$

where Re(x) denotes the real part of x. $\mathrm{Im}(\Lambda_{fifi})$ gives the line shift. The methods that will be used to calculate Λ are such that $\mathrm{Im}(\Lambda) \equiv 0$.

The above paragraphs summarize the two-state approach to analyzing high-power microwave lineshapes. If there is no collisional coupling of the m states it is clear that each of the m-component pairs connected by radiation will evolve independently of the others and a sum of Lorentzian's approximation is valid. This can be seen from the equations of motion for the density matrix when written to include the degenerate m-states(63)

$$i\frac{\partial}{\partial t}\rho(j_f m, j_i m) = \Delta\omega_{fi}\rho(j_f m, j_i m)$$

$$-E\langle j_f m|\mu|j_i m\rangle[\rho(j_i m, j_i m)-\rho(j_f m, j_f m)]$$

$$-i\sum_{j_f' j_i'}\sum_{m'}\langle\langle j_f m j_i m|\Lambda|j_f' m' j_i' m'\rangle\rangle\rho(j_f' m' j_i' m') \qquad (21)$$

$$i\frac{\partial}{\partial t}\rho(j_i m, j_i m) = -E[\langle j_i m|\mu|j_f m\rangle\rho(j_f m, j_i m)$$

$$-\rho(j_i m j_f m)\ \langle j_f m|\mu|j_i m\rangle]$$

$$-i\sum_{j'm'}\langle\langle j_i m j_i m|\Lambda|j'm'j'm'\rangle\rangle\rho(j'm'j'm') \qquad (22)$$

$|j_f m_f j_i m_i\rangle\rangle$ is a vector in Liouville space(64) and is defined by $|j_f m_f j_i m_i\rangle\rangle \equiv |j_f m_f\rangle\langle j_i m_i|$. Equations (21) and (22) assume plane polarized radiation so that matrix elements of ρ and μ are diagonal in m. The various m-component pairs are collisionally coupled unless for some reason certain of the Λ matrix elements are zero. As discussed later, within the context of first order perturbation theory it is possible to say that m-components are not collisionally coupled for dipole-dipole interaction potentials when the molecular rotational levels have definite parity. More definitive statements or statements outside the scope of first order perturbation theory are difficult to make. It is usually necessary to resort to numerical calculations.

Pickett$^{(65)}$ was apparently the first to recognize that degenerate m states are collisionally coupled and that the sum of Lorentzians may not be a valid approximation. Liu and Marcus$^{(63)}$ (hereafter denoted by LM) made the first serious attempt to deal with the m degeneracy of the rotational levels. By forming the linear combinations

$$\rho_{fi}(KQ) \quad \sum_{m_i m_f} (-1)^{j_f - m_f} (2K+1)^{1/2} \begin{pmatrix} j_f & j_i & K \\ m_f & -m_i & -Q \end{pmatrix} \rho(j_f m_f j_i m_i), \tag{23}$$

they arrived at the following two equations

$$\frac{i}{\sqrt{3}} \frac{\partial}{\partial t} \rho_{fi}(10) = \omega_{fi} \rho_{fi}(10)/\sqrt{3} - \bar{\mu}_{fi} E \cos\omega t \sum_m (-1)^{j_i + j_f} \begin{pmatrix} j_i & j_f & 1 \\ m & -m & 0 \end{pmatrix}^2$$

$$\times[\rho(j_i m j_i m) - \rho(j_f m j_f m)] - i \sum_{f'i'} \Lambda'_{fif'i'} \rho_{f'i'}(10)/\sqrt{3} \tag{24}$$

$$\frac{i}{\sqrt{2j_i+1}}\frac{\partial}{\partial t}\rho_{ii}(00) = \frac{E\cos\omega t}{\sqrt{3}(2j_i+1)}[\bar{\mu}_{if}\rho_{fi}(10)-\rho_{if}(10)\bar{\mu}_{fi}]$$

$$-i\sum_k \frac{[2j_k+1]^{1/2}}{2j_i+1}\Lambda^{o}_{iikk}\rho_{kk}(00) \quad . \qquad (25)$$

In Equations (24) and (25) $\bar{\mu}_{if}$ is defined by

$$<j_im_i|\mu|j_fm_f>=(-1)^{j_i-m_i}\begin{pmatrix} j_i & j_f & 1 \\ m_i & -m_f & 0 \end{pmatrix}\bar{\mu}_{if} \ , \qquad (26)$$

which is merely an application of the Wigner-Eckart theorem. The quantum number Q is always equal to 0 if the microwave radiation is plane-polarized. The Λ^K are defined by

$$<<j_f'm_f'j_i'm_i'|\Lambda|j_fm_fj_im_i>> = \sum_{KQ}\sum (-1)^{j_f'-m_f'+j_f-m_f}(2K+1)$$

$$\times\begin{pmatrix} j_f' & j_i' & K \\ m_f' & -m_i' & -Q \end{pmatrix}\begin{pmatrix} j_f & j_i & K \\ m_f & -m_i & -Q \end{pmatrix}\Lambda^K_{f'i'fi} \qquad (27)$$

This is a direct consequence of forming linear combinations of $|j_fm_fj_im_i>>$ in analogy with Equation (23), i.e.,

$$|j_fj_i,KQ>>=\sum_{m_fm_i}(-1)^{j_f-m_f}(2K+1)^{1/2}\begin{pmatrix} j_f & j_i & K \\ m_f & -m_i & -Q \end{pmatrix}|j_fm_fj_im_i>> \qquad (28)$$

This can be inverted to give

$$|j_f m_f j_i m_i>> = \sum_{KQ} (-1)^{j_f - m_f} (2K+1)^{1/2} \begin{pmatrix} j_f & j_i & K \\ m_f & -m_i & -Q \end{pmatrix} |j_f j_i; KQ>> \qquad (29)$$

The $\Lambda^{K}_{f'i'fi}$ are independent of the quantum number Q. This is a result of rotational invariance and has been discussed in detail by Ben-Reuven.(66)

The problem with Equations (24) and (25) is that $\rho(K,Q)$ are coupled to $\rho(jmj'm')$. To get around this, LM noted that

$$\sum_m \begin{pmatrix} j_f & j_i & 1 \\ m & -m & 0 \end{pmatrix}^2 = \frac{1}{3} \qquad (30)$$

and assumed that in Equation (24) the quantity

$$\sum_m \begin{pmatrix} j_f & j_i & 1 \\ m & -m & 0 \end{pmatrix}^2 [\rho(j_i m j_i m) - \rho(j_f m j_f m)]$$

could be replaced by

$$\frac{1}{3}[(2j_i+1)^{-1}\rho_{ii}(00) - (2j_f+1)^{-1}\rho_{ff}(00)].$$

This assumption has been shown to be inadequate for analyzing experimental data for several transitions in $^{15}NH_3$.(67) This finding spawned the introduction of an alternative to the quantity T_1/T_2, namely qT_1/T_2, where q is related to the distributions of populations among the m states.(67) This parameter has since been shown to be an impractical method of analyzing line shapes and will not be discussed further. The next progress came when Bottcher gave a set of equations involving only $\rho(KQ)$ and solved them exactly in the steady-state for the $j = 1 \leftarrow 0$ transition.(68) The lineshape for this case is proportional to

$$\frac{1}{(\Delta\omega)^2 + (\frac{1}{T_2})^2 + \frac{4}{9}\mu_{if}^2 E^2 (\frac{2T_1}{T_2} + \frac{T_4}{T_2})} \tag{31}$$

Comparison with the denominator of Equation (16) shows that the power broadening terms (the last term in the denominator are qualitatively similar. There is an additional relaxation time in (31), T_4, which describes the relaxation of ρ_{ff} (20).

Coombe and Snider(69) also considered the $j = 1 \leftarrow 0$ transition and arrive at an expression for the lineshape which is in agreement with that given by Bottcher.(68) Coombe and Snider also considered the general transition $j + 1 \leftarrow j$.(70) The set of equations of motion for the $\rho(KQ)$ becomes very large as j increases. In the interest of keeping the size of this set tractable Coombe and Snider assumed that all $\rho(KQ)$ with K greater than 2 could be ignored. This gave a set of eight equations which under two conditions reduce to a set of four equations. These give a lineshape identical to Equation (31) with the exception of numerical factors (which are a function of j) in the power broadening term. The two conditions are that plane polarized radiation be used and that the collision dynamics are the same in the j and j+1 levels. This latter condition is often referred to as a high-j approximation.

Finally, Schwendeman(55) has derived an expression for power-broadened lineshapes which is valid for plane-polarized radiation and for any j. The expression may be used for either R branch ($j = j + 1 \leftarrow j$) or Q branch ($j = j \leftarrow j$) transitions and does not make any high-j approximations. Thus, an expression is now available that exactly accounts for the m-degeneracy of the rotational levels involved in the spectral transition. The power-broadening term is a function of many Λ^K. By calculating the Λ^K and fitting the resulting lineshape to a sum of Lorentzians, the validity of this approximation may be assessed.

The equations of motion for the $\rho(KQ)$ can be written as

$$
\begin{aligned}
i\frac{\partial}{\partial t}\rho_{fi}(K) &= \Delta\omega_{fi}\rho_{fi}(K) \\
&-E\bar{\mu}_{fi}\sum_{K'}\Big\{(-1)^{j_f-j_i}[(2K+1)(2K'+1)]^{1/2}\begin{pmatrix}K & K' & 1\\ 0 & 0 & 0\end{pmatrix}\begin{Bmatrix}K' & K & 1\\ j_f & j_i & j_i\end{Bmatrix}\rho_{ii}(K') \\
&-(-1)^{j_f-j_i}[(2K+1)(2K'+1)]^{1/2}\begin{pmatrix}K & K' & 1\\ 0 & 0 & 0\end{pmatrix}\begin{Bmatrix}K' & K & 1\\ j_i & j_f & j_f\end{Bmatrix}\rho_{ff}(K')\Big\} \\
&- i\,\Lambda^{K}_{fifi}\rho_{fi}(K)\ , \qquad (32)
\end{aligned}
$$

$$
\begin{aligned}
i\frac{\partial}{\partial t}\rho_{ii}(K) &= -E\bar{\mu}_{fi}\sum_{K'}[\rho_{fi}(K')-(-1)^{j_i-j_f}\rho_{if}(K')] \\
&\times(-1)^{j_f-j_i}[(2K+1)(2K'+1)]^{1/2}\begin{pmatrix}K & K' & 1\\ 0 & 0 & 0\end{pmatrix}\begin{Bmatrix}K & K' & 1\\ j_f & j_i & j_i\end{Bmatrix} \\
&- i\sum_{k}\Lambda^{K}_{iikk}[\rho_{kk}(K)-\rho^{\circ}_{kk}(K)]\ . \qquad (33)
\end{aligned}
$$

In the above $\rho^{\circ}_{kk}(K)$ is the equilibrium value of $\rho_{kk}(K)$, $\begin{Bmatrix}\cdot & \cdot & \cdot\\ \cdot & \cdot & \cdot\end{Bmatrix}$ is a 6-j symbol,(71) and the label Q in $\rho_{fi}(KQ)$ has been deleted because it is always zero as a consequence of plane-polarized radiation.

The following points are worth noting. The relaxation of a density matrix element labelled by K is governed by

Λ^K and not by any $\Lambda^{K'}$ for $K' \neq K$. This is a result of the assumption of rotational invariance. The only coupling to different values of K arises in the field dependent terms. The 3-j symbol $\begin{pmatrix} K & K' & 1 \\ 0 & 0 & 0 \end{pmatrix}$ is zero if K + K' + 1 is odd. Therefore, the only values of K' in the summation over K' are K ± 1. For the case of plane-polarized radiation this implies that diagonal matrix elements may have only even K while off-diagonal density matrix elements may have only odd K. The set of coupled equations (32) and (33) may be solved in steady-state to give an expression for the line shape.

$$P_s(1) \sim \frac{\mu_{fi}^2 E(\frac{1}{T_2})\Delta N}{(\Delta\omega)^2 + (\frac{1}{T_2})^2 + \mu_{fi}^2 E^2 [\frac{P_s(3)}{P_s(1)}]} \tag{34}$$

where $\frac{P_s(K+2)}{P_s(K)}$ is a function of $\frac{P_s(K+4)}{P_s(K+2)}$, Λ^K_{fifi}, Λ^K_{iiii}, Λ^K_{ffff}, Λ^K_{iiff} and Λ^K_{ffii}. $P_s(K)$ is the analogue of the P_s occurring in Equations (2) and (4). The factor $[\frac{P_s(3)}{P_s(1)}]$ in Equation (34) is in the form of a continued fraction and Equation (34) will henceforth be referred to as the continued fraction lineshape. Schwendeman was able to show that the continued fraction lineshape reduces to a sum of Lorentzians for the conditions on Λ^K given in Table I.(55)

Table I. Conditions on Λ^K for the Continued Fraction Lineshape to Reduce to a Sum of Lorentzians.

<u>R Branch</u>

All Λ^K_{fifi} are equal

All Λ^K_{iiii} are equal

All $\Lambda^K_{iiff} = 0$

<u>Q Branch</u>

All Λ^K_{fifi} are equal

All T_1-like relaxation times are equal

This set of conditions may not be the only set of conditions for which the continued fraction lineshape reduces to a sum of Lorentzians.

It will be useful later to consider now the $\rho(KQ)$ and Λ^K in slightly more detail. The details of Λ^K will be given in later chapters. For the present it is satisfactory to give a brief qualitative discussion. The $\rho(KQ)$ are variously known as state multipoles or statistical tensors.(71) They were first introduced by Fano.(72) While their application in chemistry has been rather limited, their application in physics includes discussions of the production of polarized particles in nuclear reactions,(73,74) the redistribution of resonance radiation,(75) angular distributions of photoelectrons,(76-79) optical pumping(80-82) and transport properties.(83,84) Besides the previously mentioned work concerning microwave absorption, the work most closely related to this topic is that of Case et al.(85) who applied the state multipoles to the problem of determining rotational state distributions in fluorescence experiments.

The $\rho(KQ)$ formed by Equation (23) are said to be the matrix elements of an irreducible tensorial basis. All of the 2K + 1 components for a given K form an invariant set,(66) i.e., under rotations they transform only among themselves. It is easy to show from Equation (23) that

$$\rho_{ii}(00) = \sum_{m} \rho(j_i m j_i m)/\sqrt{2j_i+1} \quad . \qquad (35)$$

This follows from the relation

$$\begin{pmatrix} j & j & 0 \\ m & -m & 0 \end{pmatrix} = (-1)^{j-m}(2j+1)^{-1/2} . \qquad (36)$$

Therefore, $(2j_i+1)^{-1/2}\rho_{ii}(00)$ is an average level population. At equilibrium the $\rho(j_i m j_i m)$ are equal to each other for all m in which case the $\rho_{ii}(KQ)$ are independent of K. A level that has nonzero $\rho_{ii}(KQ)$ for K = 0 only is said to be unpolarized. A rotational level that has nonzero $\rho_{ii}(KQ)$ for K > 0 is said to be polarized with a multipole moment, or simply moment of order K. The quantum number K may also be referred to as the tensor order. The off-diagonal $\rho(KQ)$ are related to the macroscopic polarization induced by the applied radiation field. For a system of dipoles the dipole polarization may be written as

$$P = N\mathrm{tr}(\mu\rho(10)) \sim \bar{\mu}_{if}\rho_{fi}(10) + \bar{\mu}_{fi}\rho_{if}(10) \qquad (37)$$

in analogy with Equations (5) and (7). The state multipole has K = 1 here because μ is a tensor operator of tensor order 1.

The Λ^{o}_{iiii} may be interpreted as being proportional to the total collisional rate of transfer of molecules out of level i. The Λ^{o}_{iikk} are proportional to the negative of the rate of collisional transfer from level k to level i.

This is a consequence of the unitarity of the scattering matrix, which may be expressed as

$$\sum_i \Lambda^0_{iikk} \equiv 0 \ . \tag{38}$$

Equation (38) simply states that the total population of molecules remains fixed. The Λ^K_{iikk} for $K > 0$ are called multipole relaxation coefficients as they describe how the diagonal elements of a state multipole of order K relaxes due to collisions, i.e.,

$$i \frac{\partial}{\partial t} \rho_{ii}(K0) \sim -i \sum_k \Lambda^K_{iikk}\rho_{kk}(K0) \ . \tag{39}$$

Similarly, the Λ^K_{fifi} describes the relaxation of the off-diagonal elements of state multipoles of order K. For K not equal to 1 the Λ^K_{fifi} are generalizations to arbitrary tensor order of Λ^1_{fifi}. This is of interest because $\mathrm{Re}(\Lambda^1_{fifi})$ is just the traditional low power linewidth, i.e. $1/T_2$. This quantity has been the subject of considerable attention.

B. History and Summary of the Multipole Relaxation Coefficients

The first complete theory for Λ^1_{fifi} for rotation and vibration-rotation levels was given by Anderson(53) in

1949. The theory was amplified in 1962 by Tsao and Curnutte(86) (hereafter referred to as TC) who explicitly considered dipole-dipole, dipole-quadrupole, quadrupole-dipole, quadrupole-quadrupole, and dispersion intermolecular potentials. (The first four of these potentials will be abbreviated as μ-μ, μ-Q, Q-μ, and Q-Q.) Anderson made several key assumptions that are worth enumerating here. The most important assumption is that the impact approximation is valid. As mentioned above this requires that the time of collision be negligible compared to the time between collisions. This implies that only complete collisions need to be considered and in turn that only scattering matrices (or equivalently on-shell t matrices), and not off-shell t matrices are needed. Present day methods do not allow calculation of off-shell t matrices for systems of interest in microwave spectroscopy. The impact approximation has been discussed in detail by Baranger(64) who also gave several expressions for estimating the validity limits of the approximation. Obtaining numerical estimates from these expressions is almost as difficult as calculating Λ^1_{fifi} itself so that, as explained earlier, the assumption will be made here that the impact approximation is valid for the conditions considered in this work. A general expression for the Λ^K that does not depend on the impact approximation was given by Fano(87) in 1963. An equivalent expression, derived by different methods, was given by Ben-Reuven in 1975.(88)

Anderson also assumed that all molecules move along classical straight line paths. This implies that collisions resulting in changes in molecular internal states have a negligible effect on the trajectory. For rotational levels separated by energies $\leq$ kT (Boltzmann constant times temperature), this is true. A discussion of this point may be found in Reference 89. The assumption of straight line paths has practical implications for numerical calculations that are both good and bad. In the Anderson formulation the relaxation coefficient goes to infinity as the intermolecular distance goes to zero. Circumventing this difficulty requires an artificial means of imposing unitarity. The traditional method of doing this is to use a "hard sphere cutoff." Details of the cutoff procedure will be discussed later in this work and may also be found in the papers of Anderson(53) and TC.

Baranger was apparently the first to remove the restriction of classical straight line paths by treating all relative molecular motion quantum mechanically.(64)

Baranger was also the first to formally exploit the consequences of rotational invariance. These ideas were carried to completion by Ben-Reuven.(66) The key result of this work is that it is possible to write

$$\langle\langle j_f' j_i' K'Q' | \Lambda | j_f j_i KQ \rangle\rangle = \Lambda^K_{f'i'fi} \delta_{K'K} \delta_{Q'Q} \qquad (40)$$

where $\Lambda^{K}_{f'i'fi}$ is defined by Equation (27). The point is that the $\delta_{K'K}$ precludes the possibility of a sum over K' in the relaxation terms of Equations (32) and (33).

Almost all previous calculations of Λ^{K} have been for Λ^{1}_{fifi}, i.e., the cross section for low-power linewidth, $1/T_2$. By far the most common calculations are those that employ Anderson's formulation as amplified by TC.(90-98) Goldflam et al.(99) have used the close coupled (CC) and coupled states (CS) methods to calculate Raman cross sections Λ^{2}_{fifi} for H_2 perturbed by He. (The CC and CS methods will be discussed shortly.) Nielsen and Gordon(89) solved the time-dependent Schrodinger equation for a classical trajectory determined by a spherically symmetric potential. They calculated Λ^{1}_{fifi}, $\Lambda^{1}_{i'i'ii}$, and $\Lambda^{2}_{i'f'if}$ for HCl perturbed by Ar. The Λ^{K} with K greater than one were calculated to rationalize the results of NMR relaxation and Raman lineshape experiments. Shafer and Gordon(100) calculated the same cross sections for H_2 perturbed by He by using a CC method. Marcus and coworkers(101,102) have calculated Λ^{1}_{fifi} and $T_1^{-1} = \frac{1}{2}(\Lambda^{0}_{iiii} + \Lambda^{0}_{ffff} - \Lambda^{0}_{iiff} - \Lambda^{0}_{ffii}) \approx \Lambda^{0}_{iiii} - \Lambda^{0}_{iiff}$ for OCS and HCN perturbed by noble gas atoms. They used a semiclassical technique that required the calculation of complex valued trajectories. This technique was developed by Marcus(103) and Miller.(104,105) The infinite order sudden (IOS) approximation was used by Green(106) to calculate Λ^{1}_{fifi} and various Λ^{K}_{iikk} for OCS perturbed by noble gas atoms. This is the only calculation of Λ^{K}_{iikk} for a system of interest to microwave spectroscopy. The only other calculations of Λ^{K}_{iikk} are those mentioned previously for NMR relaxation. Finally, a few distorted wave Born approximation(107) calculations have been performed to rationalize experimental results for various transport experiment properties.(108)

C. Summary of Available Methods for Calculating the Scattering Matrix

The Λ^{K} are proportional to thermally averaged products of scattering matrices. The central problem in calculating Λ^{K} is to find a feasible method of obtaining the scattering matrix. There are a multitude of techniques for doing this. The close coupling method (CC) is the essentially exact, completely quantum mechanical method of calculating S, the scattering matrix.(109,110) As it is usually formulated the method consists of solving a set of N coupled second order differential equations, where N is the number of states included in the calculation. For rotational scattering the number of states increases rapidly with increasing j because of the m-degeneracy. The computer time required for solution of the differential equations rises approximately as N^3. For this reason the CC method is practical at present only for light diatoms and symmetric tops perturbed by noble gas atoms. The coupled states (CS) method attempts to reduce the number of equations by making an approximation on the orbital angular momentum operator.(111) This has the effect of reducing N by a factor of two. The next level of simplification is the infinite order sudden (IOS) approximation.(112-116) By neglecting the energy difference between rotational levels and freezing the orbital angular momentum quantum number at an arbitrary value (there are several choices possible for this quantum number, some of which appear to be better than others) the set of N coupled equations becomes completely uncoupled. This results in considerable saving in computational time so that diatomic, symmetric top, and asymmetric top molecules perturbed by noble gas atoms can be dealt with reasonably. A preliminary calculation involving H_2 - H_2 has recently been reported.(117)

At the other end of the spectrum from fully quantal methods are fully classical techniques.(118) In the typical case Hamilton's equations of motion are integrated for a given set of initial conditions. The rotational quantum numbers are treated classically (i.e., continuously) with the result that the trajectories are "binned" to obtain transition probabilities. That is, for a given set of initial conditions all trajectories with a final rotational angular momentum between, for example, 2.5 and 3.5 are lumped together and are considered to have j equal to 3. The main disadvantage of this method is that a large number of trajectories must be calculated-sometimes as many as one or two thousand. Also, any quantum effects will not be accurately considered. This is not expected to be a large problem, however, for the Λ^K, as they are relatively highly averaged quantities. A calculation of transition probabilities has been performed for OCS perturbed by H_2 treated as a structureless perturber.(118) The results were only qualitatively accurate.

In an effort to include quantum effects in a classical trajectory framework Miller(104,105) and Marcus(103) have independently developed a semiclassical technique that involves calculating complex-valued trajectories. Several calculations of Λ^K_{fifi} have been performed.(101,102) The theoretical values are smaller than the experimental low-power linewidths.

In addition to the three broad categories outlined above there are many methods which treat certain degrees of freedom classically and others quantum mechanically, each with appropriate approximations. A very brief, representative sampling of these methods is in References 119-135.

D. Choice of Methods for Calculating Λ^K

There are obviously many choices for the calculation of the scattering matrices and thereby, the Λ^K. The method of choice should be relatively simple, inexpensive and capable of giving reliable results. Two methods have been chosen with these considerations in mind. The first method is the Anderson theory, which will be extended to enable calculation not only of Λ^1_{fifi} but of all other Λ^K as well. The theory meets the above criteria and has the additional advantage of being relatively familiar to microwave spectroscopists. The Anderson theory is capable of giving good values for Λ^1_{fifi} for many molecules although for some symmetric tops, most notably NH_3, it is necessary to normalize computed values of Λ^1_{fifi} to one experimental value. The major drawbacks of the theory are that it requires an artificial method of imposing unitarity (this was discussed earlier, and will be discussed again later) and that because it is only a first order theory in the scattering matrix, a dipole-dipole potential will allow only collisional transitions where j changes by zero or one. To estimate the effect of these drawbacks the Λ^K will also be calculated using a sudden approximation.(136,137) As employed here dipole-dipole potentials and straight line paths are used so that a direct comparison with the Anderson theory may be made. The sudden approximation allows estimation of transitions where j changes by more than one. Other calculations to be presented have been outlined in the introduction.

CHAPTER II

EXTENSION OF ANDERSON THEORY TO THE CALCULATION OF Λ^K

A. Relation of the Liu-Marcus Λ^K to Anderson Theory

The Λ^K appearing in the continued fraction lineshape of Schwendeman$^{(55)}$ are the Λ^K as defined by LM. Specifically,

$$\Lambda^K_{f'i'fi} = \langle v\sigma^K_{f'i'fi}\rangle \tag{41}$$

where

$$\sigma^K_{f'i'fi} = \left(\frac{\pi}{k^2}\right) \sum_{\ell\ell'} \sum_{J_iJ_f} (-1)^{j_i-j_i'+\ell-\ell'} (2J_i+1)(2J_f+1) \times \begin{Bmatrix} J_f & J_i & K \\ j_i & j_f & \ell \end{Bmatrix} \begin{Bmatrix} J_f & J_i & K \\ j_i' & j_f' & \ell' \end{Bmatrix} [\delta_{i'i}\delta_{f'f} - S^{J_i}_{i'i} S^{J_f *}_{f'f}] \; . \tag{42}$$

In the above expressions <v . . .> denotes a thermal average, v is the relative velocity, $k = \frac{\mu v}{\hbar}$ is the magnitude of the relative collision wave vector with μ the reduced mass of the collision pair (i.e., system molecule plus perturber molecule), K is the tensor order of the relaxation process, lower case subscripted j's are rotational quantum numbers of the system molecule, ℓ and ℓ' are relative orbital angular momentum quantum numbers before and after the collision, respectively, J_k is the total angular momentum formed by coupling j_k and ℓ, and S^{J_k} is the scattering matrix which is diagonal in J_k and M. (M is the projection of J_k on a space-fixed axis.) Equation (42) is valid for the case of a molecule perturbed by a structureless (i.e., no internal states) perturber, such as a noble gas atom. Equation (42) is exact in the sense that all degrees of freedom have been treated quantum mechanically.

The $\Lambda^K_{f'i'fi}$ must be related to an expression from Anderson theory. The simplest way to do this is to recognize that Λ^1_{fifi} is $1/T_2$ for the spectroscopic transition f ← i, and that the familiar expression from Anderson theory also gives $1/T_2$. One could then assume that all other $\Lambda^K_{f'i'fi}$ correspond to certain modifications of the Anderson expressions. The Anderson theory expression for the Λ^1_{fifi} was originally given in an uncoupled basis; i.e., a basis where j_k and ℓ are not coupled to form J_k. It is shown in Appendix A that the cross section in an uncoupled basis,

$$\sigma^{KK'}_{i'f'if} = \left(\frac{\pi}{k^2}\right) \sum_{\substack{\ell\ell'mm' \\ m_i m_i' m_f m_f'}} \sum [(2K+1)(2K'+1)]^{1/2} (-1)^{j_i - j_i' - m_i' - m_i}$$

$$\times \begin{pmatrix} j_i' & j_f' & K' \\ m_i' & -m_f' & -Q \end{pmatrix} \begin{pmatrix} j_i & j_f & K \\ m_i & -m_f & -Q \end{pmatrix} [\delta_{i'i}\delta_{f'f} - S_{i'i}S^{*}_{f'f}] \, , \qquad (43)$$

is equivalent to Equation (42). In Equation (43) the possibility that K ≠ K' is allowed. The derivation in Appendix A shows that K = K'. After performing a thermal average (Equation (41)), Equation (43) can be identified with (A27) of LM:

$$\Lambda_{f'i'fi} = \frac{N_2}{2\pi} \sum_{aa'}\sum dE_a \rho_a [\delta_{f'f}\delta_{i'i}\delta_{a'a} - S_{f'a'fa}S^{*}_{i'a'ia}] \qquad (44)$$

where $\sum_a dE_a \rho_a$ constitutes a thermal average. (Although Equation (43) is written in the spherical tensor basis and Equation (44) is not, it is the thermal average which is of interest at the moment and which is the same for either Equation (43) or Equation (44).) After taking a classical limit; i.e., after replacing the quantum mechanical treatment of relative translational motion and the use of the quantum numbers ℓ and ℓ' by a classical treatment of the relative motion and the use of an impact parameter b, Equations (113a) - (115) of Ben-Reuven$^{(88)}$ may be used to convert the thermal average <v . . .> to

$$2\pi n\int vf(v)dv\int bdb\ . \qquad (45)$$

In Equation (45) v is the relative collision velocity, f(v) is the distribution function for v, and b is the impact parameter. The conversion to a classical limit is important because the Anderson theory treats the relative motion classically.

To summarize, Equations (41) and (42) may be replaced with the equivalent expressions,

$$\Lambda^{K}_{f'i'fi} = 2\pi n\int vf(v)dv\int bdb\,\sigma^{K}_{f'i'fi}\ , \qquad (46)$$

and

$$\sigma^{K}_{f'i'fi} = \sum_{\substack{m_i m_i' \\ m_f m_f'}}\sum (-1)^{j_i-j_i'-m_i-m_i'}(2K+1)\begin{pmatrix} j_i' & j_f' & K \\ m_i' & -m_f' & -Q \end{pmatrix}\begin{pmatrix} j_i & j_f & K \\ m_i & -m_f & -Q \end{pmatrix}$$

$$\times\ [\delta_{i'i}\delta_{f'f} - S_{i'i}S^{*}_{f'f}]\ , \qquad (47)$$

where the scattering matrices in Equation (47) are understood to be functions of v and b.

To make Equation (47) consistent with Anderson theory, it is necessary to "renormalize" it. The cross section $\sigma^{K}_{f'i'fi}$ is rotationally invariant. Therefore, it is independent of Q, and each of the (2K+1) Q components is equal. This implies that the factor (2K+1) can be eliminated if a sum over Q is added. Equation (47) will be written as

$$\sigma^{K}_{f'i'fi} = \sum_{\substack{m_i m_i' \\ m_f m_f' Q}} \sum (-1)^{j_i - j_i' - m_i - m_i'} \begin{pmatrix} j_i' & j_f' & K \\ m_i' & -m_f' & -Q \end{pmatrix} \begin{pmatrix} j_i & j_f & K \\ m_i & -m_f & -Q \end{pmatrix}$$

$$\times \; [\delta_{i'i}\delta_{f'f} - S_{i'i}S^{*}_{f'f}] \; . \qquad (48)$$

Finally, because of a difference in conventions for reduced matrix elements between LM and Anderson,(53) Equation (48) will be rewritten as

$$\sigma^{K}(j_i' j_f' j_i j_f) = \sum_{\substack{m_i m_i' \\ m_f m_f' Q}} \sum (-1)^{j_f - j_f' + m_f - m_f'} \left(\frac{2j_i'+1}{2j_i+1}\right)^{1/2} \begin{pmatrix} j_i & K & j_f \\ m_i & -Q & -m_f \end{pmatrix} \begin{pmatrix} j_i' & K & j_f' \\ m_i' & -Q & -m_f' \end{pmatrix}$$

$$\times [\delta_{j_f j_f'}\delta_{j_i j_i'}\delta_{m_f m_f'}\delta_{m_i m_i'} - \langle j_f' m_f' | S^{*} | j_f m_f \rangle \langle j_i' m'_i | S | j_i m_i \rangle] \; . \qquad (49)$$

The conventions for reduced matrix elements are discussed in Appendix B. Appendix C shows that Equation (49) is identical to the expression given by Anderson(53) for the interaction of a molecule with a structureless perturber.

