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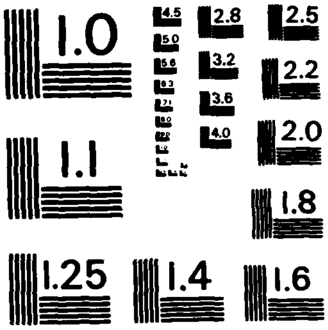

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CALCULATION OF H_2O FAR-WING ABSORPTION WITHIN THE SINGLE-PERTURBER APPROXIMATION

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Calculations of H_2O self-broadening have been carried out for near and far-wing absorption. For the far-wing case, the calculations are based on the single perturber approximation. Only collisions involving continuum states of the two-body system are considered, and an uncoupled-line approximation is assumed. An isotropic interaction potential is included exactly, while anisotropic interactions are treated in perturbation theory. For the anisotropic interaction, both dipole-dipole and dipole-quadrupole collisions are considered in detail.

Results of the present calculations indicate, in the near wings, that the dipole-dipole interaction is strongly dominant. As one progresses to the far wings, it is found that the dipole-quadrupole and (by implication) the higher-order multipole interactions become increasingly important. The general indications are that the far-wing absorption is dominated by strong, short-ranged interactions which require detailed analysis.

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Cont. of Block 11:

Within the Single-Perturber Approximation

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1.0 INTRODUCTION

The absorption of infrared radiation by water vapor in the atmosphere is of great interest since it plays a prominent role in determining atmospheric transmission to solar or laser radiation, and the heat balance of the lower atmosphere.[1] Of particular concern for