Equation (49) must be modified to include perturber states when the perturber has internal structure. This has been done by Ben-Reuven(138), TC, and Fiutak and Van-Kranendonk.(139) Modification of the notation slightly to agree with TC gives the final working expression for $\sigma^K(i'f'if)$

$$\sigma^K_{j_2}(j_i'j_f'j_ij_f) = \sum_{\substack{m_im_i'm_fm_f' \\ m_2m_2'Qj_2'}}\sum\sum (-1)^{j_f'-j_f'+m_f-m_f'}(2j_2+1)^{-1}\left(\frac{2j_i'+1}{2j_i+1}\right)^{1/2}$$

$$\times \begin{pmatrix} j_i & j_f & K \\ m_i & -m_f & -Q \end{pmatrix}\begin{pmatrix} j_i' & j_f' & K \\ m_i' & -m_f' & -Q \end{pmatrix}[\delta_{j_ij_i'}\delta_{j_fj_f'}\delta_{j_2j_2'}\delta_{m_im_i'}\delta_{m_fm_f'}\delta_{m_2m_2'}$$

$$-<j_fm_fj_2m_2|T^{-1}|j_f'm_f'j_2'm_2'><j_i'm_i'j_2'm_2'|T|j_im_ij_2m_2>] \qquad (50)$$

The T matrices in Equation (50) are analogues of the S matrices in Equation (49). The letter T has been used merely to agree with the notation of TC. In Equation (50) it should be noted that even when $j_i = j_i'$ and $j_f = j_f'$, the T matrix elements can still be off-diagonal in perturber states.

The subscript j_2 has been added to σ^K in Equation (50) because the cross section is for a given j_2 perturber level. The total cross section is

$$\sigma^K(j_i'j_f'j_ij_f) = \sum_{j_2} \rho(j_2)\sigma^K_{j_2}(j_i'j_f'j_ij_f) \qquad (51)$$

where $\rho(j_2)$ is a Boltzmann factor for the perturber level j_2. To obtain $\Lambda^K_{f'i'fi}$ Equation (46) is then used.

B. Λ^K in Terms of Anderson's P Matrix

Now that the equivalence of the quantum mechanical $\Lambda^K_{i'f'if}$ of LM and the semiclassical (i.e., classical translational motion and quantum mechanical internal motion) $\sigma^K_{i'f'if}$ of Anderson(53) theory has been established, the Anderson-like expansions of the cross sections can be carried out. Following TC, let

$$T = T_0 + T_1 + T_2 + \ldots \qquad (52)$$

where $T = (U^0)^{-1}U_m$ with U^0 and U_m the evolution operators corresponding to the Hamiltonians H^0 and H_m, respectively. Here, H^0 is the unperturbed internal state Hamiltonian for the system molecule and $H_m = H^0 + H_c$ where H_c is the Hamiltonian for the intermolecular potential. The equations of motion for T and T^{-1} are

$$i\hbar \frac{\partial T}{\partial t} = [(U^0)^{-1}H_cU^0]T$$

and

$$i\hbar \frac{\partial(T^{-1})}{\partial t} = -T^{-1}[(U^0)^{-1}H_c U^0] \ . \tag{53}$$

An iterative solution gives

$$T_0 = 1 \ , \tag{54}$$

$$T_1 = \frac{1}{i\hbar} \int [(U^0)^{-1}H_c(t)U^0]dt, \tag{55}$$

$$T_2 = \frac{-1}{\hbar^2} \int [(U^0)^{-1}H_c(t')U^0]dt' \int [(U^0)^{-1}H_c(t'')U^0]dt'' \ , \tag{56}$$

etc.

An operator P is defined by

$$P = \frac{1}{\hbar} \int_{-\infty}^{\infty} [(U^0)^{-1}H_c(t)U^0]dt \ , \tag{57}$$

in which case

$$T_1 = -iP, \qquad T_1^{-1} = -T_1 = iP, \tag{58}$$

$$T_2 = \frac{-1}{2} P^2, \text{ and } T_2^{-1} = T_2 = \frac{-1}{2} P^2 \ . \tag{59}$$

These relations enable the Anderson-like expansions to be expressed in terms of P. The expansions are analogous to the expansion in TC for σ^1_{ifif}. Details of the expansions are given in Appendix D. The results are given here.

$$\sigma^K_{j_2}(ifif) = \tfrac{1}{2}\Big[\sum_{m_i m_2} (2j_i+1)(2j_2+1]^{-1} \langle j_i m_i j_2 m_2 | P^2 | j_i m_i j_2 m_2 \rangle$$

$$+ \sum_{m_f m_2} [(2j_f+1)(2j_2+1)]^{-1} \langle j_f m_f j_2 m_2 | P^2 | j_f m_f j_2 m_2 \rangle$$

$$- \sum_{\substack{m_i m_i' m_f m_f' \\ m_2 m_2' j_2' Q}} \sum \sum (-1)^{m_f - m_f'} (2j_2+1)^{-1} \begin{pmatrix} j_i & j_f & K \\ m_i & -m_f & -Q \end{pmatrix} \begin{pmatrix} j_i & j_f & K \\ m_i' & -m_f' & -Q \end{pmatrix}$$

$$\times \langle j_f m_f j_2 m_2 | P | j_f m_f' j_2' m_2' \rangle \langle j_i m_i' j_2' m_2' | P | j_i m_i j_2 m_2 \rangle . \qquad (60)$$

$$\sigma^K_{j_2}(i'i'ii) = - \sum_{\substack{m_i m_i' n_i n_i' \\ m_2 m_2' Q j_2'}} \sum \sum (-1)^{j_i - j_i' + n_i - n_i'} (2j_2'+1)^{-1}$$

$$\times \left(\frac{2j_i'+1}{2j_i+1} \right)^{1/2} \begin{pmatrix} j_i & j_i & K \\ m_i & -n_i & -Q \end{pmatrix} \begin{pmatrix} j_i' & j_i' & K \\ m_i' & -n_i' & -Q \end{pmatrix}$$

$$\times \langle j_i n_i j_2 m_2 | P | j_i' n_i' j_2' m_2' \rangle \langle j_i' m_i' j_2' m_2' | P | j_i m_i j_2 m_2 \rangle . \qquad (61)$$

$$\sigma^{K}_{j_2}(\mathrm{iiii}) = \sum_{m_i m_2} [(2j_i+1)(2j_2+1)]^{-1} \langle j_i m_i j_2 m_2 | P^2 | j_i m_i j_2 m_2 \rangle$$

$$- \sum_{\substack{m_i m_i' n_i n_i' Q \\ m_2 m_2' j_2}} \sum \sum (-1)^{\underset{i}{\underline{n_2}}-\underset{i}{\underline{n_2'}}} (2j_2+1)^{-1} \begin{pmatrix} j_i & j_i & K \\ m_i & -n_i & -Q \end{pmatrix} \begin{pmatrix} j_i & j_i & K \\ m_i' & -n_i' & -Q \end{pmatrix}$$

$$\times \langle j_i n_i j_2 m_2 | P | j_i n_i' j_2' m_2' \rangle \langle j_i m_i' j_2' m_2' | P | j_i m_i j_2 m_2 \rangle \; . \qquad (62)$$

Some general discussion of these results is warranted. First, there are in general two types of terms in each cross section. One is independent of K and corresponds to the "outer" terms of Anderson, the other depends on K and corresponds to the "middle" terms of Anderson. The outer terms are identically zero for $\sigma^{K}_{j_2}(\mathrm{i'i'ii})$. The general form of the cross sections given here is in agreement with the equations given by Ben-Reuven(138) and Coombe, Snider and Sanctuary.(140) Their expressions are written in terms of transition (t) matrices, whereas the cross sections given here were initially in terms of scattering (T) matrices and later in terms of a P matrix. It is useful to show that the P matrix is equivalent to a 1st order perturbation approximation to the t matrix.

Let a wave function $\psi(t) = U(t,t_0)\psi(t_0)$ obey the Schrödinger equation,

$$\frac{\hbar}{i}\frac{\partial\psi(t)}{\partial t} + H'\psi(t) = 0 \quad . \tag{63}$$

Then, the equation of motion for $U(t,t_0)$ is

$$\frac{\hbar}{i}\frac{\partial U(t,t_0)}{\partial t} + H'U(t,t_0) = 0 \tag{64}$$

with initial condition $U(t_0,t_0) = 1$. This is equivalent to

$$U(t,t_0) = 1 - \frac{i}{\hbar}\int_{t_0}^{t} H'(t')U(t',t_0)dt' \ , \tag{65}$$

which has the iterative solution,

$$U^{(0)}(t,t_0) = 1,$$

$$U^{(1)}(t,t_0) = 1 - \frac{i}{h}\int_{t_0}^{t} H'(t')dt' \ , \tag{66}$$

$$\vdots$$

or,

$$U(t,t_0) = \sum_{n=0}^{\infty} U^{(n)}(t,t_0) \ , \tag{67}$$

where

$$U^{(n)} = \left(\frac{i}{\hbar}\right)^n \int_{t_0}^{t} \int_{t_0}^{t'} \cdots \int_{t_0}^{t^{(n-1)}} H'(t')H'(t'')\ldots H'(t^{(n)})dt^{(n)}\ldots dt' . \tag{68}$$

Equations (67) and (68) are equivalent to

$$U(t,t_0) = P \exp[-(\frac{i}{h})\int_{t_0}^{t} H'(t')dt'] \qquad (69)$$

where here, P is the time ordering operator; <u>i.e.</u>, P orders the upper limits of integration in Equation (68). The approximations in Equation (66) may be written

$$U^{(0)} = U_o = 1$$

$$U^{(1)} = U_0 + U_1$$

$$U^{(2)} = U_0 + U_1 + U_2 \qquad (70)$$

$$\vdots$$

Similarly, with the definition $S = U(+\infty, -\infty)$,

$$S = \sum_{n=0}^{\infty} S_n = P \exp[-(\frac{i}{h}) \int_{-\infty}^{\infty} H'(t')dt'] \qquad (71)$$

with

$$S^{(0)} = S_0 = 1,$$

$$S^{(1)} = S_0 + S_1,$$

$$S^{(2)} = S_0 + S_1 + S_2, \text{ etc.} \qquad (72)$$

The matrix elements of $S^{(n)}$ are

$$\langle f|S^{(n)}|i\rangle = \delta_{fi} + (S_1)_{fi} + \ldots + (S_n)_{fi} \ . \tag{73}$$

Then, the t matrix is defined by

$$S_{fi} = \delta_{fi} - 2\pi i\delta(E_i-E_f)t_{fi} \ . \tag{74}$$

Alternatively,

$$\Pi_{fi} = -\ 2\pi i\delta(E_i-E_f)t_{fi} \tag{75}$$

where the matrix Π is related to the scattering matrix by

$$S = 1 + \Pi \ . \tag{76}$$

The delta functions in Equations (74) and (75) are merely statements that both S and t are on the energy shell; i.e., these matrices conserve energy. Upon comparison of Equation (73) with Equations (74) and (75), the following conclusions may be drawn. First, the zeroth approximation of S is irrelevant for the scattering problem. Second, the n^{th} approximation to the t matrix on the energy shell (i.e., E_i-E_f) may be obtained from $\Pi^{(n)} = S_1 + S_2 + S_3 + \ldots + S_n$ Therefore, the matrix elements of P and/or P^2 have the same interpretation as the matrix elements of t, the transition operator. For $f \neq i$ t_{fi} is the probability amplitude for the transition $f \rightarrow i$, while $(t_{ii})^2$ is proportional to the total inelastic cross section from state i. This result is a statement of the optical theorem(141) and is the reason that Equation (38) is true.

Several other points can be made concerning Equations (60)-(62).

1) The factors $[(2j_i+1)(2j_2+1)]^{-1}$ in the outer terms arise from an average over initial collisional states of both molecule and perturber.

2) In Equation (60) the only K-dependence comes from collisions that are simultaneously elastic in levels j_i and j_f. This middle term gives rise to what have been called interference or correlation effects. If this term is zero, there is no K-dependence in the $\sigma^K_{j_2}$(ifif) cross sections. More importantly, the Rydberg-Ritz principle is valid, as discussed by Fano.(87) This means that the levels j_i and j_f relax independently of each other, and that the Liouville or "line-space" (*i.e.*, the need for four indices on Λ^K) formalism is not needed.

3) It is useful to look at $\sigma^0_{j_2}$(iiii). For this case $Q = 0$. Use of Equation (36) in Equation (62) leads to a middle term of

$$-\sum_{\substack{m_i m_i' \\ m_2 m_2' j_2'}}\sum (-1)^{m_i - m_i'}[(2j_i+1)(2j_2+1)]^{-1}$$

$$\times \langle j_i m_i j_2 m_2|P|j_i m_i' j_2' m_2'\rangle\langle j_i m_i' j_2' m_2'|P|j_i m_i j_2 m_2\rangle, \qquad (77)$$

which shows by reasoning similar to that in Reference (67) that $\sigma_{j_2}^{0}$ (iiii) is proportional to the total collisional rate out of level i.

4) It is also of interest to set K = 0 in $\sigma_{j_2}^{K}$ (i'i'ii). Then, use of Equation (36) in Equation (61) gives

$$\sigma_{j_2}^{0}(\text{i'i'ii}) = -\sum_{\substack{n_i n_i' \\ m_2 m_2' j_2'}} (2j_2+1)^{-1}[(2j_i+1)(2j'+1)]^{1/2}\left(\frac{2j_i+1}{2j_i+1}\right)^{1/2}$$

$$\times\langle j_i n_i j_2 m_2|P|j_i' n_i' j_2' m_2'\rangle\langle j_i' n_i' j_2' m_2'|P|j_i n_i j_2 m_2\rangle$$

$$= \frac{-1}{(2j_i+1)(2j_2+1)}\sum_{\substack{n_i m_2 \\ n_i' j_2' m_2'}} |\langle j_i n_i j_2 m_2|P|j_i' n_i' j_2 m_2\rangle|^2 \qquad (78)$$

This has the same form as the negative of the usual cross section for a level-to-level collisional transition.

5) The renormalization of the Liu-Marcus cross section allows a summation over Q. This in turn is the reason why the outer terms are K-independent.

C. Evaluation of the P Matrix for Multipole-Multipole Intermolecular Potentials

It remains to evaluate the matrix elements of P and P^2 and substitute the results into Equations (60)-(62).

Following TC the intermolecular potential is assumed to be expanded as

$$H_c = \sum_{\substack{k_1 k_2 \\ \lambda_1 \lambda_2}} \sum C^{k_1 k_2}_{\lambda_1 \lambda_2} Y^{k_1}_{\lambda_1}(1) Y^{k_2}_{\lambda_2}(2) \ , \tag{79}$$

where $Y^{k_1}_{\lambda_1}(1)$ is a spherical harmonic of order k_1, a function of the internal coordinates of molecule 1, and $C^{k_1 k_2}_{\lambda_1 \lambda_2}$ is a factor that depends on the intermolecular distance. The expansion (Equation 79) is valid as long as the charge distributions of the two molecules do not overlap. Therefore, it can express electrostatic, induction, and dispersion forces but not exchange forces. From TC the matrix element of P is

$$\langle j_1 m_m j_2 m_2 | P | j_1' m_1' m_2' m_2' \rangle = \sum_{\substack{k_1 k_2 \\ \lambda_1 \lambda_2}} a^{(\lambda k j)}$$

$$\times \ \langle j_1 m_1 j_2 m_2 | Y^{k_1}_{\lambda_1}(1) Y^{k_2}_{\lambda_2}(2) | j_1' m_1' j_2' m_2' \rangle$$

$$= \sum_{\substack{k_1 k_2 \\ \lambda_1 \lambda_2}} a^{(\lambda k j)} \Delta(j_1' k_1 j_1) \Delta(j_2' k_2 j_2) \langle j_1' k_1 m_1' \lambda_1 | j_1 m_1 \rangle$$

$$\times \ \langle j_2' k_2 m_2' \lambda_2 | j_2 m_2 \rangle \tag{80}$$

where $a^{(\lambda kj)}$ is a radial factor that depends on k_1 and k_2 as k, λ_1 and λ_2 as λ and j_1, j_1', j_2, and j_a' as j; it must be evaluated for each potential. $\Delta(j'kj)$ is given by

$$\Delta(j'k\,j\,) = (-1)^{j\,-j'}\left(\frac{2k+1}{4\pi}\right)^{1/2} \langle j\;k\;K\;0|j'K\,\rangle$$

$$= (-1)^{j\;-K}\left(\frac{2k+1}{4\pi}\right)^{1/2}(2j'+1)^{1/2}\begin{pmatrix} j & j' & k \\ K & -K & 0 \end{pmatrix} \quad , \quad (81)$$

where the relation

$$\langle ab\alpha\beta|c-\gamma\rangle = (-1)^{a-b-\gamma}(2c+1)^{1/2}\begin{pmatrix} a & b & c \\ \alpha & \beta & \gamma \end{pmatrix} \qquad (82)$$

has been used.

Tsao and Curnutte have evaluated $\sigma^1_{j_2}$(ifif). The other cross sections follow by analogy and are worked out in detail in Appendix D. The results are given here.

$$\sigma^K_{j_2}(\text{ifif}) = \frac{1}{32\pi^2} \sum_{\substack{j_i' j_2' k_1 k_2 \\ \lambda_1 \lambda_2}} \sum (2j_i'+1)(2j_2'+1)|a^{\lambda kj}|^2$$

$$\times \begin{pmatrix} j_i & j_i' & k_1 \\ K_i & -K_i & 0 \end{pmatrix}^2 \begin{pmatrix} j_2 & j_2' & k_2 \\ K_2 & -K_2 & 0 \end{pmatrix}^2$$

$$+ \sum_{\substack{j_f' j_2' k_1 k_2 \\ \lambda_1 \lambda_2}} \sum (2j_i'+1)(2j_2'+1)|a^{\lambda kj}|^2 \begin{pmatrix} j_f & j_f' & k_1 \\ K_f & -K_f & 0 \end{pmatrix}^2 \begin{pmatrix} j_2 & j_2 & k_2 \\ K_2 & -K_2 & 0 \end{pmatrix}^2$$

$$+ \frac{(2j_i+1)(2j_f+1)}{16\pi^2} \sum_{\substack{k_1 k_2 j_2' \\ \lambda_1 \lambda_2}} \sum (-1)^{\lambda_1+\lambda_2+k_1+K} (2j_2'+1) a(k_1 k_2 \lambda_1 \lambda_2 j)$$

$$\times \bar{a}(k_1 k_2 - \lambda_2 - \lambda_2 j') \begin{pmatrix} j_i & j_i & k_1 \\ K_i & -K_i & 0 \end{pmatrix} \begin{pmatrix} j_f & j_f & k_1 \\ K_f & -K_f & 0 \end{pmatrix} \begin{pmatrix} j_2 & j_2' & k_2 \\ K_2 & -K_2 & 0 \end{pmatrix}^2 \begin{Bmatrix} j_i & j_f & K \\ j_f & j_i & k_1 \end{Bmatrix} \tag{83}$$

$$\sigma^K_{j_2}(\text{i'i'ii}) = \frac{(2j_i+1)^{1/2}(2j_i'+1)^{3/2}}{16\pi^2} \sum_{\substack{k_1 k_2 j_2' \\ \lambda_1 \lambda_2}} \sum (-1)^{j_i - j_i' + k_1 + K + 1}$$

$$\times (2j_2'+1)|a^{\lambda kj}|^2 \begin{pmatrix} j_i & j_i' & k_1 \\ K_i & -K_i & 0 \end{pmatrix}^2 \begin{pmatrix} j_2 & j_2' & k_2 \\ K_2 & -K_2 & 0 \end{pmatrix}^2 \begin{Bmatrix} j_i & j_i & K \\ j_i' & j_i' & k_1 \end{Bmatrix}. \tag{84}$$

$$\sigma^{K}_{j_2}(\mathrm{iiii}) = \frac{1}{16\pi^2} \sum_{\substack{j_1'j_2'k_1k_2 \\ \lambda_1\lambda_2}} \sum (2j_1'+1)(2j_2'+1)|a^{\lambda kj}|^2$$

$$\times \begin{pmatrix} j_i & j_i' & k_1 \\ K_i & -K_i & 0 \end{pmatrix}^2 \begin{pmatrix} j_2 & j_2' & k_2 \\ K_2 & -K_2 & 0 \end{pmatrix}^2$$

$$+ \frac{(2j_i+1)^2}{16\pi^2} \sum_{\substack{k_1k_2\lambda_1\lambda_2 \\ j_2'}} \sum (-1)^{K+k_1+1} (2j_2'+1)|a^{\lambda kj}|^2$$

$$\times \begin{pmatrix} j_i & j_i & k_1 \\ K_i & -K_i & 0 \end{pmatrix}^2 \begin{pmatrix} j_2 & j_2' & k_2 \\ K_2 & -K_2 & 0 \end{pmatrix}^2 \begin{Bmatrix} j_i & j_i & K \\ j_i & j_i & k_1 \end{Bmatrix} . \qquad (85)$$

It is of interest to evaluate $\sigma^0_{j_2}(\mathrm{iiii})$ and $\sigma^0_{j_2}(\mathrm{i'i'ii})$. By analogy with Equation (77) and Equation (78),

$$\sigma^{0}_{j_2}(\mathrm{iiii}) = \frac{1}{16\pi^2} \sum_{\substack{j_1'j_2'k_1k_2 \\ \lambda_1\lambda_2}} \sum (2j_1'+1)(2j_2'+1)|a^{\lambda kj}|^2$$

$$\times \begin{pmatrix} j_i & j_i' & k_1 \\ K_i & -K_i & 0 \end{pmatrix}^2 \begin{pmatrix} j_2 & j_2' & k_2 \\ K_2 & -K_2 & 0 \end{pmatrix}^2$$

$$\frac{-(2j_i+1)}{16\pi^2} \sum_{\substack{k_1k_2j_2' \\ 1\ 2}} \sum (2j_2'+1)|a^{\lambda kj}|^2 \begin{pmatrix} j_i & j_i & k_1 \\ K_i & -K_i & 0 \end{pmatrix}^2 \begin{Bmatrix} j_2 & j_2' & k_2 \\ K_2 & -K_2 & 0 \end{Bmatrix}^2 \qquad (86)$$

$$\sigma^0_{j_2}(i'i'ii) = \frac{-(2j_i'+1)}{16\pi^2} \sum_{\substack{k_1k_2j_2' \\ \lambda_1\lambda_2}} \sum (2j_2'+1)|\varepsilon^{\lambda kj}|^2$$

$$\times\begin{pmatrix} j_i & j_i' & k_1 \\ K_i & -K_i & 0 \end{pmatrix}^2 \begin{pmatrix} j_2 & j_2' & k_2 \\ K_2 & -K_2 & 0 \end{pmatrix}^2 \quad . \qquad (87)$$

Equations (86) and (87) can be obtained from Equations (85) and (84), respectively, by using the relation$^{(71)}$

$$\begin{Bmatrix} j_1 & j_2 & j_3 \\ 0 & j_3 & j_2 \end{Bmatrix} = (-1)^{j_1+j_2+j_3}[(2j_2+1)(2j_3+1)]^{-1/2} \qquad (88)$$

For the K = 0 case the structure of the middle term $\sigma^0(i'i'ii)$ collapses to the structure of an outer term. This is seen by comparing Equation (87) with the first term of (86).

It should be noted that the matrix elements in Equation (80) are valid for linear molecule eigenfunctions (spherical harmonics) and for "one-ended" symmetric top eigenfunctions (proportional to rotation matrices). Proper eigenfunctions of symmetric top molecules should also be eigenfunctions of the inversion operator, which demands that they be linear combinations of the rotation matrices.

It can be easily shown that for dipole potentials, either proper or one-ended eigenfunctions give the same matrix elements. Quadrupole potentials work the same way. A discussion of these effects is relegated to Appendix F.

D. Tensor Order Dependence of the Λ^K

The motivation for studying the K-dependence of the Λ^K may be seen by examining Table I. This table gives a set of conditions - hereafter called the Karplus-Schwinger-Townes conditions - on the K-dependence of Λ^K under which the continued fraction lineshape reduces to a sum of Lorentzians. It was implied earlier that K-independence arises if there is no collisional interaction in one level. This is illustrated for $\sigma^K(ifif)$ for a structureless perturber. In this case Equation (49) is appropriate and can be rewritten as

$$\sigma^K(ifif) = 1 - \sum_{\substack{m_i m_i' \\ m_f m_f'}} \sum_Q (-1)^{m_f - m_f'} \begin{pmatrix} j_i & j_f & K \\ m_i & -m_f & -Q \end{pmatrix} \begin{pmatrix} j_i & j_f & K \\ m_i' & -m_f' & -Q \end{pmatrix}$$

$$\times \langle j_f m_f' | S^* | j_f m_f \rangle \langle j_i m_i' | S | j_i m_i \rangle \qquad (89)$$

The Kronecker deltas have been eliminated by using a sum rule over the 3-j symbols.$^{(71)}$ The technique is illustrated in Appendix D. If there is no interaction in the j_f level, $\langle j_f m_f' | S^* | j_f m_f \rangle = \delta_{m_f m_f'}$ and the second term in Equation (89) becomes

$$- \sum_{\substack{m_i m_i' \\ m_f Q}} \begin{pmatrix} j_i & j_f & K \\ m_i & -m_f & -Q \end{pmatrix} \begin{pmatrix} j_i & j_f & K \\ m_i' & -m_f & -Q \end{pmatrix} \langle j_i m_i | S | j_i m_i \rangle$$

$$= - \sum_{m_i} (2j_i+1)^{-1} \langle j_i m_i | S | j_i m_i \rangle \ . \qquad (90)$$

This is equivalent to one of the outer terms obtained previously for $\sigma^K(ifif)$. The other outer term would have been obtained if it were assumed that there was no interaction in the j_i level. The assumption $\langle j_f m_f' | S^* | j_f m_f \rangle = \delta_{m_f m_f'}$ is equivalent to setting $T_0 = 1$, (See Equation (54) and Appendix D) and it may be said that $\sigma^K(ifif)$ consists of three terms, the two outer terms, which describe how levels j_i and j_f evolve independently of each other, and the middle term, which describes the aforementioned interference effects.

It is possible to discuss the K-dependence of the cross sections in terms of various intermolecular potentials. Consider one of the products of 3-j symbols in the K-dependent middle term of $\sigma^K_{j_2}(ifif)$ in Equation (83).

If the system molecule is linear so that $K_i = K_f = 0$, the product may be written as

$$\begin{pmatrix} j_i & j_i & k_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j_f & j_f & k_1 \\ 0 & 0 & 0 \end{pmatrix} , \qquad (91)$$

which is zero if either $j_i+j_i+k_1$ or $j_f+j_f+k_1$ is odd.(71) That is, the K-dependent middle term is zero if k_1 is odd. If molecule 2 (the perturber) is linear, no definite conclusions can be reached because the middle term may be inelastic in j_2. Completely analogous arguments hold for the middle terms of Equations (84) and (85). The result for $\sigma^K(iiii)$ is the same as for $\sigma^K(ifif)$, while $\sigma^K(i'i'ii)$ is K-independent for k_1 = even.

For symmetric tops with inversion (example, NH_3) the parity of the involved levels must be taken into account. This is not explicitly indicated in the notation. The considerations are quite obvious and the results are the same as for linear molecules. For symmetric tops without inversion the situation is nebulous and no definite conclusions may be drawn. These results are summarized in Table II.

For simple potentials a more quantitative description of the K-dependence may be given. The cross section $\sigma^K(ifif)$ can be written as

$$\sigma^K(ifif) = \sigma^K(ifif)_{oi} + \sigma^K(ifif)_{of} + \sigma^K(ifif)_m \qquad (92)$$

Table II. K-Dependence of Λ^{K} for Multipole-Multipole Potentials.

R Branch ($\Delta j = \pm 1$)

Linear molecules

$\left.\begin{array}{l}\Lambda^{K}_{fifi}\\ \Lambda^{K}_{iiii}\end{array}\right\}$ no K-dependence for k_1 = odd

Λ^{K}_{iikk} no K-dependence for k_1 = even

Symmetric Tops without inversion

no definite conclusions possible except for K = 0 (reduces to linear molecule)

Q Branch ($\Delta j = 0$) (inversion levels)

results are as for linear molecules.

where the subscripts oi, of, and m denote the outer term for the i level, the outer term for the f level and the middle term, respectively. The only K-dependence is in the middle term and may be written as

$$(-1)^K \begin{Bmatrix} j_i & j_f & K \\ j_f & j_i & k_1 \end{Bmatrix} . \tag{93}$$

The major interest is in Λ^K_{ifif}. Since Λ^K is obtained by adding all σ^K for each j_2 and weighting them by a Boltzmann factor it is possible to write

$$\Lambda^K_{ifif} - \Lambda^{K-1}_{ifif} = \sum_{j_2} \sigma^K(ifif)_m - \sum_{j_2} \sigma^{K-1}(ifif)_m \tag{94}$$

where the sum over j_2 is meant also to imply weighting with a Boltzmann factor. Extraction of the K-dependent part of $\sigma^K(ifif)$ enables Equation (94) to be written as

$$\Lambda^K_{ifif} - \Lambda^{K-1}_{ifif} = \sum_{k_1} (-1)^K \begin{Bmatrix} j_i & j_f & K \\ j_f & j_i & k_1 \end{Bmatrix} F(ifk_1)$$

$$- \sum_{k_1} (-1)^{K-1} \begin{Bmatrix} j_i & j_f & K-1 \\ j_f & j_i & k_1 \end{Bmatrix} F(ifk_1) \tag{95}$$

where $F(ifk_1)$ is everything in the middle term except

$(-1)^K \begin{Bmatrix} j_i & j_f & K \\ j_f & j_i & k_1 \end{Bmatrix}$. ($F(ifk_1)$ includes $\sum\limits_{j_2}$.) For a given transition, F (ifk_1) has the same numerical value in each of the two terms on the right side of Equation (95) so that

$$\Lambda^K_{ifif} - \Lambda^{K-1}_{ifif} = \sum_{k_1} \left[(-1)^K \begin{Bmatrix} j_i & j_f & K \\ j_f & j_i & k_1 \end{Bmatrix} - (-1)^{K-1} \begin{Bmatrix} j_i & j_f & K-1 \\ j_f & j_i & k_1 \end{Bmatrix} \right] F(ifk_1) \tag{96}$$

Let $k_1 = 1$ only. As a result of the symmetry of the 6-j symbols,

$$\begin{Bmatrix} j_i & j_f & K \\ j_f & j_i & 1 \end{Bmatrix} = \begin{Bmatrix} K & j_f & j_i \\ 1 & j_i & j_f \end{Bmatrix} \text{ and } \begin{Bmatrix} j_i & j_f & K-1 \\ j_f & j_i & 1 \end{Bmatrix} = \begin{Bmatrix} K-1 & j_f & j_i \\ 1 & j_i & j_f \end{Bmatrix}. \tag{97}$$

From Table 5 of Edmonds(142)

$$\begin{Bmatrix} a & b & c \\ 1 & c & b \end{Bmatrix} = (-1)^{a+b+c+1} \frac{2[b(b+1)+c(c+1)-a(a+1)]}{[2b(2b+1)(2b+2)(2c)(2c+1)(2c+2)]^{1/2}} \tag{98}$$

After some algebra, the square bracket in the numerator of

Equation (96) can be evaluated to give

$$\Lambda^{K}_{ifif}-\Lambda^{K-1}_{ifif} = \frac{(-1)^{j_i+j_f}(4K)}{[2j_f(2j_f+1)(2j_f+2)(2j_i)(2j_i+1)(2j_i+2)]^{1/2}}$$

$$\times\ F(if1) \qquad (99)$$

The corresponding result for Λ^{K}_{iiii} is

$$\Lambda^{K}_{iiii}-\Lambda^{K-1}_{iiii} = \frac{4K}{2j_i(2j_i+1)(2j_i+2)}\, F(ii1)\ . \qquad (100)$$

The result analogous to Equation (99) for Λ^{K}_{iikk} is too cumbersome to be of use.

A more useful result for Λ^{K}_{iikk} may be obtained by realizing that it has no outer terms. For a single given potential the following ratio may be formed.

$$\frac{\Lambda^{K}_{iiff}}{\Lambda^{K-1}_{iiff}} = \frac{-\begin{Bmatrix} j_i & j_f & k_1 \\ j_f & j_i & K \end{Bmatrix}}{\begin{Bmatrix} j_i & j_f & k_1 \\ j_f & j_i & K-1 \end{Bmatrix}}\ . \qquad (101)$$

E. Some Additional Properties of the Anderson Λ^K

In anticipation of some later results concerning the application of a sudden approximation for calculating Λ^K the sudden approximation within the Anderson theory will be discussed. Also, the P operator will be expanded in terms of irreducible tensors. This will be useful later in comparing the K-dependence of the Anderson theory with that of the sudden approximation.

E1. Expansion of the P Operator in Irreducible Tensors

The matrix elements of P can be rewritten from Equation (80) as

$$<j_1m_1j_2m_2|P|j_1'm_1'j_2'm_2'>=\sum_{\substack{k_1k_2\\ \lambda_1\lambda_2}}(-1)^{-K_1-K_2-m_1-m_2}\frac{a^{(\lambda kj)}}{4\pi}$$

$$x[(2j_1+1)(2j_1'+1)(2j_2+1)(2j_2'+1)(2k_1+1)(2k_2+1)]^{1/2}$$

$$x\begin{pmatrix} j_1 & j_1' & k_1\\ K_1 & -K_1 & 0\end{pmatrix}\begin{pmatrix} j_2 & j_2' & k_2\\ K_2 & -K_2 & 0\end{pmatrix}\begin{pmatrix} j_1 & j_1' & k_1\\ m_1 & -m_1' & -\lambda_1\end{pmatrix}\begin{pmatrix} j_2 & j_2' & k_2\\ m_2 & -m_2' & -\lambda_2\end{pmatrix}. \qquad (102)$$

Consider first the simple matrix element,

$$<j_1m_1|P|j_1'm_1'>=\sum_{k_1\lambda_1}(-1)^{-K_1-m_1}\frac{\bar{a}^{(\lambda kj)}}{(4\pi)^{1/2}}[(2j_1+1)(2j_1'+1)(2k_1+1)]^{1/2}$$

$$x\begin{pmatrix} j_1 & j_1' & k_1\\ K_1 & -K_1 & 0\end{pmatrix}\begin{pmatrix} j_1 & j_1' & k_1\\ m_1 & -m_1' & -\lambda_1\end{pmatrix}. \qquad (103)$$

If the left side of Equation (103) is expanded in irreducible tensors by using equation 18.1 of Fano and Racah,(143) *i.e.*, if,

$$<j_1m_1|P|j_1'm_1'>=\sum_{KQ}(-1)^{j_1-m_1+Q}(2K+1)^{1/2}\begin{pmatrix}j_1 & j_1' & K\\ m_1 & -m_1' & -Q\end{pmatrix}P_{j_1j_1'}(KQ)$$

(104)

Then comparison of the right hand sides of Equation (103) and Equation (104) shows that they are equal if K is identified with k_1, Q with λ_1 and if

$$P_{j_1j_1'}(KQ)=(-1)^{-j_1+K_1-Q}\,\bar{a}(\lambda kj)\left[\frac{(2j_1+1)(2j_1'+1)(2k_1+1)}{4\pi\ (2K+1)}\right]^{1/2}$$

$$\times\begin{pmatrix}j_1 & j_1' & k_1\\ K_1 & -K_1 & 0\end{pmatrix}\quad . \qquad (105)$$

Here, $P_{j_1j_1'}(KQ)$ is independent of m_1 and m_1' as it should be.

Upon returning to Equation (102) and applying Equation (104) twice, it is found that

$$<j_1m_1j_2m_2|P|j_1'm_1'j_2'm_2'>=\sum_{KQ}\ \sum_{LR}(-1)^{j_1+j_2-m_1-m_2+Q+R}$$

$$\times\ [(2K+1)(2L+1)]^{1/2}\begin{pmatrix}j_1 & j_1' & K\\ m_1 & -m_1' & -Q\end{pmatrix}\begin{pmatrix}j_2 & j_2' & L\\ m_2 & -m_2 & -R\end{pmatrix}P_{j_1j_1'}(KQ)P_{j_2j_2'}(LR),$$

(106)

where

$$P_{j_1j_1'}(KQ)\ P_{j_2j_2'}(LR) = (-1)^{-j_1+j_2+K_1+K_2-Q-R}\ \frac{a^{(\lambda kj)}}{4\pi}$$

$$\times\left(\frac{(2j_1+1)(2j_1')(2j_2+1)(2j_2'+1)(2k_1+1)(2k_2+1)}{(2K+1)(2L+1)}\right)^{1/2}$$

$$\times\begin{pmatrix} j_1 & j_1' & K \\ K_1 & -K_1 & 0 \end{pmatrix}\begin{pmatrix} j_2 & j_2' & L \\ K_2 & -K_2 & 0 \end{pmatrix} \qquad (107)$$

The conclusion to be drawn from the above is that expanding the matrix elements of P into a multipole potential is equivalent to expanding the matrix elements of P into irreducible tensors.

E.2. Sudden Approximations in Anderson Theory

Some interesting sum rules may be derived from Anderson theory if the sudden approximation(136,137) is made. This approximation consists of assuming that the $a^{\lambda kj}$ factors are independent of j or the internal energy. A more detailed discussion of the sudden approximation is presented in Chapter IV. To establish notation it is useful to consider

$$\sigma^{K}_{j_2}(\mathrm{ifif})_{oi} = \frac{1}{32\pi^2} \sum_{\substack{j_i'j_2'k_1k_2 \\ \lambda_1\lambda_2}}\sum (2j_i'+1)(2j_a'+1)|a^{\lambda kj}|^2$$

$$\times \begin{pmatrix} j_i & j_i' & k_1 \\ K_i & -K_i & 0 \end{pmatrix}^2 \begin{pmatrix} j_2 & j_2' & k_2 \\ K_2 & -K_2 & 0 \end{pmatrix}^2 \tag{108}$$

$$= \frac{1}{32\pi^2} \sum_{\substack{j_i'j_2'k_1k_2 \\ 1\ 2}}\sum G(ii'22'k_1k_2)Q(\lambda kj) \tag{109}$$

where $Q(\lambda kj) = |a^{\lambda kj}|^2$. If $k_1 = 0$,

$$G(ii'22'0k_2) = (2j_i'+1)(2j_2'+1)\delta_{j_ij_i'}(2j_i+1)^{-1} \begin{pmatrix} j_2 & j_2' & k_2 \\ K_2 & -K_2 & 0 \end{pmatrix}^2$$

$$= \delta_{j_ij_i'}(2j_2'+1) \begin{pmatrix} j_2 & j_2' & k_2 \\ K_2 & -K_2 & 0 \end{pmatrix}^2 \tag{110}$$

Similarly,

$$G(ii'22'00) = \delta_{j_ij_i'}\delta_{j_2j_2'} \tag{111}$$

The last two equations simply state that if k_1 or k_2 are zero (i.e., an isotropic potential), inelastic collisions are not possible.

The middle terms of $\sigma^K(ifif)$ may be written

$$\sigma^K(ifif)_m = \frac{1}{16\pi^2} \sum_{\substack{k_1k_2j_2' \\ \lambda_1\lambda_2}} \sum G(if22'k_1k_2K)Q(\lambda kj) \tag{112}$$

where the definitions of G and Q are obvious upon comparison with Equation (83). For isotropic potentials

$$G(if22'00K) = (-1)^K(2j_i+1)(2j_f+1)(2j_2'+1)$$

$$\begin{pmatrix} j_i & j_i & 0 \\ K_i & -K_i & 0 \end{pmatrix}\begin{pmatrix} j_f & j_f & 0 \\ K_f & -K_f & 0 \end{pmatrix}\begin{pmatrix} j_2 & j_2' & 0 \\ K_2 & -K_2 & 0 \end{pmatrix}^2 \begin{Bmatrix} j_i & j_f & K \\ j_f & j_i & 0 \end{Bmatrix}$$

$$= (-1)^{K_i-K_f}\delta_{j_2j_2'} \; . \tag{113}$$

That is, the monopole (isotropic) potentials have no K-dependence. This is true even if $k_2 \neq 0$, i.e.,

$$G(if22'0k_2K) = (-1)^{K+j_i+j_f-K_i-K_f}[(2j_i+1)(2j_f+1)]^{1/2}$$

$$\times\; (-1)^{j_i+j_f-K}[(2j_i+1)(2j_f+1)]^{-1/2}(2j_2'+1)$$

$$\times \begin{pmatrix} j_2 & j_2' & k_2 \\ K_2 & -K_2 & 0 \end{pmatrix}^2 = (-1)^{-K_i-K_f}(2j_2'+1)\begin{pmatrix} j_2 & j_2' & k_2 \\ K_2 & -K_2 & 0 \end{pmatrix} \tag{114}$$

Exactly analogous analyses hold for $\sigma^K(i'i'ii)$ and $\sigma^K(iiii)$.

For $\sigma^K(i'i'ii)$ an interesting sum rule may be derived. Writing

$$\sigma^K(i'i'ii) = \frac{-1}{16\pi^2} \sum_{\substack{k_1 k_2 j_2' \\ \lambda_1 \lambda_2}} \sum G(i'i22'k_1k_2K)Q(\lambda kj) \qquad (115)$$

(compare to Equation (84)) allows G to be written for $K = 0$ as

$$G(i'i22'k_1k_20) = (2j_i'+1)(2j_2'+1)\begin{pmatrix} j_i' & j_i & k_1 \\ K_i & -K_i & 0 \end{pmatrix}^2 \begin{pmatrix} j_2 & j_2' & k_2 \\ K_2 & -K_2 & 0 \end{pmatrix}^2 . \qquad (116)$$

Also,

$$G(0i'22'k_1k_2K) = (-1)^{-j_i'-k_1+K}(2j_i'+1)^{3/2}(2j_2'+1)$$

$$\times \begin{pmatrix} 0 & j_i' & k_1 \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} j_2 & j_2' & k_2 \\ K_2 & -K_2 & 0 \end{pmatrix}^2 \begin{Bmatrix} j_i' & 0 & k_1 \\ 0 & j_i' & K \end{Bmatrix}$$

$$= (2j_2'+1)(2j_i'+1)^{1/2} \begin{pmatrix} j_2 & j_2' & k_2 \\ K_2 & -K_2 & 0 \end{pmatrix}^2 \delta_{K0}\delta_{j_i'k_1} . \qquad (117)$$

Equation (117) allows $\sigma^K(i'i'00)$ to be written as

$$\sigma^K(i'i'00) = \frac{-1}{16\pi^2} \sum_{\substack{k_2 j'_2 \\ \lambda_1\lambda_2}} \sum (2j'_2+1)(2j'_i+1)^{1/2}$$

$$\times \begin{pmatrix} j_2 & j'_2 & k_2 \\ K_2 & -K_2 & 0 \end{pmatrix}^2 \quad Q(\lambda kj)\,\delta_{K0}\,\delta_{k_1 j'_1} \tag{118}$$

Therefore,

$$\sigma^K(i'i'ii) = \sum_{k_1} (-1)^{j_i - j'_i - k_1 + K} (2j'_i+1)(2j_i+1)^{1/2}$$

$$\times \begin{pmatrix} j_i & j'_i & k_1 \\ K_i & -K_i & 0 \end{pmatrix}^2 \begin{pmatrix} j'_i & j_i & k_1 \\ j_i & j'_i & K \end{pmatrix} \sigma^K(i'i'00) \tag{119}$$

$$= \frac{-1}{16\pi^2} (-1)^{j_i+K} (2k_1+1)(2j_i+1)^{1/2} \begin{pmatrix} j_i & k_1 & k_1 \\ K_i & -K_i & 0 \end{pmatrix}^2 \begin{Bmatrix} k_1 & j_i & k_1 \\ j_i & k_1 & K \end{Bmatrix}$$

$$\times\ \sigma^0(i'i'00) \quad . \tag{120}$$

This is an interesting result because it gives a $\sigma^K(i'i'ii)$ cross section in terms of a $\sigma^K(i'i'00)$ cross section. Setting K = 0 gives

$$\sigma^0(i'i'ii) = -\sum_{k_1} (2j_i'+1)^{3/2}(2j_i+1)^{1/2}\begin{pmatrix} j_i & j_i' & k_1 \\ K_i & -K_i & 0 \end{pmatrix}^2$$

$$\times\ \sigma^0(i'i'00) \tag{121}$$

Use of the above relations is valid only when $Q(\lambda kj)$ is independent of j. This is the case in the sudden approximation. In the Anderson theory Equation (121) is of limited utility because $\sigma^0(i'i'00)$ cannot be calculated for $j_i' > 2$ (assuming potentials up to quadrupole).

An analysis similar to the above can be carried out for $\sigma^K(iiii)_m$. Defining the G function as

$$G(i22'k_1k_2K) = (-1)^{k_1+K}(2j_i+1)^2(2j_2'+1)\begin{Bmatrix} j_i & j_i & k_1 \\ j_i & j_i & K \end{Bmatrix}$$

$$\times \begin{pmatrix} j_i & j_i & k_1 \\ K_i & -K_i & 0 \end{pmatrix}^2 \begin{pmatrix} j_2 & j_2' & k_2 \\ K_2 & -K_2 & 0 \end{pmatrix}^2 \tag{122}$$

gives

$$G(022'k_1k_2K) = (2j_2'+1)\begin{pmatrix} j_2 & j_2' & k_2 \\ K_2 & -K_2 & 0 \end{pmatrix}^2 \delta_{k_1 0}\delta_{K0}\ . \tag{123}$$

Therefore,

$$\sigma^K(iiii)_m = \frac{-1}{16\pi^2} \sum_{k_1} (-1)^{k_1+K} (2j_2+1)^2 \begin{pmatrix} j_i & j_i & k_1 \\ K_i & -K_i & 0 \end{pmatrix}^2$$

$$\times \begin{Bmatrix} j_i & j_i & k_1 \\ j_i & j_i & K \end{Bmatrix} \sigma^K(0000)_m$$

$$= \frac{-1}{16\pi^2}(2j_i+1)^2 \begin{pmatrix} j_i & j_i & 0 \\ K_i & -K_i & 0 \end{pmatrix}^2 \begin{Bmatrix} j_i & j_i & 0 \\ j_i & j_i & 0 \end{Bmatrix} \sigma^0(0000)_m$$

$$= \frac{-1}{16\pi^2} \sigma^0(0000)_m \qquad (124)$$

and $\sigma^K(iiii)$ becomes K-independent in a sudden approximation. The analogous result for $\sigma^K(ifif)_m$ is

$$\sigma^K(ifif)_m = \frac{1}{16\pi^2} \sigma^K(ofof)_m(-1)^{j_f-K_i} \qquad (125)$$

and does not appear to be useful.

The sudden approximation allows simplification of the expressions given earlier for the Λ^K. If the perturber molecule is treated with the sudden approximation, the sums over j_2', m_2' and m_2 may be carried out analytically. Writing $\sigma^K(ifif)$ as

$$\sigma^K(ifif) = 1 - \Sigma\Sigma\,(-1)^{m_i - m_i'}(2j_2+1)^{-1}\begin{pmatrix} j_f & j_i & K \\ m_f & -m_f & Q \end{pmatrix}\begin{pmatrix} j_f & j_i & K \\ m_f' & -m_f' & -Q \end{pmatrix}$$

$$\times \langle j_f m_f j_2 m_2 | T^{-1} | j_f m_f' j_2' m_2' \rangle \langle j_i m_i' j_2' m_2' | T | j_i m_i j_2 m_2 \rangle \tag{126}$$

and using the relations$^{(71)}$

$$\sum_{j_2' m_2'} Y_{j_2 m_2}(\underset{\sim}{r}')Y_{j_2' m_2'}(\underset{\sim}{r}) = \delta(\underset{\sim}{r} - \underset{\sim}{r}') \tag{127}$$

and

$$(2j_2+1)^{-1} \sum_{m_2} Y_{j_2 m_2}(\underset{\sim}{r})Y_{j_2 m_2}(\underset{\sim}{r}) = \frac{1}{4\pi} \tag{128}$$

allows (126) to be written as

$$\sigma^K(ifif) = 1 - \sum_{\substack{m_i m_i' Q \\ m_f m_f'}}\Sigma\,(-1)^{m_i - m_i'}\,\frac{1}{4\pi}\begin{pmatrix} j_f & j_i & K \\ m_f & -m_i & -Q \end{pmatrix}\begin{pmatrix} j_f & j_i & K \\ m_f' & -m_i' & -Q \end{pmatrix}$$

$$\times\ \langle j_f m_f | T^{-1} | j_f m_f' \rangle \langle j_i m_i' | T | j_i m_i \rangle\ . \tag{129}$$

Analogous results clearly hold for the other cross sections. The above results are valid only in the sudden approximation, _i.e._, when the T operators do not depend on j_2. The results for the cross sections in the sudden approximation are given below. They are the analogs of

Equations (83) - (85).

$$\sigma^K(ifif) = \frac{1}{32\pi} \sum_{\substack{j_i' k_1 \lambda_1 \\ k_2 \lambda_2}} (2j_i'+1)|a^{\lambda kj}|^2 \begin{pmatrix} j_i & j_i' & k_1 \\ K_i & -K_i & 0 \end{pmatrix}^2$$

$$+ \frac{(2j_i+1)(2j_f+1)}{16\pi^2} \sum_{\substack{k_1 k_2 \\ \lambda_1 \lambda_2}} (-1)^{k_1+\lambda_1+\lambda_2+K} a(k_1 k_2 \lambda_1 \lambda_2 j)$$

$$x \quad a(k_1 k_2 -\lambda_1 -\lambda_2 j) \begin{pmatrix} j_i & j_i & k_1 \\ K_i & -K_i & 0 \end{pmatrix} \begin{pmatrix} j_f & j_f & k_1 \\ K_f & -K_f & 0 \end{pmatrix} \begin{Bmatrix} j_i & j_f & K \\ j_f & j_i & k_1 \end{Bmatrix} \tag{130}$$

$$\sigma^K(i'i'ii) = \frac{(2j_i+1)^{1/2}(2j_i'+1)^{3/2}}{16\pi^2} \sum_{\substack{k_1 k_2 \\ \lambda_1 \lambda_2}}$$

$$x \ (-1)^{j_i - j_i' + k_1 + K + 1} |a^{\lambda kj}|^2$$

$$x \begin{pmatrix} j_i & j_i' & k_1 \\ K_i & -K_i & 0 \end{pmatrix}^2 \begin{Bmatrix} j_i & j_i' & k_1 \\ j_i' & j_i & K \end{Bmatrix} \tag{131}$$

$$\sigma^K(iiii) = \frac{1}{16\pi} \sum_{\substack{k_1 k_2, \\ \lambda_1 \lambda_2 j_i'}} \sum (-1)^{k_1+K+1} |a^{\lambda k j}|^2$$

$$\times \begin{pmatrix} j_i & j_i & k_1 \\ K_i & -K_i & 0 \end{pmatrix}^2 \begin{Bmatrix} j_i & j_i & k_1 \\ j_i & j_i & K \end{Bmatrix} \qquad (132)$$

The a factors are the same as before except that now they are evaluated by neglecting the energy spacing between the rotational levels of molecule 2. Calculation of the a factors will be discussed in section F of this chapter.

The derivations in Equations (126)-(128) and the results in Equations (130)-(132) are also valid if one-ended symmetric top eigenfunctions are used. This will be shown in Chapter IV where the sudden approximation is discussed in much greater detail.

F. Numerical Results for OCS and NH_3 Systems

The theory developed in the previous sections of this chapter is applied here to the J = 2 ← 1 transition in OCS and the (J,K) = (3,3) inversion transition in NH_3. Before presenting the results the basic problem will be restated.

Most previous analyses of power-broadened microwave lineshapes have assumed that the lineshape is a sum of

Lorentzians, one for each m-component pair. This is equivalent to assuming that the m-component pairs are not collisionally coupled. Fitting an experimental lineshape to this model allows extraction of a parameter denoted $(T_1/T_2)_0$. If the model is valid, $(T_1/T_2)_0$ should be very close to the true T_1/T_2. To test this model, the Anderson-like expansions derived here are used to calculate T_1/T_2 and all of the other relaxation parameters that occur in the more exact continued fraction lineshape expression. These parameters are used to compute a lineshape which is then fit to a sum of Lorentzians(54) to obtain the parameter $(T_1/T_2)_0$. If this $(T_1/T_2)_0$ and the calculated T_1/T_2 are equal, the model is presumed valid. Alternatively, the better the fit of the lineshape the more valid the model.

There are two secondary purposes for calculating the relaxation parameters. Knowledge of all the Λ^K allows the calculation by means of Equation (27), of the $\langle\langle j_m j_m|\Lambda|j'm'j'm'\rangle\rangle$, which have an intuitive physical interpretation. In addition, knowledge of the Λ^K allows the calculation of 4-level effects, which have been discussed in Reference 55. A summary of these effects will be given shortly.

Before discussing the results of the calculations it is worthwhile to discuss the method of calculation. The calculation may be split into four parts, the calculation of the $a^{\lambda kj}$ factors (the resonance function in the parlance of TC), the calculation of the angular momentum coupling coefficients, the determination of the hard sphere cutoff and the calculation of the thermal average. The resonance functions are given explicitly in TC in terms of modified Bessel functions of the 2nd kind.(144) TC also provides a table of these functions. Rather than interpolate from this table, explicit calculation of the functions is included in the program. To do this, the Bessel functions are expanded in terms of Tchebycheff polynomials.(145) In practice, a Tchebycheff expansion is used to calculate the modified Bessel functions of the first kind, which are in turn used in another Tchebycheff expansion to calculate the desired modified Bessel functions of the second kind. The resonance functions are given in detail in Appendix H.

Some of the angular momentum coefficients were calculated by using the general formula for 3-j coefficients given in Reference 71. Other coefficients were calculated by means of special case formulas.(71)

Determination of the hard sphere cutoff has been discussed in many places.(86,93,94,98) In the present calculations separate cutoffs for each tensor order are determined. That is, the cutoffs for Λ^1_{ifif} and Λ^3_{ifif} are calculated separately. The plural "cutoffs" is used because a new cutoff is calculated for every perturber rotational level. A problem arises in the calculation of $\Lambda^{K}_{i'i'ii}$. For K = 0, the relation

$$\Lambda^{0}_{iiii} + \sum_{i'\neq i} \Lambda^{0}_{i'i'ii} \equiv 0 \qquad (133)$$

must hold. The only way to insure that this condition holds is to use for given perturber rotational levels, the same cutoffs for $\Lambda^{0}_{i'i'ii}$ as for Λ^{0}_{iiii}. The cutoffs are calculated by a simple bisection iteration procedure. Therefore, the relaxation parameters obtained in this process depend on the upper and lower limits declared for the bisection. The limits used in the calculations reported here are 0 Å and 20 Å. The uncertainty in the relaxation coefficients due to the choice of limits is estimated to be about ±2 Å^2. Further details of the hard sphere cutoff calculation are presented in Appendix G.

The thermal average consists of an average over the relative velocity distribution and a weighting by a Boltzmann factor for each perturber rotational level. The calculations presented here ignore the velocity average. The assumption is made that at a given temperature all collisions occur at the mean relative velocity. This assumption should be quite good. Calculations of Λ^{1}_{ifif} by Cattani(92) show a 2% difference for OCS between including the average and ignoring it. The difference for the (J,K) = (3,3) inversion line of NH_3 is about 8%. The

Boltzmann factors used are those given for high temperature limits by Townes and Schawlow.(146)

Table III gives the assumed parameters used in the OCS calculation. The minimum value of 4.13 Å for σ (hard sphere) is the gas kinetic diameter. If the calculated hard sphere cutoff is less than 4.13 Å, the program defaults to the value 4.13 Å and uses this as the hard sphere cutoff.

Table IV is a tabulation of many of the relaxation parameters for OCS. These parameters incorporate all multipole-multipole potentials through quadrupole. The only parameters showing marked K-dependence are the $\Lambda^{K}_{i'i'ii}$, which also show a large dependence on rotational level. Condition (133) is satisfied very closely, as can be seen by considering, for example, Λ^{0}_{2222}.

$$\Lambda^{0}_{2222} + \Lambda^{0}_{4422} + \Lambda^{0}_{3322} + \Lambda^{0}_{1122} + \Lambda^{0}_{0022} = 2.84 \text{ Å}^2,$$

a relatively small difference from zero. This is a result of the cutoff procedure described earlier. It is also worth noting that Equation (133) requires $\Lambda^{0}_{i'i'ii}$ to be negative for $i' \neq i$. Finally,

$$\frac{5}{3}\,\Lambda^{0}_{1122} = -172.2 \approx -176.0 \qquad (134)$$

where $5/3 = (2j_f+1)/(2j_i+1)$.

Table III. Assumed Parameters for OCS Calculations.

μ_D = 0.71519 D

Q = 1.0×10^{-26} esu cm^2

B_0 = 6081.49 MHz

T = 300K

$\bar{\nu}_{12}$ = 4.6×10^{4} cm/s

j (perturber) $\leq$ 90

σ (hard sphere) $\geq$ 4.13 Å

Table IV. Relaxation Parameters for OCS.[a]

iijj	K=0	K=2	K=4	K=6	K=8
0000	263.7				
1111	263.2	263.6			
2222	264.9	265.2	265.1		
3333	266.7	267.1	267.5	267.0	
4444	269.8	269.9	270.1	270.3	269.9
5555	273.0				
1100	-259.6				
2211	-176.0	-103.6			
3322	-155.6	-131.5	- 66.5		
4433	-150.0	-138.8	-104.4	- 49.5	
5544	-152.0				
0011	- 86.0				
1122	-103.3	- 60.8			
2233	-110.5	- 91.5	- 46.1		
3344	-115.8	-104.5	- 78.6	- 37.2	
4455	-119.2				
2200	- 4.4				
3311	- 2.7	- 1.3			
4422	- 2.3	- 1.7	- 0.6		
5533	- 2.1	- 1.8	- 1.1	- 0.4	
6644	- 2.0				

[a] The entries in this table are Λ^{K}_{iijj} in Å^2.

Table V gives the relaxation parameters necessary to calculate the power-broadened lineshape of the $J = 2 \leftarrow 1$ transition of OCS. Comparison of Tables I and V shows that the first three Karplus-Schwinger-Townes conditions as well satisfied, while the fourth, <u>i.e.</u>, all Λ^{K}_{iiff} and Λ^{K}_{ffii} equal zero, is not satisfied at all. The value of T_1^{-1} calculated from the equation(55)

$$T_1 = \frac{(2j+3)b_0^{ff}+(2j+1)b_0^{ii}+[(2j+1)(2j+3)]^{1/2}(b_0^{if}+b_0^{fi})}{4(j+1)(b_0^{ii}b_0^{ff}-b_0^{if}b_0^{fi})} \tag{135}$$

is very large resulting in a T_1/T_2 which is apparently quite small. The calculated T_1^{-1} was obtained by assuming the total population of the two levels is constant. This is referred to as a 2-level approximation. The T_2^{-1} is about 10 $\mathring{A}^2$ larger than the experimental values and consistent with previous calculations.(98) In equation (135) the following definitions have been used:

$$\begin{aligned} b_K^{ff} &= \Lambda^K_{ffff}, \\ b_K^{if} &= \Lambda^K_{iiff}, \\ b_K^{fi} &= \Lambda^K_{ffii} \, . \end{aligned} \tag{136}$$

The large value of T_1^{-1} in the 2-level approximation suggests that 4-level effects may be important. These

Table V. Relaxation Parameters for the OCS $J = 2 \leftarrow 1$ Transition: 2-Level Approximation.

K	a_K (Å^2)
1	264.3 = T_2^{-1}
3	264.5

K	b_K^{11}	b_K^{22}	b_K^{12}	b_K^{21} (Å^2)
0	263.2	264.9	-176.0	-103.3
2	263.6	265.2	-103.6	- 60.8
4		265.1		

$T_1^{-1} = 399.4$ Å^2

$T_1/T_2 = 0.662$

are discussed in detail in Appendix A of Reference 55. To summarize, it is noted that if the assumption of constant total population of the two levels is relaxed, the equations

$$\dot{n}_K^i = Y_i - \sum_k b_K^{ik} \, \Delta n_K^k$$

$$\dot{n}_K^f = Y_f - \sum_k b_K^{fk} \, \Delta n_K^k$$

$$\dot{n}_K^j = - \sum_k b_K^{jk} \, \Delta n_K^k \tag{137}$$

are valid. In these equations Y_i and Y_f are terms proportional to the radiation field, $n_K^j = \rho_{jj}(K)$, and Δn_K^j is the difference between n_K^j and its equilibrium value. Equations (137) have a steady-state solution of the form

$$\begin{pmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{pmatrix} \begin{pmatrix} \Delta N_1 \\ \Delta N_2 \end{pmatrix} = \begin{pmatrix} Y_1 \\ 0 \end{pmatrix} \tag{138}$$

in which the B_{ij}, ΔN_i and Y_i are appropriate submatrices of the quantities in Equation (137). Inversion of Equation (138) yields

$$Y_1 = B_{11}' \, \Delta N_1$$

in which

$$B_{11}' = B_{11} - B_{12} \, B_{22}^{-1} \, B_{21} \tag{139}$$

If all Δn_K^j for $j \neq i$ or f are assumed to be negligible (the two-level approximation), then $Y_1 = B_{11}\Delta N_1$. Therefore, the effect of including collisional transfer to levels other than those connected by radiation is to replace B_{11} by a new matrix B'_{11} which is to be used to calculate T_1^{-1}. The matrices are shown in Table VI. The resulting relaxation coefficients for the $J = 2 \leftarrow 1$ transition are given in Table VII. The new value of T_1^{-1} is much smaller than the previous case and gives a T_1/T_2 which, while still small, is much closer to the expected value. The 4-level effects are most pronounced in b_0^{11} and b_0^{22} with smaller changes in b_2^{22} and b_4^{22}. All other relaxation parameters are virtually unchanged.

The relaxation parameters have been used to calculate a lineshape according to Equation (53) of Reference 55. (This equation is the precise result described by Equation (34) of the present work.) The calculated lineshape was then numerically power-averaged to represent the power-averaging that occurs in a microwave waveguide sample cell.(54) The experimental parameters assumed for the lineshape calculation are given in Table III. The resulting lineshapes were fit to a sum of Lorentzians and the parameter $(T_1/T_2)_0$ obtained. The results for three different pressures are given in Table VIII. The calculated $(T_1/T_2)_0$ agrees fairly well with the experimental $(T_1/T_2)_0$ only when 4-level effects are included. The values of

Table VI. Matrices of b Coefficients for Calculation of 4-Level Corrections for the OCS $J = 2 \leftarrow 1$ Transition ($J \leq 4$; $K = 0$).[a]

	(1)[b]	(2)	(0)	(3)	(4)
	263.2	-176.0	-86.0	- 2.7	0
	-103.3	264.9	- 0.9	-155.6	- 2.3
$B =$	-259.6	- 4.4	263.7	0	0
	- 1.1	-110.5	0	266.7	-150.0
	0	- 1.2	0	-115.8	269.8
	(1)	(2)			
$B'_{11} =$	178.5	-178.9			
	-105.0	178.8			

[a] Values are in Å^2.

[b] The numbers in parentheses above the matrix are the J values for the corresponding columns. The rows are in the same order.

Table VII. Relaxation Parameters for the OCS $J = 2 \leftarrow 1$ Transition: 4-Level Effects, $J \leq 4$.

K	a_K ($\mathring{A}^2$)
1	$264.3 = T_2^{-1}$
3	264.5

K	b_K^{11}	b_K^{22}	b_K^{12}	b_K^{21}	($\mathring{A}^2$)
0	178.5	178.8	-178.9	-105.0	
2	263.6	208.2	-104.2	- 61.1	
		252.1			

$T_1^{-1} = 318.4\ \mathring{A}^2$

$T_1/T_2 = 0.830$

Table VIII. Summary of T_1/T_2 Calculations for the OCS $J = 2 \leftarrow 1$ Transition.

	w/o 4-Level Effects		With 4-Level Effects	
p/mtorr	T_1/T_2	$(T_1/T_2)_0^a$	T_1/T_2	$(T_1/T_2)_0^a$
60	0.662	0.732	0.830	0.930
80	0.662	0.731	0.830	0.926
100	0.662	0.729	0.830	0.925

$(T_1/T_2)_0$ (exp) = 1.04 ± 0.10

[a] Experimental parameters assumed for the determination of $(T_1/T_2)_0$ from the theoretical lineshapes are power, 10.00 Mw; attenuation, 0.800.

$(T_1/T_2)_0$ for the three pressures are approximately 12% larger than the calculated T_1/T_2 and approximately 11% smaller than the experimental value of $(T_1/T_2)_0$. For OCS it appears that T_1/T_2 should be estimated to be about 10% less than the experimentally derived $(T_1/T_2)_0$.

Finally, the relaxation parameters for the $J = 2 \leftarrow 1$ transition that are not required for the calculation of the plane-polarized radiation lineshape have been calculated. These are Λ^K_{1212} for even K and Λ^K_{1122} and Λ^K_{2211} for odd K. This allows relaxation parameters between two different m states to be obtained by means of Equation (27). The results are shown in Table IX and indicate that elastic reorienting collisions are negligible. The small contribution to these collisions is due to quadrupole interactions. Therefore, the various m-components are not coupled by this mechanism. They are, however, coupled by $\Delta j = 1$, $\Delta m = \pm 1$ collisions. This is shown in the 1122 and 2211 entries.

Table X gives the assumed parameters used in the NH_3 calculations. Only the dipole-dipole interaction potential was used. Contributions due to quadrupole potentials are negligible. Table XI gives all relaxation parameters for the $(J,K) = (3,3)$ inversion line of NH_3. The Λ^K_{iiii} and Λ^K_{ifif} have no K-dependence (for a dipole potential, this was shown earlier) while the $\Lambda^K_{i'i'ii}$ have K-dependence given as the ratio of two 6-j symbols. As for OCS, the Karplus-

Table IX. State to State Relaxation Parameters for the OCS $J = 2 \leftarrow 1$ Transition.[a]

(2121)[a]

m/m'	-1	0	1
0	91.6	105.8	91.6
1	79.4	91.6	79.4

(1111)

m/m'	-1	0	1
0	-0.1	263.5	-0.1
1	-0.3	-0.1	263.7

(2222)

m/m'	-2	-1	0	1	2
0	-0.1	0.0	265.1	0.0	-0.1
1	0.0	-0.1	0.0	265.1	-0.1
2	0.0	0.0	-0.1	-0.1	265.1

(1122)

m/m'	-2	-1	0	1	2
0	-0.1	-39.9	-53.2	-39.9	-0.1
1		-0.1	-13.4	-40.0	-79.8

(2211)

m/m'	-1	0	1
0	-22.8	-90.7	-22.8
1	-0.3	-68.1	-68.0
2	-0.3	-0.2	-135.8

[a] The values tabulated are $\langle\langle jmjm|\Lambda|j'm'j'm'\rangle\rangle$ where j and j' are the numbers in parentheses. All values are in Å^2.

Table X. Assumed Parameters for NH_3 Calculations.

$\mu_D = 1.468$ D

$Q = -1.0 \times 10^{-26}$ esu cm^2

$B_0 = 9.933$ cm^{-1}

$C_0 = 6.3$ cm^{-1}

$T = 300$ K

$\bar{v}_{12} = 8.64 \times 10^4$ cm/s

j (perturber) ≤ 15

σ (hard sphere) ≥ 4.43 Å

Table XI. Relaxation Parameters for the (J,K) = (3,3) Inversion Doublet of NH_3.[a]

${}^{K}(+-+-)$	$704.5 = T_2^{-1}$,	all K
${}^{K}(++++)$	704.4, all K	
${}^{0}(++--)$	-657.3	
${}^{1}(++--)$	-602.5	
${}^{2}(++--)$	-493.0	
${}^{3}(++--)$	-328.6	
${}^{4}(++--)$	-109.5	
${}^{5}(++--)$	164.3	
${}^{6}(++--)$	493.0	
$T_1^{-1} = 1361.7$		
$T_1/T_2 = 0.517$	2-level approximation	

[a] The values tabulated are $\Lambda^{K}_{ifi'f'}$ where ifi'f' are given in parentheses as the parity of the level. The left superscript is K (the tensor order). All values are in Å^2.

Schwinger-Townes conditions are only partially satisfied.

The inversion doublets of NH_3 are usually considered to be a very good approximation to a 2-level system. To test this approximation, 4-level effects have been included in a calculation of T_1^{-1}. The B_{11} and B'_{11} matrices are given in Table XII. The new value of T_1/T_2 of 0.582 is consistent with the view of the inversion doublet as a 2-level system. T_1 was calculated from the formula given by Schwendeman(55)

$$T_1^{-1} = \frac{2(b_K^{ii}b_K^{ff}-b_K^{if}b_K^{fi})}{(b_K^{ff}+b_K^{ii}+b_K^{if}+b_K^{fi})} \quad . \qquad (140)$$

A lineshape has been calculated by power-averaging the relaxation parameters. $(T_1/T_2)_0$ obtained from fitting the theoretical lineshape to a sum of Lorentzians is given in Table XIII for three different pressures. As for OCS, $(T_1/T_2)_0$ is a fair approximation to $(T_1/T_2)_0$(exp).

Relaxation parameters between two m states have been obtained from Equation (27). The results are given in Table XIV. As expected, the elastic reorienting collisions do not couple different m-component pairs. This is a direct result of using only dipole potentials.

Table XII. Matrices of b Coefficients for the NH_3 (J,K) = (3,3) Transition for Calculation of 4-Level Corrections: $J \leq 5$, K = 0.

	(33+)[a]	(33-)	(43+)	(43-)	(53+)	(53-)
	704.4	-657.3	0.0	- 47.0	0.0	0.0
	-657.3	704.4	- 47.0	0.0	0.0	0.0
B=	0.0	- 48.8	596.7	-489.0	0.0	- 59.0
	- 48.8	0.0	-489.0	596.7	- 59.0	0.0
	0.0	0.0	0.0	77.5	522.5	-388.3
	0.0	0.0	- 77.5	0.0	-388.3	522.5

	(33+)	(33-)
B'_{11}=	687.8	-671.8
	-671.8	687.8

T_1/T_2 = .518

---

[a] The values in parentheses are J, K, parity for the corresponding columns. The order of the rows is the same.

Table XIII. Summary of T_1/T_2 Calculations for the NH_3 $(J,K) = (3,3)$ Transition.

	w/o 4-level Effects		With 4-level Effects	
ρ/mtorr	(T_1/T_2)	$(T_1/T_2)_0^a$	(T_1/T_2)	$(T_1/T_2)_0$
20	.517	.567	.518	.568
30	.517	.550	.518	.552
40	.517	.545	.518	.546

$(T_1/T_2)_0(\text{exp}) = 0.71 \pm 0.07$

[a] Experimental parameters assumed for the determination of $(T_1/T_2)_0$ from the theoretical lineshapes are power = 15 MW, attenuation = 0.8.

Table XIV. State to State Relaxation Parameters for the NH_3 (J,K) = (3,3) Transition: Dipole-Dipole Potential.[a]

(+-+-)

m/m'	0	1	2	3
0	704.5	0	0	0
1	0	704.5	0	0
2	0	0	704.5	0
3	0	0	0	704.5

(++++)

m/m'	0	1	2	3
0	704.4	0	0	0
1	0	704.4	0	0
2	0	0	704.4	0
3	0	0	0	704.4

(++--)[b]

m/m'	0	1	2	3
0	.02	-328.66	- .01	.01
1	-328.66	- 54.77	-273.86	- 0.0
2	- .01	-273.86	-219.08	-164.33
3	- .01	- 0.0	-164.33	-492.96

(3344)

m/m'	0	1	2	3	4
0	- 24.63	- 15.38	.02	0.0	.01
1	- 9.22	- 23.07	- 23.07	0.01	0.0
2	.01	- 4.61	- 18.45	- 32.30	0.0
3	.01	0.0	- 1.54	- 10.77	- 43.07

[a] The values tabulated are $\langle\langle jmjm|\Lambda|j'm'j'm'\rangle\rangle$. For the first three tables j=j'. All values are in Å^2.

[b] The (m,m') = (0,-1) value which is not given here is -328.7. All other values not given are 0.0.

G. Numerical Results for OCS and NH_3 Systems Within the Anderson Sudden Approximation

The sudden approximation consists of neglecting internal state energy differences. When molecule 2 is treated in the sudden approximation the cross sections of interest are given by Equations (130) - (132). These equations are independent of molecule 2 quantum numbers. Therefore, weighting by a Boltzmann factor is not necessary. In addition only one hard sphere cutoff needs to be calculated for each cross section.

Tables XV and XVI summarize the results of T_1 and T_2 calculations for OCS and NH_3 in the sudden approximation for dipole-dipole potentials. The K-dependence of the relaxation parameters $\Lambda^K_{ifi'f'}$ is the same as the previous results, and values for these parameters are not given separately.

Calculated values of T_1^{-1} and T_2^{-1} are larger than those calculated by the normal Anderson theory. This is expected from the properties of the resonance function for large values of internal state frequencies. It is interesting to note that the values of T_1/T_2 are all very close to the T_1/T_2 values calculated from the Anderson theory. The only exception to this behavior occurs in NH_3 for the case that the internal energy differences in the system molecule are accounted for but those in the perturber molecule are not. That is, the sudden

Table XV. Values of T_1 and T_2 for the OCS $J = 2 \leftarrow 1$ Transition Calculated by Anderson Sudden Approximation and Dipole-Dipole Potential.[a]

SUDDEN			
SYSTEM	PERTURBER		
NO	YES	$1/T_2 = 634.0$ $T_1/T_2 = 0.659$	$1/T_1 = 961.9$
YES	YES	$1/T_2 = 614.0$ $T_1/T_2 = 0.659$	$1/T_1 = 934.6$

[a] Values of $1/T_2$ and $1/T_1$ are in $\mathring{A}^2$.

Table XVI. Values of T_1 and T_2 for the NH_3 (J,K) = (3,3) Transition Calculated by Anderson Sudden Approximation and Dipole-Dipole Potential.[a]

SUDDEN			
SYSTEM	PERTURBER		
NO	YES	$1/T_2 = 1216.5$	$1/T_1 = 2427.2$
		$T_1/T_2 = 0.501$	
YES	YES	$1/T_2 = 1401.5$	$1/T_1 = 2448.9$
		$T_1/T_2 = 0.572.$	

[a] Values of $1/T_2$ and $1/T_1$ are in Å^2.

approximation is invoked for the perturber molecule but not for the system molecule. In this case the calculated T_1/T_2 is smaller than that calculated from the full Anderson theory.

A plausible explanation of this fact is as follows. The small value of T_1/T_2 implies that T_1 is too small or equivalently that $1/T_1$ is too big. The latter quantity can be made too large if the cross sections for $J + 1 \leftarrow J$ collisional transitions are too big. In NH_3 the $J + 1 \leftarrow J$ energy gap is very large. All of this implies that the Anderson theory becomes poor at large energy gaps. The only quantity in the cross sections that depends on internal state energy differences is the resonance function which is calculated assuming a linear intermolecular trajectory. When the internal energy gap is large a large deviation from a straight line path is expected. Therefore, the above behavior of T_1/T_2 values may be taken as evidence that linear trajectories are not valid for collisional transitions exhibiting large internal energy changes.

CHAPTER III

A SIMPLE MODEL FOR THE RELAXATION COEFFICIENTS

In the previous chapter a formalism based on Anderson theory was developed to calculate multipole relaxation coefficients using multipole-multipole potentials. In this chapter a simple model will be developed which replicates the form of the Anderson theory results. The model utilizes the iterative solution to the equation of motion of the density matrix in the interaction representation. This is a common starting point for treating relaxation in nuclear magnetic resonance. The density matrix and interaction potential are expanded in irreducible tensors. In addition, the potential is assumed to have an exponential correlation function, a root mean square strength or amplitude, and a characteristic decay time. These quantities will be defined later. The resulting equations exhibit the same form as the Anderson theory results. The dependence on tensor order is identical, while the resonance function and its associated numerical factors are represented in the form of a product of a root mean square amplitude and a decay time. This latter characteristic arises from the fact that the details of the collision are in effect averaged out by the introduction of a correlation function for the potential.

The following summary of the iterative solution to the equation of motion of the density matrix and its application to relaxation in magnetic resonance is taken from Abragam,(147) Weissbluth,(148) and Redfield.(149) Since only collisions are considered here (and not the interaction of the system with a radiation field), the Hamiltonian can be written as

$$H = H_0 + V \tag{141}$$

where V is the intermolecular potential and H_0 supports the internal rotational states of the molecule. The Hamiltonian H_0 may also describe a static external field. In the interaction representation the density matrix may be written

$$\rho_I(t) = e^{iH_0t/\hbar}\rho(t)e^{-iH_0t/\hbar} \quad , \tag{142}$$

where the subscript I denotes the interaction representation. The equation of motion for $\rho_I(t)$ is

$$i\hbar \frac{\partial \rho_I(t)}{\partial t} = [V_I(t), \rho_I(t)] \quad , \tag{143}$$

which has the formal solution

$$\rho_I(t) = \rho_I(t_0) - \frac{i}{\hbar} \int_{t_0}^{t} dt[V_I(t_1),\rho_I(t_1)] \ . \tag{144}$$

Equation (144) can be iterated to give

$$\rho_I(t) = \rho_I(t_0) - \frac{i}{\hbar} \int_{t_0}^{t} dt[V_I(t_1)\rho_I(t_0)]$$

$$+ \left(\frac{-i}{\hbar}\right)^2 \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 [V_I(t_1),[V_I(t_2),\rho_I(t_0)]] + \ldots \tag{145}$$

This can in turn be differentiated, resulting in

$$\frac{d\rho_I(t)}{\partial t} = \frac{-i}{\hbar}[V_I(t),\rho_I(t_0)] + \left(\frac{-i}{\hbar}\right)^2 \int_{t_0}^{t} dt'[V_I(t),[V_I(t'),$$

$$\rho_I(t_0)]] + \ldots \tag{146}$$

Following the usual argument of nuclear magnetic resonance relaxation, it will be assumed that the ensemble average of $V_I(t)$ is zero, so that the first term in Equation (146) is zero. If this assumption is not valid, the first term merely produces a frequency shift, which may be either ignored or incorporated into a redefinition of H_0 and H_1.

Hereafter, all quantities are assumed to be in the interaction representation and the subscript I will be dropped. By assuming that the first term in Equation (146) is zero and by setting $\hbar = 1$, Equation (146) can be rewritten as

$$\frac{d\rho}{\partial t} = -[\int_0^\infty [V(t)[V(t-\tau),\rho(t)]]d\tau]_{av} \tag{147}$$

Three assumptions have been made in going from Equation (146) to Equation (147). These are: 1) it is possible to neglect correlation between $V(t)$ and $\rho(t_0)$; 2) it is then permissible to replace $\rho(t_0)$ by $\rho(t)$; and 3) it is possible to extend the upper limit of integration from t to ∞. In addition all quantities are ensemble averaged in Equation (147). All of these assumptions have been discussed by Abragam.(147)

Abragam(147) and Redfield(149) have shown that Equation (147) is equivalent to

$$\frac{d\rho}{dt} = -\sum_{q_1 q_4} [v_{q_4}^{k_4},[v_{q_1}^{k_1},\rho]]k_{q_4 q_1}(0) . \tag{148}$$

where

$$k_{qq'}(\omega) = \int_0^\infty \langle V_q^k(t)V_{q'}^k(t-\tau)\rangle e^{i\omega\tau}d\tau . \tag{149}$$

In going from Equation (147) to Equations (148) and (149) it has been assumed that the intermolecular potential has multipole character k and can be written

$$V(t) = \sum_q (-1)^q V^k_{-q}(t) v^k_q \quad . \tag{150}$$

In Equation (150), $V^k_{-q}(t)$ is an expansion coefficient and v^k_q is a unit tensor of order k and component q. Any effort to obtain an absolute numerical rate of change of the density matrix requires evaluation of Equation (149) with subsequent substitution into Equation (148).

The goal of the present work is to obtain a simple model capable of giving easily calculated numerical results and tensor order dependence of the state multipoles. To accomplish this the correlation function(150)

$$<V^k_q(t) V^k_{q'}(t-\tau)> = \frac{\delta_{q'-q}(-1)^q v^2 e^{-\tau/\tau_c}}{(2k+1)} \tag{151}$$

is introduced for the potential expansion coefficients. In Equation (151) τ_c is a correlation time and v is an average intermolecular interaction strength. With this correlation function $k_{qq'}(\omega)$ may be evaluated as

$$k_{qq'}(\omega) = \left(\frac{\delta_{q-q'}(-1)^q v^2}{(2k+1)}\right) \int_0^\infty e^{(i\omega - 1/\tau_c)\tau} d\tau$$

$$= \left(\frac{\delta_{q-q'}(-1)^q v^2}{(2k+1}\right) \frac{\tau_c}{1-i\omega\tau_c} \quad .$$

Obviously,

$$k_{qq'}(0) = \left(\frac{\delta_{q-q'}(-1)^{q}v^{2}}{2k+1}\right)\tau_c \quad . \tag{152}$$

The next step is to transform Equation (148) into a spherical tensor basis. The potential has already been expanded in such a basis. The analogue of Equation (150) for the density matrix is

$$\rho = \sum_{kq} (-1)^{q}\rho^{k}_{-q}v^{k}_{q} \ , \tag{153}$$

where, as before, v^{k}_{q} is a unit tensor of order k. Therefore, double commutators containing unit tensors of the form $[v^{k_4}_{q_4},[v^{k_1}_{q_1}, v^{k_2}_{q_2}]]$ must be evaluated. This can be accomplished by using the following relation, given by Judd:(151)

$$\begin{aligned}
[v^{k_1}_{q_1}(\ell\ell'),v^{k_2}_{q_2}(\ell''\ell''')] = {} & \sum_{k_3q_3} (-1)^{2\ell'''+\ell''-\ell'-q_3} \\
& \times [(2k_1+1)(2k_2+1)(2k_3+1)]^{1/2} \begin{pmatrix} k_1 & k_2 & k_3 \\ q_1 & q_2 & -q_3 \end{pmatrix} \\
& \times [\delta_{\ell'\ell''}(-1)^{k_1+k_2+k_3+\ell+\ell'+\ell''+\ell'''} \begin{Bmatrix} k_1 & k_2 & k_3 \\ \ell''' & \ell & \ell'' \end{Bmatrix} \\
& \times v^{k_3}_{q_3}(\ell\ell''')-\delta_{\ell\ell'''} \begin{Bmatrix} k_1 & k_2 & k_3 \\ \ell'' & \ell' & \ell \end{Bmatrix} v^{k_3}_{q_3}(\ell''\ell')] \ .
\end{aligned} \tag{154}$$

To understand the meaning of the ℓ' it is useful to consider the v^k_q in greater detail. The unit tensors v^k_q can be written

$$v^k_q = \sum_{mm'} (-1)^{j_f-m} (2k+1)^{1/2} \begin{pmatrix} j_f & j_i & k \\ m & -m' & -q \end{pmatrix} |j_f m\rangle\langle j_i m'| \quad . \qquad (155)$$

The v^k_q in Equation (155) will hereafter be denoted $v^k_q(j_f j_i)$ where the labels j_f and j_i are taken from the ket and the bra, respectively, occurring in Equation (155). Therefore, the ℓ' in Equation (154) are taken as rotational angular momentum quantum numbers. Use of Equation (154) twice allows the double commutator with all ℓ's the same, for example, $[v^{k_4}_{q_4}(\ell\ell)[v^{k_1}_{q_1}(\ell\ell),v^{k_2}_{q_2}(\ell\ell)]]$ to be evaluated as

$$[v^{k_4}_{q_4}(\ell\ell)[v^{k_1}_{q_1}(\ell\ell),v^{k_2}_{q_2}(\ell\ell)]] = \sum_{\substack{k_3 k_5 \\ q_3 q_5}} \sum (-1)^{-q_3-q_5}(2k_3+1)$$

$$\times\ [(2k_1+1)(2k_2+1)(2k_4+1)(2k_5+1)]^{1/2}[(-1)^{k_1+k_2+k_3}-1]$$

$$\times\ [(-1)^{k_3+k_4+k_5}-1] \begin{pmatrix} k_1 & k_2 & k_3 \\ q_1 & q_2 & -q_3 \end{pmatrix} \begin{pmatrix} k_4 & k_3 & k_5 \\ q_4 & q_3 & -q_5 \end{pmatrix} \begin{Bmatrix} k_1 & k_2 & k_3 \\ \ell & \ell & \ell \end{Bmatrix}$$

$$\times \begin{Bmatrix} k_4 & k_3 & k_5 \\ \ell & \ell & \ell \end{Bmatrix} v^{k_5}_{q_5}(\ell\ell) \quad . \qquad (156)$$

Equations (152) and (156) may be substituted into Equation (148), the right hand side of which becomes

$$\sum_{\substack{k_3k_5q_1q_3\\q_4q_5}}\sum\sum \delta_{-q_1q_4}(-1)^{-q_4}\frac{v^2\tau_c}{(2k_1+1)}(-1)^{-q_3-q_5}(2k_3+1)$$

$$\times\ [(2k_1+1)(2k_2+1)(2k_4+1)(2k_5+1)]^{1/2}[(-1)^{k_1+k_2+k_3}-1]$$

$$\times \begin{pmatrix} k_1 & k_2 & k_3 \\ q_1 & q_2 & -q_3 \end{pmatrix}\begin{pmatrix} k_4 & k_3 & k_5 \\ q_4 & q_3 & -q_5 \end{pmatrix}\begin{Bmatrix} k_1 & k_2 & k_3 \\ \ell & \ell & \ell \end{Bmatrix}\begin{Bmatrix} k_4 & k_5 & k_3 \\ \ell & \ell & \ell \end{Bmatrix} v^{k_5}_{q_5}(\ell\ell)$$

(157)

$$= \sum_{\substack{k_3k_5q\\q_3q_5}}\sum (-1)^{q-q_3-q_5}\, v^2\tau_c(2k_3+1)[(2k_2+1)(2k_5+1]^{1/2}$$

$$\times\ [(-1)^{k+k_2+k_3}-1][(-1)^{k_3+k+k_5}-1]\begin{pmatrix} k & k_2 & k_3 \\ q & q_2 & -q_3 \end{pmatrix}\begin{pmatrix} k & k_5 & k_3 \\ q & q_5 & -q_3 \end{pmatrix}$$

$$\times \begin{Bmatrix} k & k_2 & k_3 \\ \ell & \ell & \ell \end{Bmatrix}\begin{Bmatrix} k & k_5 & k_3 \\ \ell & \ell & \ell \end{Bmatrix} v^{k_5}_{q_5}(\ell\ell) \quad . \qquad (158)$$

In going from Equation (157) to Equation (158) the subscript on q_1 has been dropped. Also, recalling that the tensors $v^{k_4}_{q_4}$ and $v^{k_1}_{q_1}$ in Equation (156) both come from the same intermolecular potential, k_1 has been set equal to

k_4, $k_1 = k_4 = k$. This is consistent with Equations (150) and (151), in which it was assumed that the potential had a single multipole character. The two 3-j symbols demand that $q_2 = q_5$ and $-q_2 = q - q_3$, from which $(-1)^{-q-q_3-q_5}$ $= (-1)^{-2q_2}$. The q's are always integers here so that $(-1)^{-2q_2}$ is always positive. Therefore, expression (158) can be written as

$$\sum_{\substack{k_3 k_5 \\ q\ q_3}} \sum v^2 \tau_c (2k_3+1)[(2k_2+1)(2k_5+1)]^{1/2}[(-1)^{k+k_2+k_3}-1]$$

$$\times [(-1)^{k+k_3+k_5}-1] \begin{pmatrix} k & k_2 & k_3 \\ q & q_2-q_3 \end{pmatrix} \begin{pmatrix} k & k_5 & k_3 \\ q & q_2-q_3 \end{pmatrix} \begin{Bmatrix} k & k_2 & k_3 \\ \ell & \ell & \ell \end{Bmatrix}$$

$$\times \begin{matrix} k & k_5 & k_3 \\ \ell & \ell & \ell \end{matrix} \quad V^{k_5}_{q_2}(\ell\ell) \quad . \tag{159}$$

The sums over q and q_3 may be performed by using Equation (C2). The result is to eliminate the two 3-j symbols and the factor $[(2k_2+1)(2k_5+1)]^{1/2}$. Also, the product of the two square brackets is equal to $2[1-(-1)^{k+k_2+k_3}]$. Expression (159) then becomes

$$\sum_{k_3} 2v^2 \tau_c (2k_3+1)[1-(-1)^{k+k_2+k_2}] \begin{Bmatrix} k & k_2 & k_3 \\ \ell & \ell & \ell \end{Bmatrix} \begin{Bmatrix} k & k_2 & k_3 \\ \ell & \ell & \ell \end{Bmatrix} V^{k_2}_{q_2}(\ell\ell). \tag{160}$$

Use of the sum rules(71)

$$\sum_{k} (2k+1)(2f+1) \begin{Bmatrix} a & b & k \\ c & d & f \end{Bmatrix} \begin{Bmatrix} a & b & k \\ c & d & g \end{Bmatrix} = \delta_{fg} \qquad (161)$$

and

$$\sum_{k} (-1)^{f+g+k}(2k+1) \begin{Bmatrix} a & b & k \\ c & d & f \end{Bmatrix} \begin{Bmatrix} a & b & k \\ d & c & g \end{Bmatrix} = \begin{Bmatrix} a & d & f \\ b & c & g \end{Bmatrix} \qquad (162)$$

allows expression (20) to be reduced to

$$2v^2\tau_c\left[\frac{1}{(2\ell+1)} - (-1)^{k+k_2} \begin{Bmatrix} k & \ell & \ell \\ k_2 & \ell & \ell \end{Bmatrix} \right]v_{q_2}^{k_2}(\ell\ell) . \qquad (163)$$

It is useful to recall that ℓ represents a rotational angular momentum quantum number, k is the multipole order of the intermolecular potential V, and k_2 is the tensor order of one of the multipoles in the expansion of ρ, Equation (153).

The expression in (163) followed from the double commutator given just before Equation (156). If the same process is repeated for all of the needed double commutators for the case of all ℓ's the same, and the expansion for ρ in Equation (153) is used, Equation (148) becomes

$$\frac{d}{dt}\left[\sum_{k_2'q_2'}(-1)^{q_2'}\rho^{k_2'}_{-q_2'}\, v^{k_2'}_{q_2'}(\ell\ell)\right] = \sum_{k_2q_2} 2v^2\tau_c\left[\frac{1}{2\ell+1} - (-1)^{k+k_2}\right.$$

$$\times\left\{\begin{matrix} k & \ell & \ell \\ k_2 & \ell & \ell \end{matrix}\right\} v^{k_2}_{q_2}(\ell\ell)(-1)^{q_2}\rho^{k_2}_{-q_2} \qquad (164)$$

The linear independence of the v^k_q then allows corresponding terms in the sums to be equated. This leads to

$$\frac{d}{dt}\rho^{k_2}_{-q_2}(\ell\ell) = 2v^2\tau_c\left[\frac{1}{2\ell+1} - (-1)^{k+k_2}\left\{\begin{matrix} k & \ell & \ell \\ k_2 & \ell & \ell \end{matrix}\right\}\right]\rho^{k_2}_{-q_2} , \qquad (165)$$

where the $\ell\ell$ dependence of the expansion coefficients ρ^k_{-q} has been shown explicitly. Expressions for other non-zero double commutators and their corresponding relaxation terms are as follows:

$$[v^{k_4}_{q_4}(ii),[v^{k_1}_{q_i}(ii),v^{k_2}_{q_2}(fi)]] = \Sigma\Sigma A \left\{\begin{matrix} k_1 & k_2 & k_3 \\ f & i & i \end{matrix}\right\}\left\{\begin{matrix} k_4 & k_3 & k_5 \\ f & i & i \end{matrix}\right\}$$

$$\times\, v^{k_5}_{q_5}(fi) \qquad (166)$$

$$[v^{k_4}_{q_4}(ff),[v^{k_1}_{q_1}(ff),v^{k_2}_{q_2}(fi)]] = \Sigma\Sigma A(-1)^{k_1+k_2+k_4+k_5}$$

$$\times \begin{Bmatrix} k_1 & k_2 & k_3 \\ i & f & f \end{Bmatrix} \begin{Bmatrix} k_4 & k_3 & k_5 \\ i & f & f \end{Bmatrix} v^{k_5}_{q_5}(fi) \qquad (167)$$

$$[v^{k_4}_{q_4}(fi)[v^{k_1}_{q_1}(if)v^{k_2}_{q_2}(fi)]] = + \Sigma\Sigma A(-1)^{f-i} \begin{Bmatrix} k_1 & k_2 & k_3 \\ f & f & i \end{Bmatrix}$$

$$\times \begin{Bmatrix} k_1 & k_3 & k_5 \\ f & i & f \end{Bmatrix} v^{k_5}_{q_5}(fi) + \Sigma\Sigma A(-1)^{k_1+k_2+k_4+k_5+i+f}$$

$$\times \left\{ \begin{matrix} k_1 & k_2 & k_3 \\ i & i & f \end{matrix} \right. \quad \begin{Bmatrix} k_4 & k_3 & k_5 \\ i & f & i \end{Bmatrix} v^{k_5}_{q_5}(fi) \qquad (168)$$

$$[v^{k_4}_{q_4}(ii)[v^{k_1}_{q_1}(ff)v^{k_2}_{q_2}(fi)]] = -\Sigma\Sigma A(-1)^{k_1+k_2+k_3}$$

$$\times \begin{Bmatrix} k_1 & k_2 & k_3 \\ i & f & f \end{Bmatrix} \begin{Bmatrix} k_4 & k_3 & k_5 \\ f & i & i \end{Bmatrix} v^{k_5}_{q_5}(fi) \qquad (169)$$

$$[v^{k_4}_{q_4}(ff)[v^{k_1}_{q_1}(ii)v^{k_2}_{q_2}(fi)]] = -\Sigma\Sigma A(-1)^{k_3+k_4+k_5}$$

$$\begin{Bmatrix} k_1 & k_2 & k_3 \\ f & i & i \end{Bmatrix} \begin{Bmatrix} k_4 & k_3 & k_5 \\ i & f & f \end{Bmatrix} v^{k_5}_{q_5}(fi) \qquad (170)$$

$$[v^{k_4}_{q_4}(if)[v^{k_1}_{q_1}(fi)v^{k_2}_{q_2}(ii)]] = \Sigma\Sigma A(-1)^{k_1+k_2+k_3+i+f}$$

$$\times \begin{Bmatrix} k_1 & k_2 & k_3 \\ i & f & i \end{Bmatrix}[(-1)^{k_3+k_4+k_5} \begin{Bmatrix} k_3 & k_4 & k_5 \\ i & i & f \end{Bmatrix} v^{k_5}_{q_5}(ii) -$$

$$- \begin{Bmatrix} k_3 & k_4 & k_5 \\ f & f & i \end{Bmatrix} v^{k_5}_{q_5}(ff)] \qquad (171)$$

$$[v^{k_4}_{q_4}(fi)[v^{k_1}_{q_1}(if)v^{k_2}_{q_2}(ii)]] = \Sigma\Sigma A(-1)^{i-f} \begin{Bmatrix} k_1 & k_2 & k_3 \\ i & f & i \end{Bmatrix}$$

$$\times [\begin{Bmatrix} k_3 & k_4 & k_5 \\ i & i & f \end{Bmatrix} v^{k_5}_{q_5}(ii) - (-1)^{k_3+k_4+k_5} \begin{Bmatrix} k_3 & k_4 & k_5 \\ f & f & i \end{Bmatrix} v^{k_5}_{q_5}(ff)]$$

$$(172)$$

where the summations are over k_3, k_5, q_3 and q_5 and A is given by

$$A = (2k_3+1)[(2k_1+1)(2k_2+1)(2k_4+1)(2k_5+1)]^{1/2}$$

$$\times \begin{pmatrix} k_1 & k_2 & k_3 \\ q_1 & q_2-q_3 & \end{pmatrix} \begin{pmatrix} k_4 & k_3 & k_5 \\ q_4 & q_3-q_5 & \end{pmatrix} (-1)^{-q_3-q_5} . \qquad (173)$$

By using the procedure shown in detail for the case of all ℓ's equal, Equations (166) - (172), respectively, may be shown to give rise to the following relaxation terms.

$$ii\ ii\ fi \rightarrow v^2\tau_c \frac{1}{2i+1}\, \rho^{k_2}_{-q_2}(fi) \tag{174}$$

$$ff\ ff\ fi \rightarrow v^2\tau_c \frac{1}{2f+1}\, \rho^{k_2}_{-q_2}(fi) \tag{175}$$

$$fi\ if\ fi \rightarrow -v^2\tau_c \left[\frac{(-1)^{f+i}}{2i+1} + \frac{(-1)^{i+f}}{2f+1}\right]\rho^{k_2}_{-q_2}(fi) \tag{176}$$

$$ii\ ff\ fi \rightarrow -v^2\tau_c(-1)^{i+f+k+k_2} \begin{Bmatrix} k & f & f \\ k_2 & i & i \end{Bmatrix} \rho^{k_2}_{-q_2}(fi) \tag{177}$$

$$ff\ i\text{-}\ fi \rightarrow -v^2\tau_c(-1)^{i+f+k+k_2} \begin{Bmatrix} k & f & f \\ k_2 & i & i \end{Bmatrix} \rho^{k_2}_{-q_2}(fi) \tag{178}$$

$$\begin{aligned} if\ fi\ ii \rightarrow -v^2\tau_c\Big[(-1)^{k+k_2} &\begin{Bmatrix} k & f & i \\ k_2 & i & f \end{Bmatrix} \rho^{k_2}_{-q_2}(ff) - \\ &- (-1)^{i+f} \frac{1}{2i+1}\, \rho^{k_2}_{-q_2}(ii)\Big] \end{aligned} \tag{179}$$

$$\begin{aligned} fi\ if\ ii \rightarrow -v^2\tau_c\Big[(-1)^{k+k_2} &\begin{Bmatrix} k & f & i \\ k_2 & i & f \end{Bmatrix} \rho^{k_2}_{-q_2}(ff) - \\ &- (-1)^{i+f} \frac{1}{2i+1}\, \rho^{k_2}_{-q_2}(ii)\Big] \end{aligned} \tag{180}$$

$$\text{ii ii ii} \rightarrow -2v^2\tau_c[(-1)^{k+k_2}\begin{Bmatrix} k & i & i \\ k_2 & i & i \end{Bmatrix} - \frac{1}{2i+1}]\rho^{k_2}_{-q_2}(\text{ii}) \tag{181}$$

The left hand sides of expressions (174) - (181) are a shorthand for denoting the double commutator; <u>i.e.</u>, $\ell\ell' \; \ell''\ell''' \; \ell^{iv}\ell^{v} = [v^k_q(\ell\ell'), [v^k_q(\ell''\ell'''), v^{k_2}_{q_2}(\ell^{iv}\ell^{v})]]$. Also, in Expressions (174) - (181) i and f are shorthand for $\ell = j_i$ and j_f, respectively.

Through Equations (148) and (153), Equations (174) - (178) describe the time dependence of $\rho^{k_2}_{-q_2}(\text{fi})$. Comparison with the notation of Chapter II shows that $(-1)^q\rho^k_q(\text{fi}) = \rho_{\text{fi}}(KQ)$. Equations (174) - (176) have the form of an outer term of $\sigma^K(\text{ifif})$; <u>i.e.</u>, in each case the coefficient of $\rho^{k_2}_{-q_2}(\text{fi})$ is independent of tensor order and has been averaged over the degenerate initial rotational states of the system molecule. The factor $v^2\tau_c$ corresponds to the quantity

$$\frac{1}{2}\Sigma\Sigma\frac{\langle j_1m_1j_2m_2|P^2|j_1m_1j_2m_2\rangle}{(2j_2+1)}$$

of Chapter II. Equations (179) - (181) describe the time dependence of the diagonal coefficients $\rho^{k_2}_{q_2}(\text{ii})$. With these comments, each of the equations can be given an interpretation. Equations (174) and (175) correspond to the the elastic contributions to the outer terms of $\sigma^K(\mathrm{ifif})$, while Equation (176) is the inelastic contribution to this quantity. Equations (177) and (178) correspond to the middle terms of $\sigma^K(\mathrm{ifif})$ and contain elastic contributions from levels i and f simultaneously. Because k is the multipole order of the potential (k_1 of the previous chapter) and k_2 is the tensor order of the relaxation (K of Chapter II), it is seen that Equations (177) and (178) replicate the tensor order dependence of $\sigma^K(\mathrm{ifif})$. The first term of both Equations (179) and (180) corresponds to $\sigma^K(\mathrm{i'i'ii})$, while the second term of these equations corresponds to the inelastic contributions to the outer terms of $\sigma^K(\mathrm{iiii})$. Finally, the first term of Equation (181) corresponds to the middle term of $\sigma^K(\mathrm{iiii})$, while the second term is the elastic contribution to the outer term of $\sigma^K(\mathrm{iiii})$. Again, the tensor order dependence is exactly the same as the Anderson theory results.

The quantity v^2 depends on the correlation function $<V^k_q(t)V^k_{q'}(t-\tau)>$, and therefore also on the indices ℓ'. Suppose that the above results are to be applied to the calculation of $\sigma^K(\mathrm{ifif})$ for the case of a dipole-dipole potential. The relevant equations are Equations (174) - (178). In Chapter II it was noted that matrix elements of the dipole moment operator between the same rotational levels of a linear molecule are zero; <u>i.e.</u>, $<jm|\mu|jm'>=0$.

Therefore, only Equation (176) can be non-zero. The point is that the v^2 in Equations (174), (175), (177) and (178) is zero while the v^2 in Equation (176) is nonzero. Considerations such as these must be taken into account in the determination of v^2.

CHAPTER IV

APPLICATION OF AN ENERGY SUDDEN APPROXIMATION TO THE CALCULATION OF Λ^K

A. Derivation of Equations and Numerical Results

In Chapter II the Anderson theory was extended to enable the calculation of $\Lambda^K_{f'i'fi}$. The major weakness of this theory and in general any perturbation technique that uses linear trajectories is that the scattering matrix is not unitary. This necessitates the evaluation of a hard sphere cutoff. If the use of a hard sphere cutoff is satisfactory for Λ^K_{fifi} and Λ^K_{iiii}, then its use for $\Lambda^K_{i'i'ii}$ is questionable. For Λ^K_{fifi} and Λ^K_{iiii} the cutoff essentially is that value of the impact parameter for which the probability for scattering (either elastic or inelastic) is one. In calculating $\Lambda^K_{i'i'ii}$ - individual transition probabilities - the transition probability goes to zero as the impact parameter goes to zero. This is because for small b there is a large number of possible transitions, making the probability for any one transition small. (This is just the opposite case from moderately large impact parameters where only collisions with small Δj

are likely.) This behavior is not reflected in the cutoff procedure described in Chapter II. It is difficult to incorporate such behavior because the probabilities usually do not go to zero in a simple fashion.

These problems can be avoided by using an exponential approximation to the S matrix(152,154)

$$S = \exp(2i\eta) = \sum_n (2i\eta)^n/n! \ , \tag{182}$$

where an element of the phase shift matrix η is(154)

$$\eta_{ij}(b,\phi) = \eta_0(b)\delta_{ij} - \frac{1}{2\hbar}\int_{-\infty}^{\infty} \Delta V_{ij}[v(t),\theta(t),\phi]\exp(i\omega t)dt. \tag{183}$$

The integral is taken over a classical trajectory determined by a spherically symmetric potential V_0. In Equation (183) ΔV_{ij} is the matrix element of $\Delta V = V - V_0$, where V is the full potential and V_0 is the part used to determine the trajectory, η_0 is the phase shift corresponding to V_0 and $\omega = (E_i - E_j)/\hbar$ with E_i the internal energy of state i. The z-axis is assumed to be parallel to the initial velocity. This means that the polar angle, θ, and the intermolecular distance, v, depend on time, but the azimuthal angle, ϕ, does not.

This chapter will treat only linear trajectories so that comparison with the previous Anderson theory results may be made. In this case $V_0 = 0$, $\eta_0 = 0$, and $\Delta V = V$, so that the working equation for η is

$$\eta_{ij}(b,\phi) = \frac{-1}{2\hbar}\int_{-\infty}^{\infty} e^{i\omega t} V_{ij}[r(t),\theta(t),\phi]dt. \tag{184}$$

Comparison with Chapter II shows that η_{ij} is just minus one-half the P matrix element used there. Writing out the first few terms of the expansion (182) as

$$S = 1 + 2i\eta + \frac{(2i\eta)^2}{2} + \ldots \tag{185}$$

clearly shows the relation of the current results to the Anderson theory, $S = 1 - iP + (iP)^2/2 + \ldots$

It is very difficult to evaluate the infinite sum in Equation (182) analytically. (To the best of this author's knowledge it is not possible. The phase shift may be evaluated using the WKB approximation, but this requires use of numerical techniques.) If the "sudden approximation" is invoked, the problem is simplified considerably.(133,136) The sudden limit is the limit where the molecular orientation remains fixed during the collision. That is, the rotation time is slow compared to the collision time. For an atom and a rigid linear rotor, the scattering matrix in the sudden approximation is

$$S_{j'jm'm}(b,\phi) = \langle j'm'|\exp[2i\eta(\theta_m\phi_m)]|jm\rangle \tag{186}$$

where for linear trajectories the sudden phase shift is

$$\eta(b,\phi,\theta_m,\phi_m) = \frac{-1}{2\hbar}\int_{-\infty}^{\infty} V[r(t),\theta(t),\phi,\theta_m,\phi_m]dt \ . \qquad (187)$$

The free linear rotor wavefunctions are $Y_{jm}(\theta_m,\phi_m)$, so that θ_m and ϕ_m describe the (fixed) orientation of the molecule. A comparison of Equations (184) and (187) shows that in Equation (187) the exponential has been set equal to one. This implies that the sudden approximation will be valid for small internal energy spacings. It has already been mentioned that transitions with small Δj occur at large impact parameters, where the trajectories are linear to a very good approximation. At small impact parameters collisions with large Δj are possible and the corresponding trajectories will be non-linear. Therefore, collisions for large Δj will suffer in two respects when calculated in the sudden approximation with linear trajectories. First, the assumption of linear trajectories will break down, and second, ω_{ij} becomes large and setting the exponential to one may not be valid. It will be shown later that probabilities calculated in the sudden approximation are too large.

Equation (186) is difficult to use directly because many integrals must be evaluated. However, because the factor $\exp(2i\eta)$ is a function of θ_m and ϕ_m it is possible to expand it as

$$\exp(2i\eta) = \sum_{\lambda\mu} f_{\lambda\mu}\, Y_{\lambda\mu}(\theta_m \phi_m) \qquad (188)$$

with the coefficients $f_{\lambda\mu}$ given by

$$f_{\lambda\mu} = \int_0^{\pi} \sin\theta_m d\theta_m \int_0^{2\pi} \exp[2i\eta(b,\phi,\theta_m,\phi_m)] Y^*_{\lambda\mu}(\theta_m \phi_m) d\phi_m \; . \qquad (189)$$

The S matrix results from taking matrix elements of exp(2iη); <u>i.e.</u>, matrix elements of Equation (188). If this is done,

$$\begin{aligned} S_{j'jm'm} &= \langle j'm' | \exp(2i\eta) | jm \rangle \\ &= \sum_{\lambda\mu} f_{\lambda\mu} \langle j'm' | Y_{\lambda\mu}(\theta_m,\phi_m) | jm \rangle \\ &= \sum_{\lambda\mu} (-1)^{m'} \left[\frac{(2j'+1)(2j+1)(2\ \ +1)}{4\pi}\right]^{1/2} \\ &\quad \times \begin{pmatrix} j & j' & \lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j & j' & \lambda \\ m & -m' & \mu \end{pmatrix} f_{\lambda\mu} \end{aligned} \qquad (190)$$

The last step is a standard result and was used earlier when the matrix elements of the P operator were evaluated for multipole-multipole potentials.

Cross$^{(155)}$ has used the above formulation to evaluate transition probabilities $P_{j'j}$ for dipole-dipole potentials. After integrating $P_{j'j}$ over the impact parameter, these quantities correspond to $\Lambda^0_{i'i'ii}$. (It is important to note however, that P_{jj} does not correspond to Λ^0_{iiii}; this will be discussed later.) A brief review of Cross' derivation will be given before developing the formulas for the general relaxation coefficients $\Lambda^K_{i'f'if}$.

The transition probability from state j to state j' is given by

$$P_{j'j}(b) = T^2_{j'j} = |S_{j'j} - \delta_{j'j}|^2 \; . \tag{191}$$

If the $P_{j'j}$ are averaged over the degenerate m states, the probability is

$$P_{j'j}(b) = (2j+1)^{-1} \sum_{m'm} T^2_{j'jm'm}. \tag{192}$$

By using Equations (190), (191) and (192) it is easy to show that

$$P_{j'j}(b) = \sum_{\lambda} (2j'+1) \begin{pmatrix} j & j' & \lambda \\ 0 & 0 & 0 \end{pmatrix}^2 F_\lambda(b) \; , \tag{193}$$

where

$$F_\lambda = \sum_{\mu} |(4\pi)^{-1/2} f_{\lambda\mu} - \delta_{\lambda 0}|^2. \tag{194}$$

Equation (193) is valid for a linear molecule - atom system.

It will be generalized to symmetric tops later. If Equation (193) is integrated over the impact parameter, the result is $\Lambda^{0}_{j'j'jj}$.

$$\Lambda^{0}_{j'j'jj} = 2\pi \sum_{\lambda} (2j'+1) \begin{pmatrix} j & j' & \lambda \\ 0 & 0 & 0 \end{pmatrix}^{2} \int_{0}^{\infty} F_{\lambda}(b)\,b\,db \qquad (195)$$

For a system of two linear rotors the transition probability may be written

$$P_{j_1'j_1}(b) = [(2j_1+1)(2j_2+1)]^{-1} \sum_{\substack{m_1m_1'm_2m_2' \\ j_2'}} \sum |\langle j_1'm_1'j_2'm_2'|$$

$$\times\ |\exp(2i\eta)-1|j_1m_1j_2m_2\rangle|^{2} \qquad (196)$$

where exp(2iη)-1 is just the T operator. Since only molecule 1 is observed, the internal states of molecule 2 may be summed over by using Equations (127) and (128). This gives

$$P_{j_1'j_1}(b) = \frac{1}{4\pi} \int\int (2j_1+1)^{-1} \sum_{m_1m_1'} |\langle j_1'm_1'|\exp(2i\eta)-1|j_1m_1\rangle|^{2}$$

$$\times\ d\Omega_2 \qquad (197)$$

For linear perturbers the volume element $d\Omega_2$ is $\sin\theta_2 d\theta_2 d\phi_2$.

Cross[(155)] showed that for a dipole-dipole potential, the function $F_\lambda(b)$ may be evaluated as

$$F_\lambda(b) = (\lambda+\tfrac{1}{2}) \int_0^\pi [j_\lambda(y \sin\theta) - \delta_{\lambda 0}]^2 \sin\theta_2 d\theta_2 \qquad (198)$$

where

$$y = \frac{2\mu_1\ \mu_2}{\hbar b^2 v}\ , \qquad (199)$$

and $j_\lambda(x)$ is a spherical Bessel function. It is related to the normal Bessel function by

$$j_\lambda(x) = (\frac{\pi}{2x})^{1/2}\ J_{\lambda+1/2}(x)\ . \qquad (200)$$

Finally, $\Lambda^0_{j'j'jj}$ is given as

$$\Lambda^0_{j'j'jj} = (2\pi\mu_1\mu_2/\hbar v)\sum_\lambda (2j_1'+1) \begin{pmatrix} j_1 & j_1' & \lambda \\ 0 & 0 & 0 \end{pmatrix}^2 A_\lambda, \qquad (201)$$

where

$$A_0 = \frac{\pi^2}{24}$$

$$A_\lambda = \frac{\pi^2}{4}[(2\lambda+3)(2\lambda-1)]^{-1} \qquad (\lambda \neq 0)$$

$$A_{tot} = \sum_\lambda A_\lambda = \frac{\pi^2}{8}\ . \qquad (202)$$

The derivation of Equation (201) followed that given by Cross. A corresponding equation for a general relaxation coefficient may be evaluated in the following manner. The general cross section is

$$\sigma^K(i'f'if) = \sum_{\substack{m_i m_i' m_2 m_2' \\ m_f m_f' Q j_2'}} \sum \sum (-1)^{j_f - j_f' + m_f - m_f'} (2j_2+1)^{-1}$$

$$\times \begin{pmatrix} j_i & j_f & K \\ m_i & -m_f & -Q \end{pmatrix} \begin{pmatrix} j_i' & j_f' & K \\ m_i' & -m_f' & -Q \end{pmatrix} \left[\frac{2j_i'+1}{2j_i+1}\right]^{1/2}$$

$$\times [\delta_{j_i j_i'} \delta_{j_f j_f'} \delta_{j_2 j_2'} \delta_{m_i m_i'} \delta_{m_f m_f'} \delta_{m_2 m_2'} - \langle j_f' m_f' j_2' m_2' | S^* | j_f m_f j_2 m_2 \rangle$$

$$\times \langle j_i' m_i' j_2' m_2' | S | j_i m_i j_2 m_2 \rangle] \qquad (203)$$

After the molecule 2 states have been summed over (by again using Equation (127) and (128)), (203) can be written as

$$\sigma^K(i'f'if) = \frac{1}{4\pi} \int\int \sum_{\substack{m_i m_i' \\ m_f m_f' Q}} \sum (-1)^{j_f - j_f' + m_f - m_f'} \begin{pmatrix} j_i & j_f & K \\ m_i & -m_f & -Q \end{pmatrix}$$

$$\times \begin{pmatrix} j_i' & j_f' & K \\ m_i' & -m_f' & -Q \end{pmatrix} \left[\frac{2j_i'+1}{2j_i+1}\right]^{1/2} [\delta_{j_i j_i'} \delta_{j_f j'} \delta_{m_i m_i'} \delta_{m_f m_f'} - \quad j_f' m_f' | S^* | j_f m_f$$

$$\times \langle j_i' m_i' | S | j_i m_i \rangle] d\Omega_2 \qquad (204)$$

Use of the relation

$$\delta_{j'j}\delta_{m'm} = \sum_{\lambda} (-1)^{m}[(2j+1)(2j'+1)]^{1/2}\begin{pmatrix} j & j' & \lambda \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} j & j' & \lambda \\ m & -m' & \mu \end{pmatrix}\delta_{\lambda 0} \tag{205}$$

for $\delta_{j_i j_i'}\delta_{m_i m_i'}$ and $\delta_{j_f j_f'}\delta_{m_f m_f'}$, use of Equation (190) for the matrix elements of the scattering operator, and use of Equation (D8) enables the cross section to be written as

$$\sigma^{K}(i'f'if) = \frac{-1}{4\pi} \iint \sum_{\lambda\mu} (-1)^{K+\mu+j_f-j_f'}(2j_i'+1)[(2j_f+1)(2j_f'+1)]^{1/2}$$

$$\times \begin{pmatrix} j_i & j_i' & \lambda \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} j_f & j_f' & \lambda \\ 0 & 0 & 0 \end{pmatrix}\begin{Bmatrix} j_i & j_i' & \lambda \\ j_f' & j_f & K \end{Bmatrix} [(\tfrac{1}{4\pi}f^{2}_{\lambda\mu} - \delta_{\lambda 0}]d\Omega_2 \tag{206}$$

By using Equation (206) $\sigma^{K}(i'i'ii)$ and $\Lambda^{K}_{i'i'ii}$ can be obtained as

$$\sigma^{K}(i'i'ii) = -\sum_{\lambda}(-1)^{K}(2j_i'+1)^{3/2}(2j_i+1)^{1/2}$$

$$\times \begin{pmatrix} j_i & j_i' & \lambda \\ 0 & 0 & 0 \end{pmatrix}^{2} \begin{Bmatrix} j_i & j_i' & \lambda \\ j_i' & j_i & K \end{Bmatrix} F_{\lambda} \tag{207}$$

and

$$\Lambda^{K}_{i'i'ii} = -(2\pi\mu_1\mu_2/\hbar v) \sum_{\lambda} (-1)^{K}(2j_i'+1)^{3/2}(2j_i+1)^{1/2}$$

$$\times \begin{pmatrix} j_i & j_i' & \lambda \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{Bmatrix} j_i & j_i' & \lambda \\ j_i' & j_i & K \end{Bmatrix} A_{\lambda} \; . \qquad (208)$$

The coefficients Λ^{K}_{ifif} and Λ^{K}_{iiii} cannot be written in terms of A_{λ}. This is seen by comparing Equations (206) and (198). When $\lambda = 0$, the terms in square brackets in these equations are not the same. It is shown in Appendix H that Λ^{K}_{ifif} and Λ^{K}_{iiii} can be written in a form similar to Equation (208) with A_{λ} replaced by B_{λ} where $B_{\lambda} = A_{\lambda}$ for $\lambda \neq 0$ and $B_0 = \frac{-\pi^2}{12}$.

If the system molecule is a symmetric top with one-ended symmetric top eigenfunctions, the results are almost the same as those given above. In particular, the sudden S matrix element is now

$$S_{j'jk'km'm} = \langle j'k'm' | \exp(2i\eta) | jkm \rangle$$

$$= \sum_{\lambda\mu} f_{\lambda\mu} \langle j'k'm' | Y_{\lambda\mu}(\theta_m, \phi_m) | jkm \rangle$$

$$= \sum_{\lambda\mu} (-1)^{k'+m'} \left[\frac{(2j'+1)(2j+1)(2\lambda+1)}{4\pi}\right]^{1/2}$$

$$\times \begin{pmatrix} j & j' & \lambda \\ k-k' & 0 & \end{pmatrix} \begin{pmatrix} j & j' & \lambda \\ m-m' & \mu & \end{pmatrix} f_{\lambda\mu} \; . \qquad (209)$$

In the cross section, $\delta_{j_i j_i'}\delta_{k_i k_i'}\delta_{m_i m_i'}$ is replaced by

$$\delta_{j_i j_i'}\delta_{k_i k_i'}\delta_{m_i m_i'} = \sum_{\lambda\mu} (-1)^{k_i'+m_i'}[(2j_i+1)(2j_i'+1)]^{1/2}$$

$$\times \begin{pmatrix} j_i & j_i' & \lambda \\ k_i & -k_i' & 0 \end{pmatrix}\begin{pmatrix} j_i & j_i' & \lambda \\ m_i & -m_i' & \mu \end{pmatrix}\delta_{\lambda 0} \qquad (210)$$

The angular momentum algebra is the same as that leading to Equation (206). The analogue of Equation (206) is

$$\sigma^K(i'f'if) = \frac{-1}{4\pi} \iint \sum_{\lambda\mu} (-1)^{K+\lambda+j_f-j_f'}(2j_i'+1)$$

$$\times [(2j_f+1)(2j_f'+1)]^{1/2} \begin{pmatrix} j_i & j_i' & \lambda \\ k_i & -k_i' & 0 \end{pmatrix}\begin{pmatrix} j_f & j_f' & \lambda \\ k_f & -k_f' & 0 \end{pmatrix}\begin{Bmatrix} j_i & j_i' & \lambda \\ j_f' & j_f & K \end{Bmatrix}$$

$$\times [\frac{1}{4\pi} f^2_{\lambda\mu} - \delta_{\lambda 0}]d\Omega_2 \qquad (211)$$

The same comments regarding the functions A_λ and B_λ for the coefficients Λ^K_{iiii} and Λ^K_{ifif} for the linear rotor case apply to the present case.

Proper consideration of symmetric top molecules involves the parity-adapted symmetric top eigenfunctions

$$|jkm\varepsilon> = N_\varepsilon[|jkm> + \varepsilon|\ j-km>] \qquad (212)$$

where

$$N_\varepsilon = 1 \quad \text{for } k = \varepsilon = 0$$

$$N_\varepsilon = 1/\sqrt{2} \text{ for } k > 0 \text{ and } \varepsilon = \pm 1$$

By using these functions, the scattering matrix in the sudden approximation may be written as

$$S_{j'jk'km'm\varepsilon'\varepsilon} = \langle j'k'm'\varepsilon' | S | jkm\varepsilon \rangle$$

$$= N_\varepsilon N_{\varepsilon'} (-1)^{k'+m'} \sum_{\lambda\mu} \left[\frac{(2j+1)(2j'+1)(2\lambda+1)}{4\pi}\right]^{1/2} \begin{pmatrix} j & j' & \lambda \\ m & -m' & \mu \end{pmatrix} f_{\lambda\mu}$$

$$\times \left\{ \begin{pmatrix} j & j' & \lambda \\ k & -k' & 0 \end{pmatrix} + \varepsilon' \begin{pmatrix} j & j' & \lambda \\ -k & -k' & 0 \end{pmatrix} + \varepsilon \begin{pmatrix} j & j' & \lambda \\ k & k' & 0 \end{pmatrix} + \varepsilon\varepsilon' \begin{pmatrix} j & j' & \lambda \\ -k & k' & 0 \end{pmatrix} \right\}. \qquad (218)$$

In this discussion only k = k' will be considered. In this case

$$S_{j'jk'km'm\varepsilon'\varepsilon} = N_\varepsilon N_{\varepsilon'} (-1)^{k+m'} \sum_{\lambda\mu} \left[\frac{(2j+1)(2j'+1)(2\lambda+1)}{4\pi}\right]^{1/2}$$

$$\times \begin{pmatrix} j & j' & \lambda \\ k & -k & 0 \end{pmatrix} \begin{pmatrix} j & j' & \lambda \\ m & -m' & \mu \end{pmatrix} [1 + \varepsilon\varepsilon'(-1)^{j+j'+\lambda}] f_{\lambda\mu} \qquad (214)$$

The cross section in Equation (211) becomes

$$\sigma^K(i'f'if) = \frac{-1}{4\pi} N_{\varepsilon_f} N_{\varepsilon_f'} N_{\varepsilon_i} N_{\varepsilon_i'} \iint \sum_{\lambda\mu} (-1)^{K+\lambda+j_f-j_f'}$$

$$\times\ [1+\varepsilon_f\varepsilon_f'(-1)^{j_f+j_f'+\lambda}][1+\varepsilon_i\varepsilon_i'(-1)^{j_i+j_i'+\lambda}](2j_i'+1)$$

$$\times\ [(2j_f+1)(2j'+1)]^{1/2} \begin{pmatrix} j_i & j_i' & \lambda \\ k_i & -k_i & 0 \end{pmatrix} \begin{pmatrix} j_f & j_f' & \lambda \\ k_f & -k_f & 0 \end{pmatrix} \begin{Bmatrix} j_i & j_i' & \lambda \\ j_f' & j_f & K \end{Bmatrix}$$

$$\times\ [\frac{1}{4\pi} f^2_{\lambda\mu} - \delta_{\lambda 0}]d\Omega_2 \quad . \tag{215}$$

All of the previous equations are valid for the case that molecule 2 is a symmetric top. Instead of Equations (127) and (128) the following two equations are used to sum over the internal states of molecule 2.

$$\sum_{j_2'k_2'm_2'} \frac{2j_2'+1}{8\pi^2} D^{j_2'}_{k_2'm_2'}(\alpha\beta\gamma) D^{j_2'^{*}}_{k_2'm_2'}(\alpha'\beta'\gamma') = \delta(\alpha-\alpha')$$

$$\times\ \delta(\beta-\beta')\delta(\gamma-\gamma') \tag{216}$$

$$\frac{1}{2j_2+1} \sum_{k_2m_2} \frac{2j_2+1}{8\pi^2} D^{j_2}_{k_2m_2}(\alpha\beta\gamma) D^{j_2}_{k_2m_2}(\alpha\beta\gamma) = \frac{1}{8\pi^2} \sum_{k_2} 1$$

$$= (2j_2+1)/8\pi^2 \tag{217}$$

In the application of these two equations two points must be considered. First, the factor $(4\pi)^{-1}$ in Equation (197) becomes $(8\pi^2)^{-1}$ in the present case. However, the volume element $d\Omega_2$ for a symmetric top is $d\alpha \sin\beta \, d\beta \, d\gamma$ so that after integration over α the $(4\pi)^{-1}$ factor remains. Second, it appears from Equation (217) that an additional factor of $(2j_2+1)$ will be introduced. However, since the quantity $P_{j'j}$ of Equation (196) is averaged over all degenerate states of the perturber an extra factor of $(2j_2+1)^{-1}$ should be inserted in Equation (196) when the perturber is a symmetric top. This additional factor is necessary because of the average over k_2.

The preceding analysis has been applied to the calculation of all relaxation coefficients for the $J = 2 \leftarrow 1$ transition of OCS and the $(J,K) = (3,3)$ inversion transition of NH_3. The coefficients are given in Table XVII. The assumed parameters for the calculations are the same as for the extended Anderson theory calculations and are given in Tables III and X, respectively. The values of T_1 for OCS and NH_3 were calculated from Equations (135) and (140), respectively. All of the relaxation coefficients here are larger than the corresponding quantities obtained from the modified Anderson theory of Chapter II. In addition the Λ^1_{ifif} are larger than the experimental low-power linewidth. It is expected that cross sections calculated from a sudden approximation will be larger than those calculated from a theory where the energy differences between internal states

Table XVII. Relaxation Coefficients for the J = 2 ← 1 Transition of OCS and the (J,K) = (3,3) Inversion Transition of NH_3 Calculated in the Sudden Approximation.[a]

	K						
$j_i j_f j'_i j'_f$	0	1	2	3	4	5	6
				OCS			
1111	505.2	551.1	532.7	-----	-----	-----	-----
2222	508.0	528.8	538.8	548.7	529.5	-----	-----
1122	-137.8	-106.1	- 77.6	-----	-----	-----	-----
2211	-229.6	-176.8	-129.4	-----	-----	-----	-----
1212	------	520.5	551.1	531.4	-----	-----	-----
	T_1 = 0.00146	T_2^{-1} = 520.5		T_1/T_2 = 0.7613			
				NH_3[b]			
$\underset{++++}{3333}$	1147.9	1168.0	1201.0	1235.4	1258.2	1253.8	1192.5
$\underset{++--}{3333}$	-564.1	-511.2	-410.4	-268.5	- 89.4	130.8	415.0
	T_1 = .000584	T_2^{-1} = 1168.0		T_1/T_2 = 0.6821			

---

[a] The coefficients are $\Lambda^K_{ifi'f'}$ in $\mathring{A}^2$. [b] The entries for $\underset{----}{3333}$ and $\underset{+-+-}{3333}$ are identical to the entries for $\underset{++++}{3333}$. The entries $\underset{--++}{3333}$ are the same as the entries for $\underset{++--}{3333}$.

are considered. This will be discussed later. The other major difference from the Anderson theory results is in the tensor order dependence of the cross sections. While the K-dependence of $\Lambda^K_{i'i'ii}$ is similar in both theories, the Λ^K_{ifif} and Λ^K_{iiii} show a larger variation with K in the sudden approximation. (The fact that the $3_-3_-3_-3_-$, $3_+3_+3_+3_+$ and $3_+3_-3_+3_-$ cross sections are the same may be easily demonstrated by using Equation (214).)

Table XVIII gives the B matrices obtained from four-level corrections to OCS and NH_3. Tables XX and XXII describe and compare the fits of the theoretical lineshapes to a sum of Lorentzians. The procedure is the same as that used in Chapter II. As before, the four-level effects are larger for OCS than for NH_3. However, the effects of four-level corrections for OCS are smaller than the same effects in the Anderson theory calculations. A plausible explanation of this is that because the sudden approximation neglects all internal state energy differences it effectively already treats the system as a many level one. The sudden value of 0.68 for T_1/T_2 gives rise to a $(T_1/T_2)_0$ of 0.71 which is in excellent agreement with the experimental value. If one assumes that the sudden approximation is a valid description of the collision dynamics, the value of T_1/T_2 obtained from a lineshape experiment which has been analyzed by fitting to a sum of Lorentzians would be 0.68.

Table XVIII. Matrices of b Coefficients in Sudden Approximation for Calculation of 4-Level Corrections. OCS J = 2 ← 1 Transition ($J \leq 4$; K = 0) and NH_3 (J,K) = (3,3) Inversion Doublet ($J \leq 5$; K = 0.

OCS

	(1)[a]	(2)	(0)	(3)	(4)
	505.17	-137.77	-321.47	- 23.66	- 8.89
	-229.62	507.95	- 76.54	-147.55	- 26.58
B =	-107.16	- 15.31	535.79	- 5.10	- 2.32
	- 55.20	-206.57	- 35.72	509.31	-152.68
	- 26.66	- 47.85	- 20.87	-196.30	510.03

	(1)	(2)
B'_{11}	435.37	-163.07
	-271.79	424.91

NH_3

	(33+)[b]	(33-)	(43+)	(43-)	(53+)	(53-)
	1147.9	-564.1	-170.6	- 69.8	-28.0	- 22.6
	-564.1	1147.9	- 69.8	-170.6	-22.6	- 28.0
B =	-219.3	- 89.8	1204.6	-342.4	-226.3	- 61.8
	- 89.8	-219.3	-342.4	1204.6	- 61.8	-226.3
	- 43.9	- 35.6	-276.6	- 75.5	1212.0	-238.0
	- 35.6	- 43.9	- 75.5	-276.6	-238.0	1212.0

	(33+)	(33-)
B'_{11} =	1084.72	-618.56
	-618.56	1084.72

[a] The numbers in parentheses above the matrix are the J values for the corresponding columns. The rows are in the same order.

[b] The symbols in parentheses above the matrix are J, K, parity for the corresponding columns. The rows are in the same order.

Table XIX. Relaxation Parameters in Sudden Approximation for the OCS $J = 2 \leftarrow 1$ Transition: 4-Level Effects, $J \leq 4$.

K	a_K (Å^2)
1	520.5
3	531.4

K	b_K^{11}	b_K^{22}	b_K^{12}	b_K^{21} (Å^2)
0	435.37	424.91	-163.07	-271.79
2	532.01	498.41	- 81.71	-136.17
4		518.92		

$T_1^{-1} = 644.38$

$T_1/T_2 = .8078$

Table XX. Summary of T_1/T_2 Calculations in Sudden Approximation for the OCS J = 2 ← 1 Transition.

	w/o 4-Level Effects		With 4-Level Effects	
p/mtorr	T_1/T_2	$(T_1/T_2)_0$[a]	T_1/T_2	$(T_1/T_2)_0$[a]
60	.761	.802	.808	.850
80	.761	.800	.808	.848
100	.761	.799	.808	.846

$(T_1/T_2)_0$ (exp) = 1.04 ± 0.10

[a] Experimental parameters assumed for the determination of $(T_1/T_2)_0$ from the theoretical lineshapes are power = 10.00 Mw, attenuation = 0.800.

Table XXI. State to State Relaxation Parameters in Sudden Approximation for the OCS $J = 2 \leftarrow 1$ Transition.[a]

(2121)[a]

m/m'	-1	0	1
0	184.1	212.6	184.1
1	159.4	184.1	159.4

(1111)

m/m'	-1	0	1
0	-9.2	523.5	-9.2
1	-18.4	-9.2	532.7

(2222)

m/m'	-2	-1	0	1	2
0	-7.0	3.0	527.9	-3.0	-7.0
1	-1.5	-11.2	-3 0	533.4	-9.8
2	-3.0	-1.5	-7.0	-9.8	529.2

(1122)

m/m'	-2	-1	0	1	2
0	-1.7	-52.5	-69.4	-52.5	-1.7
1	-5.1	-3.4	-18.6	-50.8	-100.0

(2211)

m/m'	-1	0	1
0	-31.0	-115.8	-31.0
1	-5.6	-87.5	-84.7
2	-8.5	-2.8	-166.6

---

[a] The values tabulated are $\langle\langle jmjm|\Lambda|j'm'j'm'\rangle\rangle$ where j and j' are the numbers in parentheses. All values are in Å^2.

Table XXII. Summary of T_1/T_2 Calculations in Sudden Approximation for the NH_3 (J,K) = (3,3) Inversion doublet.

	w/o 4-Level Effects		With 4-Level Effects	
p/mtorr	(T_1/T_2)	$(T_1/T_2)_0$[a]	(T_1/T_2)	$(T_1/T_2)_0$
20	.682	.705	.686	.720
30	.682	.705	.686	.712
40	.682	.704	.686	.709

$(T_1/T_2)_0(\text{exp}) = 0.71 \pm 0.07$

[a] Experimental parameters for the determination of $(T_1/T_2)_0$ from the theoretical lineshapes are power = 15.0 Mw, attenuation = 0.800.

Table XXIII. State to State Relaxation Parameters in Sudden Approximation for the NH$_3$ (J,K) = (3,3) Inversion Doublet.[a,b]

(+-+-)[b]

m/m'	-3	-2	-1	0	1	2	3
0	-0.7	-24.3	- 2.6	1203.1	- 2.6	- 24.3	- 0.7
1	-0.5	- 0.2	-29.6	- 2.6	1212.0	- 18.6	-12.7
2	0.0	- 0.8	- 0.2	- 24.3	- 18.6	1222.4	-30.6
3	0.0	0.0	- 0.5	- 0.7	- 12.7	- 30.6	1192.5

(++--)[c]

m/m'	-3	-2	-1	0	1	2	3
0	-2.3	- 2.3	-277.4	0.0	-277.4	- 2.3	- 2.3
1	-0.1	- 4.5	0.0	-277.4	- 48.2	-229.4	= 4.5
2	-0.1	0.0	- 4.5	- 2.3	-229.4	-185.7	-142.1
3	0.0	-00.1	- 0.1	- 2.3	- 4.5	-142.1	-415.0

[a] The values tabulated are <<jmjm|Λ|jm'jm>> where j = 3 and the parity is indicated in the parentheses. All values are in Å^2.

[b] The values for (++++) and (----) are the same as the values for (+-+-).

[c] The values for (--++) are the same as the values for (++--).

State to state relaxation parameters are given in Tables XXI and XXIII. It is interesting to note that the elements $\langle\langle jmjm|\Lambda|jm'jm'\rangle\rangle$ (where j may also denote parity for the case of NH_3) for $\Delta m \geq 1$ are all very small relative to those elements diagonal in m. This is reminiscent of the results obtained from the Anderson calculations. In the latter case the elements for $\Delta m \geq 1$ are small because the Anderson theory is a first order theory. One might expect that in an infinite order theory such as the sudden approximation the off-diagonal elements would be large. That they are small implies that the m-component pairs are not significantly coupled by collisions.

B. Application of the Sudden Approximation to Four-Level Double Resonance Experiments

The most powerful and general method of observing rotationally inelastic scattering is microwave-microwave double resonance. A brief summary of a four-level double resonance experiment in NH_3 will be presented here. Oka has published a complete review of these experiments.(15)

A four-level double resonance experiment on NH_3 is depicted schematically in Figure 1. The double arrow represents a microwave pump beam which tends to equalize the populations of the pair of inversion levels that it connects. This change in populations is transferred to

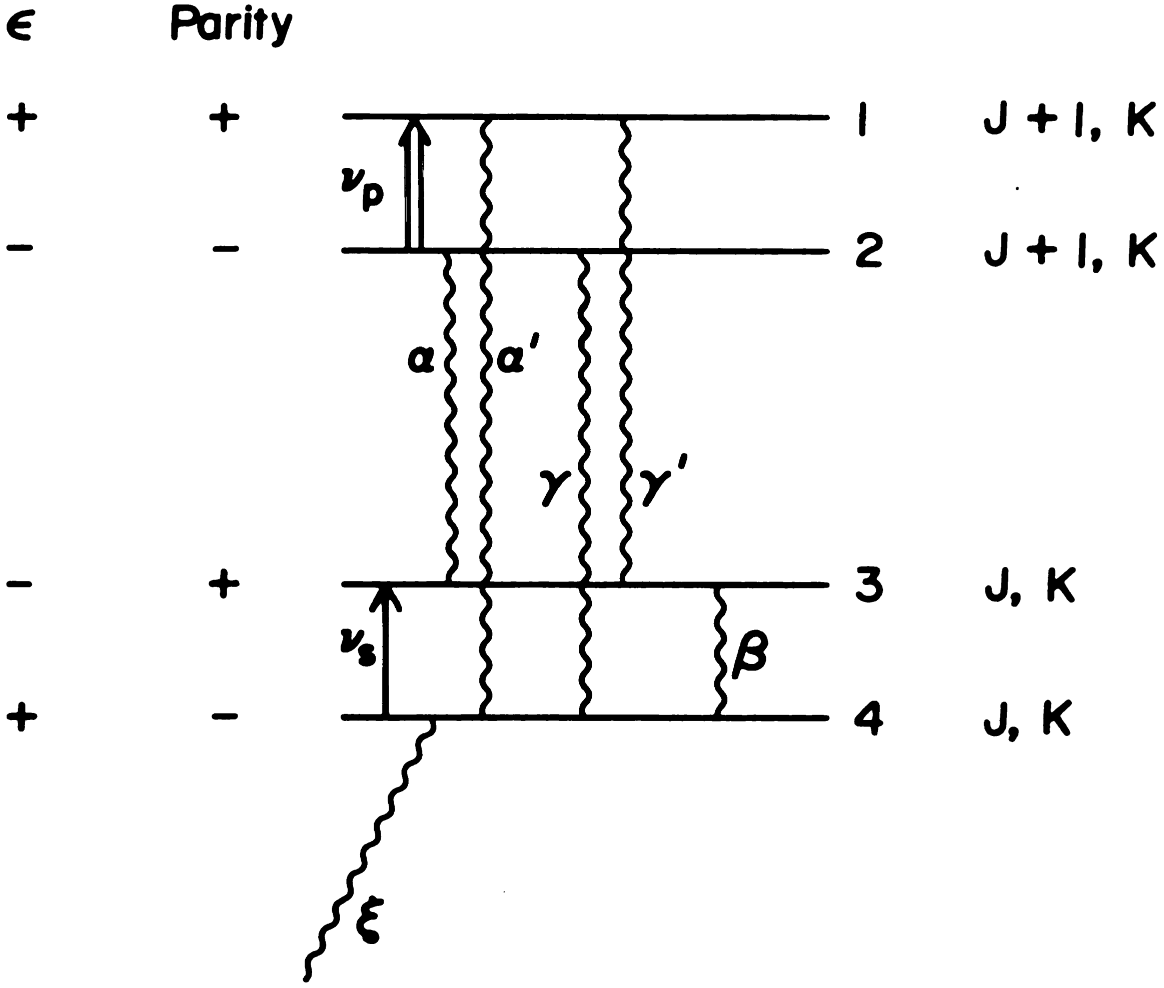

Figure 1. Energy level scheme for a four-level double resonance experiment in NH_3.

other levels by collisions, and is monitored by observing the change in absorption intensity, ΔI, of a weak radiation field (the signal). To a good first approximation the observed change in intensity can be related to collisional rates among four levels, the two pump levels and the two signal levels.

The quantity which is measured experimentally is $\eta = \Delta I/I$. Oka$^{(15)}$ has shown that

$$\eta = \frac{-\nu_\infty}{\nu_s} \frac{k_\alpha^\uparrow - k_\gamma^\uparrow}{k_\alpha^\uparrow + k_\gamma^\uparrow + 2k_\beta + k_\xi} \tag{218}$$

if the following conditions hold.

$$k_{13} \cong k_{24} = k_\gamma^\downarrow$$
$$k_{14} \cong k_{23} = k_\alpha^\downarrow$$
$$k_{34} \cong k_{43} = k_\beta$$
$$k_\beta^\uparrow \cong k_\beta^\downarrow$$

In these equations k_{nm} is the rate constant for collisionally-induced transitions from state n to m. The symbol $k_\alpha^\downarrow$ denotes the collisional rate from a higher to a lower level and is related to $k_\alpha^\uparrow$ by

$$\frac{k_\alpha^\uparrow}{k_\alpha^\downarrow} = \exp(-\Delta E/kT) \quad . \tag{220}$$

The condition $k_\beta^\uparrow \cong k_\beta^\downarrow$ is a statement that the energy difference between the levels of an inversion doublet is very small.

Oka has calculated η by using a simplified Anderson theory with dipole-dipole potentials.(156) For this case, $k_\gamma \equiv 0$ and $k_\xi \equiv 0$, so that

$$\eta = \frac{-\nu_\rho}{\nu_s} \frac{k_\alpha^\uparrow}{k_\alpha^\uparrow + 2k_\beta} \quad . \tag{221}$$

Although this calculation gives the algebraic sign of η in agreement with experiment the calculated magnitude of η is about five times too large. With the sudden approximation developed in this chapter it is possible to calculate η by using Equation (218)

The collisional rates k occurring in Equation (218) are just the $\Lambda^0_{i'i'ii}$ with the appropriate i and i' indices given earlier in this chapter. Specifically,

$$\Lambda^0_{i'i'ii} = \left(\frac{2\pi\mu_1\mu_2}{\hbar v}\right)(2j_i'+1)N^2_{\varepsilon_i}N^2_{\varepsilon_i'} \sum_\lambda \left[1+\varepsilon_i\varepsilon_i'(-1)^{j_i+j_i'+\lambda}\right]$$

$$\times \left[1+\varepsilon_i\varepsilon_i'(-1)^{j_i+j_i'+\lambda}\right](-1)^{j_i+j_i'+\lambda} \begin{pmatrix} j_i & j_i' & \lambda \\ k & -k & 0 \end{pmatrix} \begin{pmatrix} j_i & j_i' & \lambda \\ k & -k & 0 \end{pmatrix} A_\lambda \tag{222}$$

Four rates need to be considered. These are Λ^0(jk- → j+1k-) and Λ^0(jk+ → j+1k+), which are dipole allowed in first order perturbation theory, and Λ^0(jk- → j+1k+) and Λ^0(jk+ → j+1k-), which are dipole forbidden. The minus and plus signs in the current notation denote ε and not the parity of the level. Equation (222) can be used to give the following expressions for the rate constants.

$$\Lambda^0(jk- \rightarrow j+1k-) = C \sum_\lambda [1+(-1)^{\lambda+1}]^2 \begin{pmatrix} j+1 & j & \lambda \\ k & -k & 0 \end{pmatrix}^2 A_\lambda, \tag{223}$$

$$\Lambda^0(jk+ \rightarrow j+1k+) = C \sum_\lambda [1+(-1)^{\lambda+1}]^2 \begin{pmatrix} j+1 & j & \lambda \\ k & -k & 0 \end{pmatrix}^2 A_\lambda, \tag{224}$$

$$\Lambda^0(jk- \rightarrow j+1k+) = C \sum_\lambda [1-(-1)^{\lambda+1}]^2 \begin{pmatrix} j+1 & j & \lambda \\ k & -k & 0 \end{pmatrix}^2 A_\lambda, \tag{225}$$

$$\Lambda^0(jk+ \rightarrow j+1k-) = C \sum_\lambda [1-(-1)^{\lambda+1}]^2 \begin{pmatrix} j+1 & j & \lambda \\ k & -k & 0 \end{pmatrix}^2 A_\lambda, \tag{226}$$

where

$$C = \left(\frac{2\pi\mu_1\mu_2}{\hbar v}\right)(2j+1)\left(\frac{1}{4}\right) . \tag{227}$$

In Equations (223) and (224) only terms with λ odd contribute, while in Equations (225) and (226) only terms with λ even contribute. Also Equations (223) and (224) are equal, as are Equations (225) and (226). Therefore, in the sudden approximation the first two conditions given in Equation (219) are satisfied.

It is useful to compare these results with the Anderson theory expression for $\Lambda^0(i'i'ii)$ (dipole-dipole interaction)

$$\sigma^0(i'i'ii) \sim \frac{1}{16\pi^2} \sum_{j_2'} (2j_i'+1) \begin{pmatrix} j_i & j_i' & 1 \\ k_i & -k_i & 0 \end{pmatrix}^2 \begin{pmatrix} j_2 & j_2' & 1 \\ k_2 & -k_2 & 0 \end{pmatrix}^2$$

$$\times \quad |a^{\lambda kj}|^2 \tag{228}$$

The only part of this expression that depends on ε is $|a^{\lambda kj}|^2$. The dependence on ε is due to the energy spacing of the inversion doublets. Therefore, there should be differences between the two dipole allowed transitions. However, the computational results presented in Chapter II show that to a resolution of about 0.2 Å^2 there are no differences.

The results of the sudden approximation calculation of the rate constants k are summarized in Table XXIV. Oka's calculation using a simplified Anderson theory shows the best agreement with the experimental value. The agreement is probably merely fortuitous, because only resonant collisions have been considered. Inclusion of non-resonant collisions would lead to a larger value as discussed by Oka.(156)

Table XXIV. Sudden Approximation Calculations of Rate Constants for Four-Level Double Resonance Experiments in NH_3.[a]

$k_\alpha^\uparrow = 170.6$

$k_\gamma^\uparrow = 69.8$

$k_\beta = 564.1$

$k_\xi = 103.0$

$$\left(\frac{k_\alpha^\uparrow - k_\gamma^\uparrow}{k_\alpha^\uparrow + k_\gamma^\uparrow + 2k_\beta + k_\xi}\right)_{\text{SUDDEN}} = 0.0685$$

$$\left(\frac{k_\alpha^\uparrow}{k_\alpha^\uparrow + 2k_\beta}\right)_{\text{OKA}} = 0.0567$$

OBSERVED = 0.0112

---

[a] The levels involved are J = 3 and K = 3 in Figure 1.

C. Energy Corrections to the Sudden Approximation Scattering Matrix

The sudden approximation to the scattering matrix neglects energy differences between internal states. Therefore, it is expected to give transition probabilities that are too large. Because the sudden approximation relaxation coefficients are so easy to calculate it is of interest to try to correct the approximation by reintroducing consideration of internal state energy differences. De Pristo et al.(157) have made an attempt at doing this. A brief description of their approach and applications to relaxation coefficients will be given here. Later, some other ways of incorporating energy corrections will be considered.

It is difficult to evaluate the accuracy of energy corrections because there is little experimental data on transition probabilities and because there are very few accurate fully quantum mechanical calculations of transition probabilities for systems of interest to microwave spectroscopists.

The argument of DePristo et al. is as follows. The perturbation series for the exact S matrix in the interaction representation is

$$S_{mm'} = \delta_{mm'} - i\hbar^{-1} \int_{-\infty}^{\infty} \exp(i\omega_{mm'}t)V^{s}_{mm'}(t)dt$$
$$- \hbar^{-2} \sum_{m''} \int_{-\infty}^{\infty} \exp(i\omega_{mm''}t)V^{s}_{mm''}(t) \int_{-\infty}^{t} \exp(i\omega_{m''m'}t')$$
$$\times V^{2}_{m''m'}(t')dt'dt + \ . \ . \ . \tag{229}$$

where

$$V_{mm'}(t) = \exp(i\omega_{mm'}t)V^{s}_{m'}(t) \ . \tag{230}$$

In the sudden approximation all $\exp(i\omega_{mm'}t)$ factors are set equal to one. The energy correction consists of setting the limits of integration to $\pm\tau_c/2$ (τ_c is the collision duration) and keeping the exponential factors in the first integrals only. That is, the S matrix is written as

$$S_{mm'} = \delta_{mm'} - i\hbar^{-1} \int_{-\tau_c/2}^{\tau_c/2} \exp(i\omega_{mm'}t)V^{s}_{mm'}(t)dt$$
$$- \hbar^{-2} \sum_{m''} \int_{-\tau_c/2}^{\tau_c/2} \exp(i\omega_{mm'}t)V^{s}_{mm''}(t) \int_{-\tau_c/2}^{t} V^{s}_{m''m'}(t')dt'dt$$
$$\tag{231}$$

The integral $\int_{-\tau_c/2}^{\tau_c/2} \exp(i\omega t)V^{s}(t)dt$ is approximated by

$$\frac{1}{\tau_c} \int_{-\tau_c/2}^{\tau_c/2} (1+i\omega t-\omega^2 t^2/2)dt \int_{-\tau_c/2}^{\tau_c/2} V^s(t)dt \ . \qquad (232)$$

The first integral in Equation (232) is $1-\omega^2(\tau_c/2)^2/6$ which is rewritten as $6[6+(\omega\tau_c(2)^2]^{-1}$. (This is a Padé approximant.) The second integral is identified as the n^{th} term in the expansion of the sudden S matrix. The result of this is an energy corrected sudden approximation.

$$S_{mm'} = 6[6 + (\omega_{mm'}\tau_c/2)^2]^{-1} S^s_{mm'} \qquad (233)$$

where $S^s_{mm'}$ is the sudden S matrix. The collision time can be approximated as

$$\tau_c = \frac{\chi_c \ b}{v} \qquad (234)$$

where for a r^{-3} potential $\chi_c = 1.5$.

It is of interest to carry the results of DePristo et al. a step further by substituting Equation (233) into the equation for a general relaxation cross section $\sigma^K(i'f'if)$. Both $\sigma^K(iiii)$ and $\sigma^K(ifif)$ contain only elastic S matrix elements S_{mm}. For elastic S matrix elements ω_{mm} is zero and Equation (233) shows that there is no energy correction to S^s_{mm}. Therefore in the context of the above correction only $\sigma^K(i'i'ii)$ for $i' \neq i$ will be considered. (Several calculations of Λ^1_{ifif} have been performed by using a fully quantum mechanical sudden method - the infinite order sudden (IOS) method.(115,116) These calculations were for vibration-rotation lines of He-HD, He-HCl, He-CO, and He-HCN systems and were compared to exact close coupled calculations. It is interesting to note that the IOS results range from 7 to 500% higher than the CC results. This suggests that there may be room for improvement in the energy correction given in Equation (233).)

If j' ≠ j in Equation (192), the T matrix may be replaced by the S matrix. By using Equations (193), (194) and (233) the energy corrected cross section for the transition probability from j' to j may be written as

$$\sigma^0(j'j'jj)_{ECS} = \frac{36}{\{6+[\frac{\omega_{j'j}b}{2v}]^2\ 2.25\}^2} \sum_{\lambda\mu} (2j'+1)$$

$$\times \begin{pmatrix} j & j' & \lambda \\ 0 & 0 & 0 \end{pmatrix} \frac{f^2_{\lambda\mu}}{4\pi} \tag{235}$$

Equation (235) must be integrated over the impact parameter and θ_2 to obtain $\Lambda^0_{j'j'jj}$. After expanding the denominator of the correction factor, the following integral must be evaluated

$$\frac{\pi}{2} \int_0^\pi \int_0^\infty \frac{yJ^2_{\lambda+1/2}(y\sin\theta)\sin\theta\, dy\, d\theta}{a_0y^4 + a_1y^2 + a_2} \tag{236}$$

where

$$a_0 = 36$$

$$a_1 = \frac{24\mu_1\mu_2}{\hbar v}\,\frac{\omega^2_{j'j}(1.5)^2}{4v^2}$$

$$a_2 = \frac{4\mu_1^2\mu_2^2}{\hbar^2 v^2}\,\frac{\omega^4_{j'j}(1.5)^4}{16\ v^4} \qquad (237)$$

and all other symbols have been previously defined. Attempts to evaluate Equation (236) analytically have failed. While Equation (236) could be evaluated numerically, the value of such an effort is probably not worthwhile until accurate values of transition probabilities for dipole-dipole systems are available.

An alternative to the integral in Equation (236) is simply to set b in the correction factor equal to some average inelastic impact paramebeer b_0. This is similar in principle to the hard sphere cutoff used in the Anderson theory. Unfortunately, the desire to bypass such a concept is one motivation for using the sudden approximation in the first place.

It is undoubtedly possible to devise many different energy corrections to the sudden S matrix. An alternative to the approach discussed above has as its starting point the Anderson approximation to the scattering operator,

$$S \approx 1 - iP$$
$$S^s \approx 1 - iP^s \tag{238}$$

where P is the same P as used in Chapter II; P^s is the P operator in the sudden limit. The precise form of P^s will be given shortly.

It is convenient to consider matrix elements of the above operators. For the case $m \neq n$, Equation (238) gives the following

$$S_{mn} \tilde{=} -iP_{mn}$$

$$S^s_{mn} \approx -iP^s_{mn} \tag{239}$$

From Equation (239)

$$S^2_{mn} = \frac{P^2_{mn}}{(P^s_{mn})^2} (S^s_{mn})^2 \ . \tag{240}$$

Each of the quantities in Equation (240) is understood to be evaluated at a given impact parameter. It is also worthwhile to note that although Equation (240) has been written with Anderson theory in mind it is a much more general result in that P_{mn} may be evaluated within a different set of approximations than those used in Anderson theory. For example, P_{mn} may be the fully quantum mechanical first Born Approximation. Also, the correction in Equation (240) may be extended to terms higher than first order by writing

$$S_{mn}^{2} = \frac{(-iP_{mn} - \frac{1}{2} P_{mn}^{2} + \ldots)^{2}}{(-iP_{mn}^{s} - \frac{1}{2}(P_{mn}^{s})^{2} + \ldots)^{2}} (S_{mn}^{s})^{2} . \qquad (241)$$

The quantities of interest are cross sections. These may be obtained from S_{mn}^{2} and the analogous quantities by taking the absolute value of S_{mn}, squaring it, summing over m, m', m_2, m_2' and j_2', and multiplying by $[(2j+1)(2j_2+1)]^{-1}$. Following this prescription the first of Equations (239) may be written as

$$\sum_{\substack{mm' \\ m_2 m_2'}} \sum_{j_2'} [(2j+1(2j_2+1)]^{-1} |\langle jmj_2m_2|S|j'm'j_2'm_2'\rangle|^{2}$$

$$= \sum_{\substack{mm' \\ m_2 m_2}} \sum_{j_2'} [(2j+1)2j_2+1)]^{-1} |\langle jmj_2m_2|P|j'm'j_2'm_2'\rangle|^{2}, \qquad (242)$$

with a similar equation involving S^{s} and P^{s}. The analogue of Equation (240), written in terms of cross sections, is

$$\sigma(S) = \frac{\sigma(P)}{\sigma(P^{s})} \sigma(S^{s}) \qquad (243)$$

In Equation (243) $\sigma(S^{s})$ is the cross section evaluated from a scattering matrix computed in the sudden approximation.

The quantity $\sigma(S)$ is an exact value of the corresponding cross section. Now, $\sigma(P)$ and $\sigma(P^S)$ are cross sections calculated by using the approximation in Equation (238). Equation (243) will be useful if the ratio $\sigma(P)/\sigma(P^S)$ is more exact than either of its factors. From Chapter II $\sigma(P)$ may be written (for a dipole-dipole potential)

$$\sigma(P) = \sum_{\substack{mm'\\ m_2m'_2}} \sum_{j'_2} [(2j+1(2j_2+1)]^{-1} |<jmj_2m_2|P|j'm'j'_2m'_2>|^2$$

$$= C \sum_{\substack{j'_2\;1\\ \lambda_2}} B^2_{\lambda_1\lambda_2} (2j'+1)(2j'_2+1) \begin{pmatrix} j & j' & 1 \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} j_2 & j'_2 & 1 \\ 0 & 0 & 0 \end{pmatrix}^2 \qquad (244)$$

where

$$C = (\mu_1\mu_2/3\hbar vb^2)^2$$

It was shown by TC that

$$\sum_{\lambda_1\lambda_2} B^2_{\lambda_1\lambda_2} = 2[K^2_2(k) + 4K^2_1(k) + 3K^2_0(k)] \; . \qquad (245)$$

Defining f(k) as

$$f(k) = \frac{1}{8}\, k^4 \sum_{\lambda_1\lambda_2} B^2_{\lambda_1\lambda_2}$$

enables $\sigma(P)$ to be written as

$$\sigma(P) = 8C \sum_{j_2'} f(k)(2j'+1)(2j_2'+1) \begin{pmatrix} j & j' & 1 \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} j_2 & j_2' & 1 \\ 0 & 0 & 0 \end{pmatrix}^2 . \tag{246}$$

In the sudden limit ω and therefore k goes to zero and f(0) is one. Therefore

$$(P^S) = 8C \sum_{j_2'} (2j'+1)(2j_2'+1) \begin{pmatrix} j & j' & 1 \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} j_2 & j_2' & 1 \\ 0 & 0 & 0 \end{pmatrix}^2$$

$$= 8C(2j'+1) \begin{pmatrix} j & j' & 1 \\ 0 & 0 & 0 \end{pmatrix}^2 \tag{247}$$

Substitution of Equations (246) and (247) into Equation (243) gives

$$\sigma(S) = [\sum_{j_2'} f(k)(2j_2'+1) \begin{pmatrix} j_2 & j_2' & 1 \\ 0 & 0 & 0 \end{pmatrix}^2]\sigma(S^S) . \tag{248}$$

In Equation (248), σ(S), f(k) and $\sigma(S^S)$ are understood to be evaluated at the same given impact parameter.

The interesting features of Equation (248) are most clearly seen if molecule two is considered to be adequately described by the sudden approximation. In this case the sum over j_2' in Equation (248) may be carried out giving

$$\sigma(S) = f(k)\sigma(S^S) .$$

A qualitative plot of f(k) vs. (k) is given in Figure 2 for a dipole-dipole potential. The most significant difference between Equation (248) and Equation (235) is that while in Equation (235) $\sigma(S)$ is smaller than $\sigma(S^s)$ for all values of ω at a given b, this is no longer true in Equation (248). ($\omega_{j'j} \geq 0$ in Equation (235).) For values of ω such that k is less than k_0 Equation (248) predicts that $\sigma(S)$ is larger than $\sigma(S^s)$.

If it is desired to extend Equation (248) to relaxation coefficients, the equation must be averaged over the impact parameter; <u>i.e.</u>,

$$2\pi \int_0^\infty b\sigma(S)db = 2\pi \sum_{j_2'} (2j_2'+1) \begin{pmatrix} j_2 & j_2' & 1 \\ 0 & 0 & 0 \end{pmatrix}^2 \int_0^\infty bf(k)\sigma(S^s)db \tag{249}$$

The integral on the right side of Equation (249) involves integrals of the form

$$\int_0^\infty b^7 J_\lambda^2(\frac{C}{b^2}) K_n^2(\frac{\omega b}{v})db \ , \tag{250}$$

where C is a constant, n is an integer and λ is a half-integer. All attempts to integrate Equation (250) analytically have failed.

It is possible to analytically evaluate an approximation to Equation (249). Because $\sigma(S^s)$ is proportional to F_λ, the integral on the right side of Equation (249) is

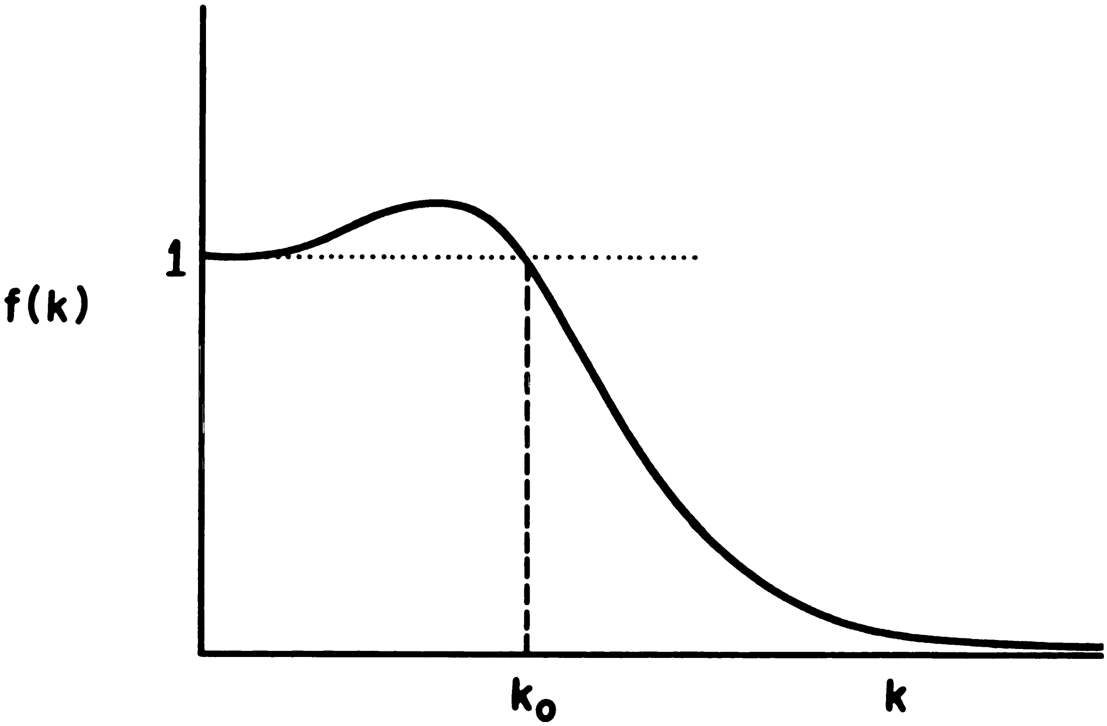

Figure 2. Qualitative plot of f(k) vs k for a dipole-dipole potential. $k = \frac{\omega b}{v}$.

$$\int_0^\infty bf(k)F_\lambda db \quad ,$$

which may be approximated as

$$\int_0^\infty f(k)db\int_0^\infty bF_\lambda db \ . \qquad (251)$$

The second integral in Equation (251) is just the integral that was evaluated earlier for the pure sudden approximation. (If the integral was approximated as $\int_0^\infty bf(k)db\int_0^\infty F_\lambda db$, the introduction of a hard sphere impact parameter would be necessary.) The first integral may be evaluated analytically. The details are given in Appendix I. The result is

$$\int_0^\infty f(k)db = (\frac{v}{\omega})(\frac{4}{3})(1.5)^3[\Gamma(1.5)]^4 \qquad (252)$$

$$= 2.77586(\frac{v}{\omega})$$

In this approximation Equation (249) becomes

$$\Lambda(S) = \sum_{\substack{j_2'\\ j_2}} (2j_2'+1)\begin{pmatrix} j_2 & j_2' & 1 \\ 0 & 0 & 0 \end{pmatrix}^2 (\frac{v}{\omega})(\frac{4}{3})(1.5)^3[\Gamma(1.5)]^4\rho_{j_2}$$

$$\times\ \Lambda(S^S) \qquad (253)$$

where ρ_{j_2} is a Boltzmann factor.

One of the advantages of the sudden approximation is that the sum over j_2 and j_2' may be neglected. (The perturber states have been summed over by using the closure relations for spherical harmonics and rotation matrices given earlier.) This advantage is lost in Equation (253).

The essential prediction of Equation (253) is that

$$\Lambda(S) \sim (\frac{v}{\omega})\Lambda(S^s) \qquad (254)$$

When ω is small, $\Lambda(S)$ is much greater than $\Lambda(S^s)$ while when ω is large, $\Lambda(S)$ is much less than $\Lambda(S^s)$. Intuitively, only the latter limit seems reasonable.

To attempt to establish the validity of approximation (Equation (251)) the exact integral should be evaluated numerically at least once. To compute a cross section, however, the exact integral will have to be evaluated for every allowed value of λ. Because $|j-j'|\leq\lambda\leq j+j'$, this could become very expensive.

CHAPTER V

ADDITIONAL RESULTS

In this chapter two additional results will be presented. They are concerned with the equations of motion for the density matrix. First, the equations of motion for a symmetric top Q-branch transition in a static external electric field will be derived. The second part of the chapter discusses some phase conventions for reduced matrix elements and their relation to previously derived equations of motion for state multipoles.

A. Comparison of T_2 for Transitions in a Static Electric Field in Linear and Symmetric Top Molecules

The case of a linear rotor in a static external electric field has been discussed in LM. Before discussing the analogous case for symmetric tops, a brief summary of the LM results will be presented.

In a static electric field and plane polarized radiation the $(j_f m) \leftarrow (j_i m)$ and $(j_f -m) \leftarrow (j_i -m)$ spectral transitions are coupled. By using the Wigner-Eckart theorem it is possible to show that

$$\langle j_i m|\mu|j_f m\rangle = \langle j_i -m|\mu|j_f -m\rangle \tag{255}$$

This result and the following linear combination of density matrix elements

$$\rho\pm(j_i j_f) = \rho(j_i m j_f m)\pm\rho(j_i -m j_f -m) \tag{256}$$

can be used to write the equations of motion as

$$\begin{aligned} i\,\frac{\partial}{\partial t}\rho\pm(j_f j_i) &= \omega_{fi}\rho\pm(j_f j_i)-\langle j_f m|\mu|j_i m\rangle\varepsilon\cos\omega t \\ &\quad \times\,[\rho\pm(j_i j_i)-\rho\pm(j_f j_f)] \\ &\quad -\,i\lambda^{\pm}_{fifi}\rho\pm(j_f j_i)\ -i\lambda^{\pm}_{fiif}\rho\pm(j_i j_f) \end{aligned} \tag{257}$$

$$\begin{aligned} i\,\frac{\partial}{\partial t}\rho\pm(j_i j_i) &= -\varepsilon\cos\omega t[\langle j_i m|\mu|j_f m\rangle\rho\pm(j_f j_i)-\rho\pm(j_i j_f) \\ &\quad \times\,\langle j_f m|\mu|j_i m\rangle]-i\lambda^{\pm}_{iiii}\rho\pm(j_i j_i)-i\lambda^{\pm}_{iiff}\rho\pm(j_f j_f) \end{aligned} \tag{258}$$

In the above equations the m-dependence of $\rho\pm(j_i j_f)$ has been suppressed. The $\lambda^{\pm}$ are defined as

$$\lambda^{\pm}_{fifi}=\langle\langle j_f m j_i m|\Lambda|j_f m j_i m\rangle\rangle\pm\langle\langle j_f -m j_i -m|\Lambda|j_f m j_i m\rangle\rangle \tag{259}$$

with analogous equations for $\lambda^{\pm}_{fiif}$, $\lambda^{\pm}_{iiff}$ and $\lambda^{\pm}_{iiii}$. Equation (27) may be used in Equation (259) to give

$$\lambda^{\pm}_{fifi} = \sum_{K} (2K+1) \begin{pmatrix} j_f & j_i & K \\ m- & m & 0 \end{pmatrix}^2 [1\pm(-1)^{K+j_f+j_i}]\Lambda^{K}_{fifi} \qquad (260)$$

with similar equations for $\lambda^{\pm}_{fiif}$, $\lambda^{\pm}_{iiff}$ and $\lambda^{\pm}_{iiii}$. Equations (257) and (258) decouple the pair of transitions $(j_f m) \leftarrow (j_i m)$ and $(j_f -m) \leftarrow (j_i -m)$ from the other possible transitions among m states. They also show that ρ_+ and ρ_- are uncoupled. The polarization for this case can be written

$$P = \langle j_f m|\mu|j_i m\rangle \rho_+(j_i j_f) + \langle j_i m|\mu|j_f m\rangle \rho_+(j_f j_i) \qquad (261)$$

so that only the equations of motion for ρ_+ are needed. The system can be treated analogously to a two-state system and gives for relaxation times

$$\frac{1}{T_2} = \mathrm{Re}\lambda^{+}_{fifi}$$

$$\frac{1}{T_1} = \frac{1}{2}(\lambda^{+}_{iiii} - \lambda^{+}_{ffii} + \lambda^{+}_{ffff} - \lambda^{+}_{iiff}) \ . \qquad (262)$$

In the above it was assumed that the strength of the field was such that the spectral lines arising from different values of m are non overlapping.

The dipole moment matrix element for a symmetric top evaluated with a parity-adapted basis may be written

$$\langle j_i km+|\mu|j_f km-\rangle = (-1)^{j_i-m}\begin{pmatrix} j_i & j_f & 1 \\ m & -m & 0 \end{pmatrix}\bar{\mu}_{if} \ . \tag{263}$$

The following discussion is restricted to Q-branch transitions in a symmetric top with inversion (like NH_3). For this case,

$$\langle jkm+|\mu|jkm-\rangle = (-1)^{j-m}\begin{pmatrix} j & j & 1 \\ m & -m & 0 \end{pmatrix}\bar{\mu}_{if} \ . \tag{264}$$

Also

$$\langle jk-m+|\mu|jk-m-\rangle = (-1)^{j+m}\begin{pmatrix} j & j & 1 \\ -m & m & 0 \end{pmatrix}\bar{\mu}_{if}$$

$$= (-1)^{j-m+1}\begin{pmatrix} j & j & 1 \\ m & -m & 0 \end{pmatrix}\bar{\mu}_{if} \tag{265}$$

where the symmetry properties of the 3-j symbols and the fact that m is an integer have been used. The conclusion from Equations (264) and (265) is that

$$\langle jkm+|\mu|jkm-\rangle = -\langle jk-m+|\mu|jk-m-\rangle \ . \tag{266}$$

The polarization can be written

$$P = \mathrm{tr}(\mu\rho)$$

$$= \sum_m [<j_i m|\mu|j_f m>\rho(j_f m j_i m)+<j_f m|\mu|j_i m>\rho(j_i m j_f m)] \tag{267}$$

where the sum over m is restricted to m and -m. In Equation (267) the symbols j_i and j_f include, in addition to the j value of the state, the quantum number k and the parity. Equation (267) can be evaluated to give

$$P = <j_i m|\mu|j_f m>\rho_-(j_f j_i)+\rho_-(j_i j_f)<j_f m|\mu|j_i m>. \tag{268}$$

Therefore, the equations of motion for ρ_- are needed. Use of Equation (21) of Chapter I and Equation (266) of the present chapter gives the equation of motion for $\rho_-(j_f j_i)$ as

$$i \frac{\partial}{\partial t}\rho_-(j_f j_i)=\omega_{fi}\rho_-(j_f j_i)-\varepsilon\cos\omega t<j_f m|\mu|j_i m>$$

$$\mathrm{x}\ [\rho_+(j_i j_i)-\rho_+(j_f j_f)]$$

$$- i\lambda^-_{fifi}\rho_-(j_f j_i) - i\lambda^-_{fiif}\rho_-(j_i j_f) \tag{269}$$

This result differs from Equation (257) in that here $\rho_-(j_f j_i)$ is coupled to $\rho_+(j_i j_i)$ and $\rho_+(j_f j_f)$. In a manner similar to that used to obtain Equation (269) the equation of motion for $\rho_+(jj)$ is

$$i\,\frac{\partial}{\partial t}\rho_+(j_ij_i) = -\varepsilon\cos\omega t[\langle j_im|\mu|j_fm\rangle\rho_-(j_fj_i)-\rho_-(j_ij_f)$$

$$\times \langle j_fm|\mu|j_im\rangle]$$

$$- i\lambda^+_{iiii}\rho_+(j_ij_i) - i\lambda^+_{iiff}\rho_+(j_fj_f) \qquad (270)$$

$\rho_+(j_ij_i)$ is coupled to $\rho_-(j_fj_i)$ which is given in Equation (269). Therefore Equation (269) and Equation (270) are the equations of motion necessary to describe this system. The relaxation times are seen to be

$$\frac{1}{T_2} = \mathrm{Re}(\lambda^-_{fifi})$$

$$\frac{1}{T_1} = \frac{1}{2}(\lambda^+_{iiii} - \lambda^+_{ffii} + \lambda^+_{ffff} - \lambda^+_{iiff}) \qquad (271)$$

This is the same T_1 as for the linear rotor. The $1/T_2$ differs from the linear rotor case in that here the minus combination is needed. For comparison λ^-_{fifi} and λ^+_{fifi} are given as

$$\lambda^-_{fifi} = \sum_K (2K+1)\begin{pmatrix} j_f & j_i & K \\ m & -m & 0 \end{pmatrix}^2 [1-(-1)^{j_f+j_i+K}]\Lambda^K_{fifi} \qquad (272)$$

and

$$\lambda^{+}_{fifi} = \sum_{K} (2K+1) \begin{pmatrix} j_f & j_i & K \\ m & -m & 0 \end{pmatrix}^2 [1+(-1)^{j_f+j_i+K}]\Lambda^{K}_{fifi} \quad . \quad (273)$$

For Q-branch transitions in a symmetric top with inversion, λ^{-}_{fifi} is needed for $1/T_2$ and only terms with odd K contribute to Equation (272). For R-branch transitions in a linear rotor, λ^{+}_{fifi} is needed and again only terms with K odd contribute to Equation (273).

Equations (272) and (273) suggest a way of experimentally obtaining Λ^{K}_{fifi} for K greater than 1. To be concrete, Equation (273) will be considered for R-branch transitions in linear rotors. The following comments apply equally well to Equation (272) for Q-branch symmetric top transitions. $\mathrm{Re}(\Lambda^{1}_{fifi})$ is the low-power linewidth obtained in zero field. For a 1 ← 0 transition K = 1 only for Λ^{K}_{fifi}. For a 2 ← 1 transition and plane-polarized radiation K = 1, 3 for Λ^{K}_{fifi}. Re Λ^{1}_{fifi} may be obtained from a zero field lineshape experiment. This enables Λ^{3}_{fifi} to be obtained when a non-zero field lineshape experiment is performed. For a 3 ← 2 transition K = 1, 3, 5. After Re Λ^{1}_{fifi} is obtained from a zero field experiment there are two remaining unknowns. However, there are three different m-components pairs which may be probed. This enables a set of linear equations to be set up from Equation (273), with one equation for each $|m|$. Obtaining Λ^{K}_{fifi}

in this way would be a useful check on the theoretical calculations presented earlier. In the Anderson theory the Λ^K_{fifi} and Λ^K_{iiii} are similar in form so that indirect comparison with the Λ^K_{iiii} may also be made.

B. Phase Conventions for Reduced Matrix Elements

In this section a discussion of conventions for reduced matrix elements and their relation to equations of motion for the density matrix is presented. Equations (4.1) and (4.2) of LM may be written for plane-polarized radiation and non-overlapping lines as

$$\begin{aligned} i\,\frac{\partial}{\partial t}\rho(j_f m j_i m) &= \omega_{fi}\rho(j_f m j_i m) - \varepsilon\cos\omega t \langle j_f m|\mu_z|j_i m\rangle \\ &\quad \times [\rho(j_i m j_i m) - \rho(j_f m j_f m)] \\ &\quad - i\sum_{j_f' j_i'}\sum_{m'} \langle\langle j_f m j_i m|\Lambda|j_f' m' j_i' m'\rangle\rangle \rho(j_f' m' j_i' m') \end{aligned} \tag{274}$$

$$\begin{aligned} i\,\frac{\partial}{\partial t}\rho(j_i m j_i m) &= -\varepsilon\cos\omega t[\langle j_i m|\mu_z|j_f m\rangle\rho(j_f m j_i m) \\ &\quad - \rho(j_i m j_f m)\langle j_f m|\mu_z|j_i m\rangle] \\ &\quad - i\sum_{j'}\sum_{m'} \langle\langle j_i m j_i m|\Lambda|j' m' j' m'\rangle\rangle \rho(j' m' j' m') \quad . \end{aligned} \tag{275}$$

Equation (274) is identical to Equation (1) of

Schwendeman.(55) Equation (2) of Schwendeman is

$$i\,\frac{\partial}{\partial t}\rho(j_i m j_i m) = -\varepsilon\cos\omega t\langle j_f m|\mu_z|j_i m\rangle[\rho(j_f m j_i m)-\rho(j_i m j_f m)]$$

$$-i\sum_{j'}\sum_{m'}\langle\langle j_i m j_i m|\Lambda|j'm'j'm'\rangle\rangle\rho(j'm'j'm') \qquad (276)$$

Comparing Equation (276) with Equation (275) shows that in Equation (276) the assumption

$$\langle j_i m|\mu_z|j_f m\rangle = \langle j_f m|\mu_z|j_i m\rangle \qquad (277)$$

has been made.

The adjoint of a tensor operator is defined as

$$\langle jm|T_{kq}|j'm'\rangle = (-1)^{p-q}\langle jm|T^{\dagger}_{k-q}|j'm'\rangle$$

$$= (-1)^{p-q}\langle j'm'|T_{k-q}|jm\rangle^{*} \qquad (278)$$

where q is the z-component of the tensor order k. As discussed in Brink and Satchler,(71) there are two choices for the parameter p; p = 0 or p = k. These choices will be denoted convention I and II, respectively. If p = 0, the following relations hold:

$$\langle jm|T_{kq}|j'm'\rangle = (-1)^{-q}\langle j'm'|T_{k-q}|jm\rangle^{*}\ , \qquad (279)$$

$$\langle j||T_k||j'\rangle = (-1)^{j-j'}\langle j'||T_k||j\rangle^{*}\ ; \qquad (280)$$

while if p = k,

$$\langle jm|T_{kq}|j'm'\rangle = (-1)^{k-q}\langle j'm'|T_{k-q}|jm\rangle^* \qquad (281)$$

and

$$\langle j||T_k||j'\rangle = (-1)^{j-j'-k}\langle j'||T_k||j\rangle^* \;. \qquad (282)$$

In the previous four equations $\langle j||T_k||j'\rangle$ is a reduced matrix element and obeys the same equation as $\bar{\mu}_{fi}$ of Chapter I(Equation (26)). It is noted that if Equation (279) is adopted then Equation (280) and not Equation (28) must be used. (Equations (280) and (282) follow from Equations (271) and (281), respectively, by use of the Wigner-Eckart theorem.) In the following the z-component (<u>i.e.</u>, q = 0) of the dipole moment will be considered. It will also be assumed that $\langle jm|\mu_z|j'm'\rangle$ is real. Then, Equations (279) - (282) give the following results.

Convention I (p = 0):

$$\langle j_i m|\mu_{10}|j_f m\rangle = \langle j_f m|\mu_{10}|j_i m\rangle \qquad (283)$$

$$\bar{\mu}_{if} = (-1)^{j_i - j_f}\,\bar{\mu}_{fi} \qquad (284)$$

Convention II $(p = 1)$:

$$\langle j_i m|\mu_{10}|j_f m\rangle = -\langle j_f m|\mu_{10}|j_i m\rangle \tag{285}$$

$$\bar{\mu}_{if} = \bar{\mu}_{fi} \tag{286}$$

Equation (34) of Schwendeman$^{(55)}$ is

$$i\,\frac{\partial}{\partial t}\rho_{ii}(K) = -\varepsilon\bar{\mu}_{fi}\cos\omega t \sum_{K'} C^{fi}_{KK'}[\rho_{fi}(K')-(-1)^{j_i-j_f}\rho_{if}(K')]$$

$$-i\sum_{k}\Lambda^{K}_{iikk}\rho_{kk}(K) \tag{287}$$

In Equation (287) the $C^{fi}_{KK'}$ are defined as

$$C^{fi}_{KK'} = (-1)^{j_f-j_i}[(2K+1)(2K'+1)]^{1/2}\begin{pmatrix} k & k' & 1 \\ 0 & 0 & 0 \end{pmatrix}\begin{Bmatrix} K & K' & 1 \\ j_f & j_i & j_i \end{Bmatrix}. \tag{288}$$

It is possible to derive an equation of motion for $\rho_{ii}(K)$ without choosing a convention. This is (neglecting collisions)

$$i\,\frac{\partial}{\partial t}\rho_{ii}(K) = -\varepsilon\cos\omega t \sum_{K'} (-1)^{j_f-j_i}C^{fi}_{KK'}$$

$$\times\ [\bar{\mu}_{if}\rho_{fi}(K') - \bar{\mu}_{fi}\rho_{if}(K')]\quad . \tag{289}$$

If convention I is used in Equation (289), the result is

Equation (287); i.e., the result is Equation (34) of Schwendeman.(55) This establishes the phase conventions used in that work.

Finally, it is interesting to note that the commutation relation given in Equation (154) of Chapter III may be used to obtain the equations of motion for the state multipoles. This is done by recognizing that these equations are essentially just the commutators $[\rho_{ii}(K)\mu_{fi}(1)]$, $[\rho_{ff}(K)\mu_{fi}(1)]$ and $[\rho_{if}(K),\mu_{fi}(1)]$. These commutators may be easily evaluated to give, respectivelv,

$$\sqrt{3}\sum_{K'}[(2K+1)(2K'+1)]^{1/2}(-1)^{j_f-j_i}\begin{pmatrix}K & 1 & K'\\ 0 & 0 & 0\end{pmatrix}\begin{Bmatrix}K & 1 & K'\\ j_f & j_i & j_i\end{Bmatrix}$$

$$\times\ \rho_{fi}(K') \tag{290}$$

$$\sqrt{3}\sum_{K'}[(2K+1)(2K'+1)]^{1/2}(-1)^{j_f-j_i}\begin{pmatrix}K & 1 & K'\\ 0 & 0 & 0\end{pmatrix}\begin{Bmatrix}K & 1 & K'\\ j_i & j_f & j_f\end{Bmatrix}$$

$$\times\ \rho_{fi}(K') \tag{291}$$

$$\sqrt{3}\sum_{K'}[(2K+1)(2K'+1)]^{1/2}\begin{pmatrix}K & 1 & K'\\ 0 & 0 & 0\end{pmatrix}\begin{Bmatrix}K & 1 & K'\\ j_i & j_i & j_f\end{Bmatrix}$$

$$\times\ \rho_{ii}(K') - \begin{Bmatrix}k & 1 & K'\\ j_f & j_f & j_i\end{Bmatrix}\rho_{ff}(K')] \quad . \tag{292}$$

The factor $\sqrt{3}$ arises from a different normalization of reduced matrix elements.

APPENDICES

APPENDIX A

EQUIVALENCE OF EQUATIONS (42) AND (43)

In this appendix the equivalence between Equations (42) and (43) of Chapter II is established. By using the four equations,

$$\langle j_f' m_f' \ell' m' | = \sum_{J_f' M_f'} (-1)^{\ell' - j_f' - M_f'} (2J_f' + 1)^{1/2} \begin{pmatrix} j_f' & \ell' & J_f' \\ m_f' & m' - M_f' & \end{pmatrix}$$

$$\times \langle j_f' \ell' J_f' M_f' | \quad , \qquad \text{(A1)}$$

$$| j_f m_f \ell m \rangle = \sum_{J_f M_f} (-1)^{\ell - j_f - M_f} (2J_f + 1)^{1/2} \begin{pmatrix} j_f & \ell & J_f \\ m_f & m - M_f & \end{pmatrix}$$

$$\times | j_f \ell J_f M_f \rangle \quad , \qquad \text{(A2)}$$

$$| j_i m_i \ell m \rangle \sum_{J_i M_i} (-1)^{\ell - j_i - M_i} (2J_i + 1)^{1/2} \begin{pmatrix} j_i & \ell & J_i \\ m_i & m - M_i & \end{pmatrix}$$

$$\times | j_i \ell J_i M_i \rangle \quad , \qquad \text{(A3)}$$

and

$$<j_i' m_i' \ell' m'| = \sum_{J_i' M_i'} (-1)^{\ell' - j_i' - M_i'} (2J'+1)^{1/2} \begin{pmatrix} j_i' & \ell' & J_i' \\ m_i' & m'-M_i' & \end{pmatrix}$$

$$\times <j_i' \ell' J_i' M_i'| \quad , \tag{A4}$$

$\delta_{i'i}\delta_{f'f}$ can be written as

$$\delta_{i'i}\delta_{f'f} = <j_i' m_i' \ell' m' | j_i m_i \ell m><j_f' m_f' \ell' m' | j_f m_f \ell m>$$

$$= \sum_{\substack{J_i J_i' J_f J_f' \\ M_i M_i' M_f M_f'}} \sum \sum (-1)^{j_i - j_i' - j_f - j_f' - M_i - M_i' - M_f - M_f'} [(2J_i+1)(2J_i'+1)$$

$$\times (2J_f+1)] (2J_f'+1)]^{1/2} \begin{pmatrix} j_i' & \ell' & J_i' \\ m_i' & m'-M_i' & \end{pmatrix} \begin{pmatrix} j_i & \ell & J_i \\ m_i & m-M_i & \end{pmatrix}$$

$$\times \begin{pmatrix} j_f' & \ell' & J_f' \\ m_f' & m'-M_f' & \end{pmatrix} \begin{pmatrix} j_f & \ell & J_f \\ m_f & m-M_f & \end{pmatrix} j_i' \ell' J_i' M_i' | j_i \ell J_i M_i>$$

$$\times <j_f' \ell' J_f' M_f' | j_f \ell J_f M_f> \ . \tag{5}$$

Also, $S_{i'i} S^*_{f'f}$ can be written as

$$S_{i'i}S^{*}_{f'f} = \sum_{\substack{J_iJ_i'J_fJ_f'\\ M_iM_i'M_fM_f'}} \sum \sum (-1)^{j_i-j_i'+j_f-j_f'-M_i-M_i'-M_f-M_f'}$$

$$\times\ [(2J_i+1)(2J_i'+1)(2J_f+1)(2J_f'+1)]^{1/2}$$

$$\times \begin{pmatrix} j_i' & \ell' & J_i' \\ m_i' & m' & -M_i' \end{pmatrix} \begin{pmatrix} j_i & \ell & J_i \\ m_i & m & -M_i \end{pmatrix} \begin{pmatrix} j_f' & \ell' & J_f' \\ m_f' & m' & -M_f' \end{pmatrix} \begin{pmatrix} j_f & \ell & J_f \\ m_f & m & -M_f \end{pmatrix}$$

$$\times\ S^{J_i}_{i'i}\ S^{J_f *}_{f'f} \tag{A6}$$

Use of Equations (A5) and (A6) and the fact that the scattering matrix must be diagonal in J_k and M_k allows $\sigma_{i'f'if}$ to be written as

$$\sigma_{i'f'if} = \left(\frac{\pi}{k^2}\right) \sum_{\substack{J_iJ_fM_iM_f\ell\ell'\\ mm'm_im_i'm_fm_f'}} \sum \sum \sum$$

$$\times\ (-1)^{j_i-j_i'+j_f-j_f'-j_i-j_f'-M_i-M_i'-M_f-M_f'-m_i-m_i'}(2J_i+1)(2J_f+1)$$

$$\times\ [(2K+1)(2K'+1)]^{1/2} \begin{pmatrix} j_i & j_f & K \\ m_i & -m_f & -Q \end{pmatrix} \begin{pmatrix} j_i' & j_f' & K' \\ m_i' & -m_f' & -Q \end{pmatrix} \begin{pmatrix} j_i & \ell & J_i \\ m_i & m & -M_i \end{pmatrix}$$

$$\times \begin{pmatrix} j_i' & \ell' & J_i \\ m_i' & m' & -M_i \end{pmatrix} \begin{pmatrix} j_f & \ell & J_f \\ m_f & m & -M_f \end{pmatrix} \begin{pmatrix} j_f' & \ell' & J_f \\ m_f' & m' & -M_f \end{pmatrix} [\delta_{i'i}\delta_{f'f} - S^{J_i}_{i'i} S^{J_f *}_{f'f}] \tag{A7}$$

Finally, use of the relation

$$\sum_{m_i} \sum_{m_f m} (-1)^{j_i+j_f+\ell+m_i+m_f+m} \begin{pmatrix} j_f & \ell & J_f \\ m_f & m & -M_f \end{pmatrix} \begin{pmatrix} j_i & \ell & J_i \\ m_i & m & -M_i \end{pmatrix} \begin{pmatrix} J_i & j_f & K \\ m_i & -m_f & -Q \end{pmatrix}$$

$$= \begin{pmatrix} J_f & J_i & K \\ -M_f & M_i & -Q \end{pmatrix} \begin{Bmatrix} J_f & J_i & K \\ j_i & j_f & \ell \end{Bmatrix} \qquad \text{(A8)}$$

twice and summation over the resulting two 3-j symbols results in Equation (42).

APPENDIX B

CONVENTIONS FOR REDUCED MATRIX ELEMENTS

In this appendix the LM and TC conventions for reduced matrix elements are compared.

According to Equation (4.10) of LM, the LM convention for reduced matrix elements is

$$<\gamma'j'm'|T(KQ)|\gamma jm> = (-1)^{j'-m'}\begin{pmatrix} j' & K & j \\ -m & Q & m \end{pmatrix}<\gamma'j'||T||\gamma j> \tag{B1}$$

This is Equation (5.4.1) of Edmonds.(142)

The TC convention is obtained from Equation (81) of TC as

$$\begin{aligned}<j_i m_i|\mu_z|j_f m_f> &= <j_f 1 m_f 0|j_i m_i>F' \\ &= (-1)^{j_f+m_i+1}(2j_i+1)^{1/2}\begin{pmatrix} j_f & 1 & j_i \\ m_f & 0 & -m_i \end{pmatrix}F' \\ &= (-1)^{j_i-m_i}(2j_i+1)^{1/2}\begin{pmatrix} j_i & 1 & j_f \\ -m_i & 0 & m_f \end{pmatrix}F' \end{aligned} \tag{B2}$$

Equation (B2) differs from Equation (B1) by the factor $(2j_i+1)^{1/2}$.

APPENDIX C

REDUCTION OF EQUATION (49) TO THE ANDERSON RESULT

This appendix shows that Equation (49) of the text reduces to the expression given by Anderson (Equation (47') of Reference (53)) and TC (Equation (88)) for $\sigma^1(j_i j_f j_i j_f)$. If the appropriate substitutions (<u>i.e.</u>, K = 1, $j_i' = j_i$, etc.) are made in Equation (49), then

$$\sigma^1(ifif) = \sum_{\substack{m_i m_i' \\ m_f m_f'}} \sum_{Q} (-1)^{m_f - m_f'} \begin{pmatrix} j_i & K & j_f \\ m_i & -Q & -m_f \end{pmatrix} \begin{pmatrix} j_i & K & j_f \\ m_i' & -Q & -m_f' \end{pmatrix} \delta_{m_f m_f'} \delta_{m_i m_i'}$$

$$- \sum_{\substack{m_i m_i' \\ m_f m_f'}} \sum_{Q} (-1)^{m_f - m_f'} \begin{pmatrix} j_i & K & j_f \\ m_i & -Q & -m_f \end{pmatrix} \begin{pmatrix} j_i & K & j_f \\ m_i' & -Q & -m_f' \end{pmatrix} \langle j_f m_f' | S^* | j_f m_f \rangle$$

$$\times \langle j_i m_i' | S | j_i m_i \rangle \quad . \qquad \text{(C1)}$$

The first term of Equation (C1) is just

$$\sum_{m_i m_f} \sum_{Q} \begin{pmatrix} j_i & K & j_f \\ m_i & -Q & -m_f \end{pmatrix} \begin{pmatrix} j_i & K & j_f \\ m_i & -Q & -m_f \end{pmatrix} = \sum\sum \begin{pmatrix} j_i & j_f & K \\ m_i & -m_f & -Q \end{pmatrix} \begin{pmatrix} j_i & j_f & K \\ m_i & -m_f & -Q \end{pmatrix}$$

$$= \sum_{Q} \frac{1}{(2K+1)} = 1 \qquad \text{(C2)}$$

Use in turn of the three relations,

$$\begin{pmatrix} a & b & c \\ \alpha & \beta & \gamma \end{pmatrix} = (-1)^{a-b-\gamma}(2c+1)^{-1/2}\langle ab\alpha\beta|c-\gamma\rangle \quad , \qquad \text{(C3)}$$

$$\langle ab\alpha\beta|c\gamma\rangle = (-1)^{b+\beta}\left[\frac{2c+1}{2a+1}\right]^{1/2}\langle cb-\gamma\beta|a-\alpha\rangle \quad , \qquad \text{(C4)}$$

and

$$\langle ab\alpha\beta|c\gamma\rangle = (-1)^{a+b-c}\langle ab-\alpha-\beta|c-\gamma\rangle \quad , \qquad \text{(C5)}$$

allows the second term of (C1) to be expressed such that (C1) can be written

$$\sigma^1(ifif) = 1 - \sum_{\substack{m_i m_i' \\ m_f' m_f}} \sum_{Q} \frac{\langle j_f 1 m_f Q|j_i m_i\rangle\langle j_f 1 m_f' Q|j_i m_i'\rangle}{(2j_i+1)}$$

$$\times \langle j_f m_f'|S^*|j_f m_f\rangle\langle j_i m_i'|S|j_i m_i\rangle \qquad \text{(C6)}$$

which in a slightly different notation is exactly the expression given by Anderson and Tsao and Curnutte.

APPENDIX D

DERIVATION OF ANDERSON-LIKE EXPRESSIONS FOR Λ^K

This appendix presents the details of the Anderson-like expansions of the cross sections given above in Equations (60)-(62) and Equations (83)-(85). The terminology follows that of TC. The expansion $T = T_0 + T_1 + T_2 + \ldots$ is substituted into the product $T^{-1}T$ giving $[(T^{-1})_0 + (T^{-1})_1 + (T^{-1})_2 + \ldots](T_0 + T_1 + T_2 + \ldots)$. The order of the expansion of σ^K is determined by the sum of the subscripts on the various terms of T and will be denoted as σ_n.

$\underline{\sigma^K(ifif)}$

Zeroth order: let $T = T_0 = 1$ and $T^{-1} = T_0^{-1} = 1$.

$$\sigma_0 = 1 - \sum_{\substack{m_i m_i' m_f m_f' \\ m_2 m_2' Q\ j_2'}} \sum \sum (-1)^{m_f - m_f'} (2j_2+1)^{-1} \begin{pmatrix} j_i & j_f & K \\ m_i & -m_f & -Q \end{pmatrix}$$

$$\times \begin{pmatrix} j_i & j_f & K \\ m_i' & -m_f' & -Q \end{pmatrix} \delta_{m_f m_f'} \delta_{m_i m_i'} \delta_{m_2 m_2'} \delta_{j_2 j_2'}$$

$$= 1 - \sum_{\substack{m_i m_f \\ m_2 Q}} \sum (2j_2+1)^{-1} \begin{pmatrix} j_i & j_f & K \\ m_i & -m_f & -Q \end{pmatrix} \begin{pmatrix} j_i & j_f & K \\ m_i & -m_f & -Q \end{pmatrix}$$

$$= 1 - \sum_{\substack{m_i m_f \\ Q}} \sum \begin{pmatrix} j_i & j_f & K \\ m_i & -m_f & -Q \end{pmatrix} \begin{pmatrix} j_i & j_f & K \\ m_i & -m_f & -Q \end{pmatrix}$$

$$= 1 - \sum_{Q=-K}^{+K} \frac{\delta_{KK}\delta_{QQ}}{(2K+1)} = 0 \ .$$

First order: let $T^{-1} = T_0^{-1} = 1$ and $T = T_1 = -iP$ or

$$T^{-1} = iP \text{ and } T = 1.$$

The first combination (i.e., $T_0^{-1} = 1$ and $T_1 = -iP$) gives

$$\sigma_1 = - \sum_{\substack{m_i m_i' m_f m_f' \\ m_2 m_2' Q \; j_2'}} \sum \sum (-1)^{m_f - m_f'} (2j_2+1)^{-1} \begin{pmatrix} j_i & j_f & K \\ m_i & -m_f & -Q \end{pmatrix} \begin{pmatrix} j_i & j_f & K \\ m_i' & -m_f' & -Q \end{pmatrix}$$

$$\times \ \delta_{j_2 j_2'} \delta_{m_2 m_2'} \delta_{m_f m_f'} \langle j_i m_i' j_2' m_2' | -iP | j_i m_i j_2 m_2 \rangle$$

If $m_f = m_f'$, as required by the factor $\delta_{m_f m_f'}$, the two 3-j symbols require that $m_i = m_i'$. Therefore, σ_1 can be written

$$\sigma_1 = i \sum_{\substack{m_i m_f \\ m_2 Q}} \sum (2j_2+1)^{-1} \begin{pmatrix} j_i & j_f & K \\ m_i & -m_f & -Q \end{pmatrix} \begin{pmatrix} j_i & j_f & K \\ m_i & -m_f & -Q \end{pmatrix}$$

$$\times \langle j_f m_f j_2 m_2 | P | j_i m_i j_2 m_2 \rangle \quad ,$$

or

$$\sigma_1 = i \sum_{m_i m_2} \sum [(2j_i+1)(2j_2+1)]^{-1} \langle j_i m_i j_2 m_2 | P | j_i m_i j_2 m_2 \rangle , \tag{D1}$$

where

$$\sum_{m_f Q} \begin{pmatrix} j_i & j_f & K \\ m_i & -m_f & -Q \end{pmatrix} \begin{pmatrix} j_i & j_f & K \\ m_i & -m_f & -Q \end{pmatrix} = \frac{\delta_{j_i j_i} \delta_{m_i m_i}}{(2j_i+1)}$$

has been used. By a completely analogous procedure, the combination $T_0 = 1, T_i^{-1} = iP$ gives

$$- i \sum_{m_f m_2} [(2j_f+1)(2j_2+1)]^{-1} \langle j_f m_f j_2 m_2 | P | j_f m_f j_2 m_2 \rangle \ . \tag{D2}$$

Second Order: Let $T^{-1} = 1$, $T = -P\,\frac{2}{2}$; $T^{-1} = -P\,\frac{2}{2}$, $T = 1$; or $T^{-1} = iP$, $T = -iP$.

The first combination gives

$$\sigma_2 = - \sum_{\substack{m_i m_i' m_f m_f' \\ m_2 m_2' Q\ j_2'}} \sum \sum (-1)^{m_f - m_f'} (2j_2+1)^{-1} \begin{pmatrix} j_i & j_f & K \\ m_i & -m_f & -Q \end{pmatrix} \begin{pmatrix} j_i & j_f & K \\ m_i' & -m_f' & -Q \end{pmatrix}$$

$$\times\ \delta_{j_2 j_2'} \delta_{m_f m_f'} \delta_{m_i m_i'} \langle j_i m_i' j_2' m_2' | -\tfrac{1}{2} P^2 | j_i m_i j_2 m_2 \rangle$$

$$= \frac{1}{2} \sum_{\substack{m_i m_f \\ m_2 Q}} \sum (2j_2+1)^{-1} \begin{pmatrix} j_i & j_f & K \\ m_i & -m_f & -Q \end{pmatrix} \begin{pmatrix} j_i & j_f & K \\ m_i & -m_f & -Q \end{pmatrix}$$

$$\times\ \langle j_i m_i j_2 m_2 | P^2 | j_i m_i j_2 m_2 \rangle$$

$$= \frac{1}{2} \sum_{m_i m_2} \sum [(2j_i+1)(2j_2+1]^{-1} \langle j_i m_i j_2 m_2 | P^2 | j_i m_i j_2 m_2 \rangle\ . \qquad \text{(D3)}$$

Similarly, the second combination gives

$$\frac{1}{2} \sum_{m_f m_2} \sum [(2j_f+1)(2j_2+1)]^{-1} \langle j_f m_f j_2 m_2 | P^2 | j_f m_f j_2 m_2 \rangle\ . \qquad \text{(D4)}$$

For $T^{-1} = iP$ and $T = -iP$,

$$\sigma_2 = - \sum_{\substack{m_i m_i' m_f m_f' \\ m_2 m_2' Q\ j_2'}} \sum \sum (-1)^{m_f - m_f'} (2j_2+1)^{-1} \begin{pmatrix} j_i & j_f & K \\ m_i & -m_f & -Q \end{pmatrix} \begin{pmatrix} j_i & j_f & K \\ m_i' & -m_f' & -Q \end{pmatrix}$$

$$\times\ \langle j_f m_f j_2 m_2 | P | j_f m_f' j_2' m_2' \rangle \langle j_i m_i' j_2' m_2' | P | j_i m_i j_2 m_2 \rangle\ , \qquad \text{(D5)}$$

which cannot be simplified further. This completes the Anderson-like expansion of $\sigma^K(ifif)$. The first order term is pure imaginary and therefore contributes only to the lineshift. It will not be considered further here. Combination of Equations (D3)-(D5) gives Equation (60) of Chapter II.

$\underline{\sigma^K(i'i'ii)}$

In Equation (50) of Chapter II the symbol j in $\sigma^K(j_i'j_f'j_ij_f)$ and in $\delta_{j_ij_i'}$, <u>etc</u>. should be considered to be a set of quantum numbers. If $j \neq j'$, the outer terms drop out giving the purely middle term, Equation (50).

Both zeroth and first order contributions to $\sigma^K(i'i'ii)$ are zero in the same manner as for $\sigma^K(i'f'if)$.

Second Order: Let $T^{-1} = 1$ and $T = -\frac{1}{2}P^2$; $T = 1$ and $T^{-1} = -\frac{1}{2}P^2$; and $T^{-1} = iP$ and $T = -iP$.

Again, the first two combinations are zero, while the last combination gives

$$- \sum_{\substack{m_im_i'n_in_i' \\ m_2m_2'Q\; j_2'}} \sum \sum (-1)^{j_i-j_i'+n_i-n_i'}(2j_2+1)^{-1} \left[\frac{2j_i'+1}{2j_i+1}\right]^{1/2}$$

$$\times \begin{pmatrix} j_i & j_i & K \\ m_i & -n_i & -Q \end{pmatrix} \begin{pmatrix} j_i' & j_i' & K \\ m_i' & -n_i' & -Q \end{pmatrix}$$

$$\times \langle j_in_ij_2m_2|P|j_i'n_i'j_2'm_2'\rangle\langle j_i'm_i'j_2'm_2'|P|j_im_ij_2m_2\rangle \,, \qquad \text{(D6)}$$

which is Equation (61) of Chapter II.

σ^K(iiii)

The zeroth order term is zero by reasoning analogous to that used for the other cross sections.

First Order: Let $T^{-1} = 1$ and $T = -iP$; $T = 1$ and $T^{-1} = iP$.

The first combination gives

$$\sigma_1 = - \sum_{\substack{m_i m_i' n_i n_i' \\ m_2 m_2' Q\ j_2'}} \sum \sum (-1)^{n_i - n_i'} (2j_2+1)^{-1} \begin{pmatrix} j_i & j_i & K \\ m_i & -n_i & -Q \end{pmatrix} \begin{pmatrix} j_i & j_i & K \\ m_i' & -n_i' & -Q \end{pmatrix}$$

$$\times\ \delta_{n_i n_i'} \delta_{m_2 m_2'} \delta_{j_2 j_2'} \langle j_i m_i' j_2' m_2' | -iP | j_i m_i j_2 m_2 \rangle$$

$$= i \sum_{m_i m_2} \sum [(2j_i+1)(2j_2+1)]^{-1} \langle j_i m_i j_2 m_2 | P | j_i m_i j_2 m_2 \rangle \ .$$

A similar calculation shows that the second combination gives the negative of this result, so that the first order term is identically zero.

Second Order: Let $T^{-1} = 1$ and $T = -\frac{1}{2}P^2$; $T = 1$ and $T^{-1} = -\frac{1}{2}P^2$; and $T^{-1} = iP$ and $T = -iP$.

The first two combinations are completely analogous to the corresponding part of the second order expansion of σ^K(ifif) and give

$$\frac{1}{2} \sum_{m_i m_2} [(2j_i+1)(2j_2+1)]^{-1} \langle j_i m_i j_2 m_2 | P^2 | j_i m_i j_2 m_2 \rangle \qquad \text{(D7)}$$

and

$$\frac{1}{2} \sum_{n_i m_2} [(2j_i+1)(2j_2+1)]^{-1} \langle j_i n_i j_2 m_2 | P^2 | j_i n_i j_2 m_2 \rangle \ , \qquad \text{(D8)}$$

respectively. The third combination gives

$$- \sum_{\substack{m_i m'_i n_i n'_i \\ m_2 m'_2 Q \ j'_2}} \sum \sum (-1)^{n_i - n'_i} (2j_2+1)^{-1} \begin{pmatrix} j_i & j_i & K \\ m_i & -n_i & -Q \end{pmatrix} \begin{pmatrix} j_i & j_i & K \\ m'_i & -n'_i & -Q \end{pmatrix}$$

$$\times \langle j_i n_i j_2 m_2 | P | j_i n'_i j'_2 m'_2 \rangle \langle j_i m'_i j'_2 m'_2 | P | j_i m_i j_2 m_2 \rangle . \qquad \text{(D9)}$$

Equations (D7)-(D9) give Equation (62) of Chapter II.

The next step is to evaluate the matrix elements of the P operator. Tsao and Curnutte have done this for $\sigma^1(ifif)$. The result may be immediately generalized to $\sigma^K(ifif)$. The outer term is

$$\frac{1}{32\pi} \sum_{\substack{j'_i j'_2 k_1 k_2 \\ \lambda_1 \lambda_2}} \sum |a^{(\lambda k j)}|^2 \langle j_i k_1 K_i 0 | j'_i K_i \rangle^2 \langle j_2 k_2 K_2 0 | j'_2 K_2 \rangle^2$$

$$= \frac{1}{32\pi} \sum_{\substack{j'_i j'_2 k_1 k_2 \\ \lambda_1 \lambda_2}} \sum |a^{(\lambda k j)}|^2 (2j'_i+1)(2j'_2+1) \begin{pmatrix} j_i & j'_i & k_1 \\ K_i & -K_i & 0 \end{pmatrix}^2$$

$$\times \begin{pmatrix} j_2 & j'_2 & K_2 \\ K_2 & -K_2 & 0 \end{pmatrix}^2 \qquad \text{(D10)}$$

with a similar term for j_f. The middle term is

$$(-1)^{j_i+j_f+K}\frac{[(2j_i+1)(2j_f+1)]^{1/2}}{16\pi^2}\sum\sum_{\substack{k_1k_2j_2'\\ \lambda_1\lambda_2}}(-1)^{k_1+\lambda_1+\lambda_2}$$

$$\times\ a(k_1k_2\lambda_1\lambda_2j)\bar{a}(k_1k_2-\lambda_1\lambda_2j')\langle j_ik_1K_i0|j_iK_i\rangle\langle j_fk_1K_f0|j_fK_f\rangle$$

$$\times\ \langle j_2k_2K_20|j_2'K_2\rangle^2W(j_ij_fj_ij_f;Kk_1)$$

$$=\frac{(2j_i+1)(2j_f+1)}{16\pi^2}\sum\sum_{k_1k_2\lambda_1\lambda_2j_2'}(-1)^{\lambda_1+\lambda_2+k_1+K}(2j_2'+1)$$

$$\times\ a(k_1k_2\lambda_1\lambda_2j)\bar{a}(k_kk_2-\lambda_1-\lambda_2j')\begin{pmatrix}j_i & j_i & k_1\\ K_i & -K_i & 0\end{pmatrix}\begin{pmatrix}j_f & j_f & k_1\\ K_f & -K_f & 0\end{pmatrix}$$

$$\times\ \begin{pmatrix}j_2 & j_2' & k_2\\ K_2 & -K_2 & 0\end{pmatrix}^2\begin{Bmatrix}j_i & j_f & K\\ j_f & j_i & k_1\end{Bmatrix}, \qquad \text{(D11)}$$

where W(abcd;ef) is a Racah symbol, related to the 6-j symbol by(71)

$$W(abcd;ef) = (-1)^{a+b+c+d}\begin{Bmatrix}a & b & e\\ d & c & f\end{Bmatrix}.$$

Substitution of the matrix elements of P given in Equation (80) into the expression for $\sigma^K(i'i'ii)$ gives

$$\sigma^K(i'i'ii) = - \sum_{\substack{m_i m_i' k_1 k_2 k_1' k_2' \\ n_i n_i' \lambda_1 \lambda_2 \lambda_1' \lambda_2' \\ m_2 m_2' j_2' Q}} \Sigma\,\Sigma\,\Sigma \; (-1)^{j_i - j_i' + m_i - m_i'} (2j_2+1)^{-1}$$

$$\times \begin{pmatrix} j_i & j_i & K \\ m_i & -n_i & -Q \end{pmatrix} \begin{pmatrix} j_i' & j_i' & K \\ m_i' & -n_i' & -Q \end{pmatrix} |a^{\lambda k j}|^2 \, \Delta(j_i k_i j_i') \Delta(j_2 k_2 j_2')$$

$$\times \Delta(j_i k_1' j_i') \Delta(j_2 k_2' j_2') \langle j_i k_1 m_i \lambda_1 | j_i' m_i' \rangle \langle j_2 k_2 m_2 \lambda_2 | j_2' m_2' \rangle$$

$$\times \langle j_i k_1' n_i \lambda_1' | j_i' n_i' \rangle \langle j_2 k_2' \pi_2 \lambda_2' | j_2' m_2' \rangle \left[\frac{2j_i'+1}{2j_i+1}\right]^{1/2} .$$

After using the definition of $\Delta(abc)$ given in Equation (81), using Equation (82), and setting $k_1 = k_1'$, $k_2 = k_2'$, $\lambda_1 = \lambda_1'$ and $\lambda_2 = \lambda_2'$ (the validity of which is discussed in Appendix E), the above expression may be written

$$\sigma^K(i'i'ii) = - \sum_{\substack{m_i m_i' k_1 k_2 \\ n_i n_i' \lambda_1 \lambda_2 \\ j_2' Q}} \Sigma\,\Sigma \; (-1)^{j_i - j_i' + m_i - n_i'} \frac{|a^{(\lambda k j)}|^2}{16\pi^2}$$

$$\times \left[\frac{2j_i'+1}{2j_i+1}\right]^{1/2} (2k_1+1)(2j_i+1)(2j_i'+1)(2j_2'+1) \begin{pmatrix} j_i & j_i' & k_1 \\ K_i & -K_i & 0 \end{pmatrix}^2$$

$$\times \begin{pmatrix} j_2 & j_2' & k_2 \\ K_2 & -K_2 & 0 \end{pmatrix}^2 \begin{pmatrix} j_i & j_i & K \\ m_i & -n_i & -Q \end{pmatrix} \begin{pmatrix} j_i' & j_i' & K \\ m_i' & -n_i' & -Q \end{pmatrix} \begin{pmatrix} j_i & j_i' & k_1 \\ m_i & -m_i' & \lambda_1 \end{pmatrix} \begin{pmatrix} j_i & j_i' & k_1 \\ n_i & -n_i' & \lambda_1 \end{pmatrix} .$$

The product of the last four 3-j symbols and the factor $(-1)^{m_i-n_i'}$ may be written as

$$(-1)^{j_i+j_i'+k_1+m_i-n_i'} \begin{pmatrix} j_i' & j_i' & K \\ -m_i' & n_i' & Q \end{pmatrix} \begin{pmatrix} j_i & j_i & K \\ +n_i & -m_i & -Q \end{pmatrix} \begin{pmatrix} j_i & j_i' & k_1 \\ -m_i & m_i' & -\lambda_1 \end{pmatrix}$$

$$\times \begin{pmatrix} j_i & j_i' & k_1 \\ -n_i & n_i' & -\lambda_1 \end{pmatrix} \qquad \text{(D12)}$$

Now, the sum rule$^{(71)}$

$$\sum_{\alpha\beta\gamma\alpha'\beta'} \sum (-1)^{\alpha+\beta+\gamma+c+C} \begin{pmatrix} A & b & C \\ -\alpha & \beta' & \gamma \end{pmatrix} \begin{pmatrix} a & B & C \\ \alpha' & \beta & -\gamma \end{pmatrix} \begin{pmatrix} B & A & c \\ -\beta & \alpha & \gamma' \end{pmatrix}$$

$$\times \begin{pmatrix} a & b & c_1 \\ \alpha' & \beta' & \gamma_1' \end{pmatrix} = \frac{\delta_{cc_1}\delta_{\gamma'\gamma_1'}}{(2c+1)} \begin{Bmatrix} a & b & c \\ A & B & C \end{Bmatrix} \qquad \text{(D13)}$$

is used with $A = j_i$, $B = j_i'$, $C = K$, $a = j_i'$, $b = j_i$, $c = k_1$, $\alpha = m_i$, $\beta = m_i'$, $\gamma = Q$, $\alpha' = -m_i'$, $\beta' = m_i$, and $\gamma' = \lambda_1$. With this rule and the observations that

$\alpha+\beta+\gamma = m_i' + m_i + Q$ and $-m_i' + n_i' + Q = 0$, which in turn implies that $n_i' = m_i'-Q$ and therefore that $m_i-n_i' = m_i-m_i' + Q$, it is possible to sum Equation (D12) over m_i, m_i', n_i, n_i', and Q to give the right side of Equation (D13). This gives the final expression for $\sigma^K(i'i'ii)$ as Equation (84).

The outer term of $\sigma^K(iiii)$ is just twice one outer term of $\sigma^K(ifif)$. Therefore, it can be written

$$\frac{1}{16\pi^2} \sum_{\substack{k_1 k_2 j_i' \\ \lambda_1 \lambda_2 j_2'}} \sum |a^{(\lambda k j)}|^2 (2j_i'+1)(2j_2'+1) \begin{pmatrix} j_i & j_i' & k_1 \\ K_i & -K_i & 0 \end{pmatrix}^2 \times \begin{pmatrix} j_2 & j_2' & k_2 \\ K_2 & -K_2 & 0 \end{pmatrix}^2 .$$

The middle term of $\sigma^K(iiii)$ may be obtained by the same procedure used to obtain $\sigma^K(i'i'ii)$. The only change is that j_i' is replaced by j_i.

APPENDIX E

PROOF OF RESTRICTIONS ON MULTIPOLE ORDER OF POTENTIALS IMPOSED IN APPENDIX D

In appendix D the restrictions $k_1 = k_1'$, $k_2 = k_2'$, $\lambda_1 = \lambda_1'$ and $\lambda_2 = \lambda_2'$ were imposed in the derivation of $\sigma^K(i'i'ii)$. In this appendix these restrictions are shown to be rigorous. If the assumption is made that the above conditions do not hold, $\sigma^0(i'i'ii)$ may be written as

$$\sigma^0(i'i'ii) = - \sum_{\substack{m_i m_i' k_1 k_2 k_1' k_2' \\ m_2 m_2' \lambda_1 \lambda_2 \lambda_1' \lambda_2'}} \Sigma \Sigma \Sigma \; (-1)^{j_i - j_i' + m_i - m_i'} (2j_2+1)^{-1}$$

$$\times \; a^{(\lambda k j)} a^{(\lambda' k' j)}$$

$$\times \; \Delta(j_i k_1 j_i')\Delta(j_i k_1' j_i')\Delta(j_2 k_2 j_2')\Delta(j_2 k_2' j_2')$$

$$\times \begin{pmatrix} j_i' & j_i' & 0 \\ m_i' & -m_i' & 0 \end{pmatrix} \begin{pmatrix} j_i & j_i & 0 \\ m_i & -m_i & 0 \end{pmatrix} \langle j_i k_1 m_i \lambda_1 | j_i' m_i' \rangle \langle j_i k_1' m_i \lambda_1' | j_i' m_i' \rangle$$

$$\times \; \langle j_2 k_2 m_2 \lambda_2 | j_2' m_2' \rangle \langle j_2 k_2' m_2 \lambda_2' | j_2' m_2' \rangle \quad .$$

The symmetry properties of the Clebsch-Gordon coefficients demand that $\lambda_1 = \lambda_1'$ and $\lambda_2 = \lambda_2'$. With these restrictions, rewriting the above expression in terms of 3-j symbols gives

$$\frac{-(2j_i+1)(2j_i'+1)}{16\pi^2} \sum_{\substack{m_i m_i' k_1 k_2 \\ m_2 m_2' k_1' k_2' \\ j_2' \lambda_1 \lambda_2}} \sum a^{\lambda k j} a^{\lambda k' j} (2j_2'+1) \begin{pmatrix} j_i' & j_i' & 0 \\ m_i' & -m_i' & 0 \end{pmatrix}$$

$$\times \begin{pmatrix} j_i & j_i & 0 \\ m_i & -m_i & 0 \end{pmatrix} (-1)^{j_i - j_i' + m_i - m_i'} [(2k_1+1)(2k_1'+1)(2k_2+1)$$

$$\times (2k_2'+1)]^{1/2} \begin{pmatrix} j_i' & j_i & k_1 \\ K_i & -K_i & 0 \end{pmatrix} \begin{pmatrix} j_i' & j_i & k_1' \\ K_i & -K_i & 0 \end{pmatrix} \begin{pmatrix} j_2' & j_2 & k_2 \\ K_2 & -K_2 & 0 \end{pmatrix}$$

$$\times \begin{pmatrix} j_2' & j_2 & k_2' \\ K_2 & -K_2 & 0 \end{pmatrix} \begin{pmatrix} j_i & j_i' & k_1 \\ m_i & -m_i' & \lambda_1 \end{pmatrix} \begin{pmatrix} j_i & j_i' & k_1' \\ m_i & -m_i' & \lambda_1 \end{pmatrix} \begin{pmatrix} j_2 & j_2' & k_2' \\ m_2 & -m_2' & \lambda_2 \end{pmatrix}$$

$$\times \begin{pmatrix} j_2 & j_2' & k_2 \\ m_2 & -m_2' & \lambda_2 \end{pmatrix} .$$

Summation over m_2 and m_2' then demands that $k_2 = k_2'$ and gives

$$\sigma^0(i'i'ii) = \frac{-(2j_i+1)(2j_i'+1)}{16\pi^2} \sum_{\substack{m_i m_i' k_1 k_2 \\ j_2' k_1' \lambda_1 \lambda_2}} \sum \sum (-1)^{j_i - j_i' + m_i - m_i'}$$

$$\times\ a^{\lambda kj}\ a^{\lambda k'j}(2j_2'+1)[(2k_1+1)(2k_1'+1)]^{1/2} \begin{pmatrix} j_i' & j_i' & 0 \\ m_i' & -m_i' & 0 \end{pmatrix}$$

$$\times \begin{pmatrix} j_i & j_i & 0 \\ m_i & -m_i & 0 \end{pmatrix} \begin{pmatrix} j_i & j_i' & k_1 \\ m_i & -m_i' & \lambda_1 \end{pmatrix} \begin{pmatrix} j_i & j_i' & k_1' \\ m_i & -m_i' & \lambda_1 \end{pmatrix} \begin{pmatrix} j_i' & j_i & k_1 \\ K_i & -K_i & 0 \end{pmatrix} \begin{pmatrix} j_i' & j_i & k_1' \\ K_i & -K_i & 0 \end{pmatrix}$$

$$\times \begin{pmatrix} j_2' & j_2 & k_2 \\ K_2 & -K_2 & 0 \end{pmatrix}^2 .$$

Finally, Equation (D13) may be used to show that $k_1 = k_1'$. These results may be easily generalized to arbitrary K and also applied to $\sigma^K(iiii)_m$.

APPENDIX F

MATRIX ELEMENTS OF MULTIPOLE MOMENT OPERATORS FOR ONE-ENDED AND PARITY ADAPTED SYMMETRIC TOP EIGENFUNCTIONS

This appendix considers matrix elements of dipole and quadrupole moments for both "one-ended" and proper symmetric top eigenfunctions.

Following the notation of Anderson(53) parity-adapted symmetric top eigenfunctions are written as

$$\psi_+ = \frac{1}{\sqrt{2}} (\psi_{+K} + \psi_{-K}); \quad \psi_- = \frac{1}{\sqrt{2}} (\psi_{+K} - \psi_{-K}) \tag{F1}$$

where $\psi_{\pm K}$ are the usual symmetric top eigenfunctions for $J = J$ and $k = \pm K$. Therefore,

$$\psi_{+K} = \frac{1}{\sqrt{2}} (\psi_+ + \psi_-); \qquad \psi_{-K} = \frac{1}{\sqrt{2}} (\psi_+ - \psi_-) \ . \tag{F2}$$

By using these relations and the fact that the dipole moment μ has odd parity, it is easy to show that

$$\langle K|\mu|K\rangle = \tfrac{1}{2}[\langle +|\mu|-\rangle + \langle -|\mu|+\rangle] \ ,$$

$$\langle -K|\mu|-K\rangle = -\tfrac{1}{2}[\langle +|\mu|-\rangle + \langle -|\mu|+\rangle] \ .$$

That is,

$$<K|\mu|K> = -<-K|\mu|-K>. \qquad (F3)$$

Equation (F3) can be demonstrated directly using

$$<J'K'M'|Y^{j}_{m}(\theta\phi)|JKM>$$

$$= (-1)^{K'+M'} \left[\frac{(2J+1)(2J'+1)(2j+1)}{4\pi}\right]^{1/2}$$

$$\times \begin{pmatrix} J & J' & j \\ K & -K' & 0 \end{pmatrix} \begin{pmatrix} J & J' & j \\ M & -M' & m \end{pmatrix} \qquad (F4)$$

with j = 1 and m = 0. Equations (F1) and (F2) can also be used to show that

$$<+|\mu|-> = \frac{1}{2}[<K|\mu|K>-<K|\mu|-K> + <-K|\mu|K> -<-K|\mu|-K\ ]$$

$$= <K|\mu|K>\ . \qquad (F5)$$

The last step follows from application of Equation (F4) to obtain

$$<K|\mu|-K> = <-K|\mu|K> = 0$$

and

$$\langle K|\mu|K\rangle = -\langle -K|\mu|-K\rangle \quad . \tag{F6}$$

Equation (F5) shows that the matrix elements of the dipole moment operator may be taken using either "one-ended" or proper eigenfunctions.

By using Equations (F1) and (F2) and the fact that the quadrupole moment Q has even parity, it is easy to show that

$$\langle K|Q|K\rangle = \langle -K|Q|-K\rangle \tag{F7}$$

and

$$\langle +|Q|+\rangle = \frac{1}{2}[\langle +K|Q|+K\rangle + \langle -K|Q|-K\rangle + \langle +K|Q|-K\rangle + \langle -K|Q|+K\rangle].$$

Equation (F4) may be used with $j = 2$ to show that

$$\langle +|Q|+\rangle = \langle +K|Q|+K\rangle \tag{F8}$$

APPENDIX G

SUMMARY OF RESONANCE FUNCTIONS AND HARD-SPHERE CUTOFF CALCULATIONS

This appendix will give explicit expressions for the $a^{\lambda kj}$ factors occurring in the expressions for $\sigma^K(i'f'if)$ in Chapter II. Comparison in turn of Equation (108) of TC with Equations (133), (150) and (161) of TC leads to the following identifications for dipole-dipole, dipole-quadrupole and quadrupole-quadrupole interactions, respectively:

$$\frac{1}{32\pi^2}|a^{\lambda kj}|^2 = \frac{4}{9}\left(\frac{\mu_1\mu_2}{\hbar v}\right)^2 \frac{1}{b^4} f_1(k), \quad \mu\text{-}\mu; \tag{G1}$$

$$\frac{1}{32\pi^2}|a^{\lambda kj}|^2 = \frac{4}{45}\left(\frac{\mu_1 Q_2}{\hbar v}\right)^2 \frac{1}{b^6} f_2(k), \quad \begin{matrix}\mu\text{-}Q\\ Q\text{-}\mu\end{matrix}\ ; \tag{G2}$$

and

$$\frac{1}{32\pi^2}|a^{\lambda kj}|^2 = \frac{1}{25}\left(\frac{Q_1 Q_2}{\hbar v}\right)^2 \frac{1}{b^8} f_3(k)\ , \quad Q\text{-}Q\ . \tag{G3}$$

In the above equations $k = \frac{\omega b}{v}$, where ω is an internal state energy difference, and b is the impact parameter. The functions $f_1(k)$, $f_2(k)$ and $f_3(k)$ are defined as

$$f_1(k) = \frac{1}{4} k^4[K_2^2(k) + 4K_1^2(k) + 3K_0^2(k)]$$

$$f_2(k) = \frac{1}{64} k^2[K_3^2(k) + 6K_2^2(k) + 15K_1^2(k) + 10K_0^2(k)]$$

$$f_3(k) = \frac{1}{2304} k^8[K_4^2(k) + 8K_3^2(k) + 28K_2^2(k) + 56K_1^2(k) + 35K_0^2(k)]$$

$$f_n(0) = 1 \qquad n = 1,2,3$$

As regards the middle terms, TC show that

$$\sum_{\lambda_1\lambda_2} (-1)^{\lambda_1+\lambda_2} a(k_1k_2\lambda_1\lambda_2j)a'(k_1k_2-\lambda_1-\lambda_2j') = \sum_{\lambda_1\lambda_2} x\ |a^{\lambda kj}|^2 \quad ,$$

so that the above equations may also be used to compute middle terms of $\sigma^K(i'f'if)$.

The hard sphere cutoff is determined by the condition

$$\sigma_{j_2}^K(b_0) = 1 \ .$$

That is, the hard sphere cutoff is that value of b (denoted b_0) such that $\sigma_{j_2}^K$ is one. Integration of $\sigma_{j_2}^K(b)$

over b gives

$$\sigma^K_{j_2} = \pi b_0^2 + \int_{b_0}^{\infty} 2\pi b \ \sigma^K_{j_2}(b)db$$

If, (for simplicity) only a μ-μ potential is considered the integral to be evaluated is

$$\int_{b_0}^{\infty} b[K_2^2 + 4K_1^2 + 3K_0^2]db$$

$$= \frac{1}{2} b_0^2[K_3K_1 + 4K_2K_0 - K_2^2 - K_1^2 - 3K_0^2]_{k=k_0} \quad .$$

The notation $[\quad]_{k=k_0}$ indicates that the K functions are to be evaluated at $k = k_0 = \frac{\omega b_0}{v}$. As a result of these integrations $\sigma^K_{j_2}$ may be written as

$$\sigma^K_{j_2} = \pi b_0^2\{1 + \frac{1}{b_0^4} [\sum_{j_i' j_2'} Ali(j_i' j_2')F_1(k_0) +$$

$$+ \sum_{j_f' j_2'} Alf(j_f' j_2')F_1(k_0) + \sum_{j_2'} Alm(j_2')F_1(k_0)]\}.$$

The above equation is specific for $\sigma^K_{j_2}$(ifif) and a μ-μ potential. Similar expressions for $\sigma^K_{j_2}$(ifi'f') are easily obtained from expressions in Chapter II. With the following expressions for $F_n(k)$ the A coefficients are easily obtained.

$$F_1(k) = \frac{1}{4} k^4 [K_3K_1 + 4K_2K_0 - K_2^2 - K_1^2 - 3K_0^2]; \quad \mu\text{-}\mu$$

$$F_2(k) = \frac{1}{64} k^6 [K_4K_2 + 6K_3K_1 + 15K_2K_0 - K_3^2 - 6K_2^2$$

$$- 5K_1^2 - 10K_0^2]; \quad \begin{matrix}\mu\text{-}Q \\ Q\text{-}\mu\end{matrix}$$

$$F_3(k) = \frac{1}{2304} k^8 [K_5K_3 + 8K_4K_2 + 28K_3K_1 + 56K_2K_0$$

$$- K_4^2 - 8K_3^2 - 28K_2^2 - 21K_1^2 - 35K_0^2]; \quad Q\text{-}Q$$

$$F_1(0) = 1$$
$$F_2(0) = \frac{1}{2}$$
$$F_3(0) = \frac{1}{3}$$

The values of $f_n(0)$ and $F_n(0)$ are necessary when the internal energy state differences are zero, <u>i.e.</u>, $\omega = 0$. This is the case in the sudden approximation.

APPENDIX H

DETERMINATION OF THE SUDDEN APPROXIMATION B_0

The objective of this appendix is to obtain the correct A_λ function for the relaxation coefficients Λ^K_{ifif} and Λ^K_{iiii}. By using Equations (20) and (21) of Chapter IV $\sum_{j'} \Lambda^0_{j'j'jj}$ can be written as

$$\sum_{j'} \Lambda^0_{j'j'jj} = -\left(\frac{2\pi\mu_1\mu_2}{\hbar v}\right) \sum_{j'\lambda} (2j'+1) \begin{pmatrix} j & j' & \lambda \\ 0 & 0 & 0 \end{pmatrix}^2 A_\lambda \qquad \text{(H1)}$$

$$= -\left(\frac{2\pi\mu_1\mu_2}{\hbar v}\right) A_\lambda$$

$$= -\left(\frac{2\pi\mu_1\mu_2}{\hbar v}\right) \frac{\pi^2}{8} \quad . \qquad \text{(H2)}$$

Also,

$$\sum_{j'} \Lambda^0_{j'j'jj} = L^0_{jjjj} + \sum_{j'\neq j} \Lambda^0_{j'j'jj} \quad . \qquad \text{(H3)}$$

The symbol L^0_{jjjj} is used instead of Λ^0_{jjjj} because the term in the sum for $j = j'$ is not what has been defined previously as Λ^0_{jjjj}; <u>i.e.</u>, L^0_{jjjj} is not proportional to the total collisional rate of transfer out of level j.

From the discussion of $\Lambda^K_{i'i'ii}$ of Chapter I, the following relation must hold:

$$\Lambda^0_{jjjj} = - \sum_{j'\neq j} \Lambda^0_{j'j'jj} \quad . \tag{H4}$$

Therefore,

$$\sum_{j'} \Lambda^0_{j'j'jj} = +L^0_{jjjj} - \Lambda^0_{jjjj} = -C \frac{\pi^2}{8} \; , \tag{H5}$$

and

$$\Lambda^0_{jjjj} = L^0_{jjjj} + C \frac{\pi^2}{8}$$

$$= C[-(2j+1) \begin{pmatrix} j & j & \lambda \\ 0 & 0 & 0 \end{pmatrix}^2 A_\lambda + \frac{\pi^2}{8}] \; . \tag{H6}$$

In the above

$$C = \frac{2\pi\mu_1\mu_2}{\hbar v} \; .$$

Considering the case j = 0 in Equation (I6) gives

$$\Lambda^0_{0000} = C[-A_0 + \frac{\pi^2}{8}]$$

$$= +C(\frac{\pi^2}{12}) \; . \tag{H7}$$

Therefore, the quantity B_0 of Chapter V is

$$B_0 = \frac{-\pi^2}{12} \quad . \tag{H8}$$

In the above argument only the case for K = 0 and linear rotors was considered. However, the argument is valid for any tensor order and for symmetric tops as well, because the A_λ and B_0 functions do not depend on these factors.

APPENDIX I

ANALYTICAL EVALUATION OF IMPACT PARAMETER INTEGRATION IN THE ENERGY CORRECTION TO THE SUDDEN APPROXIMATION

The integral

$$g(s) = \int_0^\infty \chi^{s-1} K_\mu(ax) K_\nu(ax)dx$$

is given in reference (158) as

$$g(s) = \frac{2^{s-3}\ a^{-s}}{\Gamma(s)}\ \Gamma[\tfrac{1}{2}(s+\nu+\mu)]\Gamma[\tfrac{1}{2}(s-\mu+\nu)]\Gamma[\tfrac{1}{2}(s+\mu-\nu)]$$

$$\times\ \Gamma[\tfrac{1}{2}(s-\mu-\nu)] \quad . \tag{I1}$$

The first integral in Equation (251) becomes

$$\int_0^\infty f(k)db = \frac{1}{4} \int_0^\infty k^4[K_2^2 + 4K_1^2 + 3K_0^2]db$$

$$= (\frac{\omega}{v})^4[\frac{1}{4} \int_0^\infty b^4K_2^2(\frac{\omega}{v}b)db + \int_0^\infty b^4K_1^2(\frac{\omega}{v}b)db$$

$$+ \frac{3}{4} \int_0^\infty b^4K_0^2(\frac{\omega}{v}b)db]$$

Repeated use of Equation (I1) leads to

$$= (\frac{v}{\omega}) (\frac{4}{3}) (\frac{3}{2})^3 [\Gamma(\frac{3}{2})]^4$$

In the above the following relations concerning gamma functions have been used.

$$\Gamma(p+1) = p!, \quad p \text{ integer}$$

$$\Gamma(\chi+1) = \chi\Gamma(\chi) \quad .$$

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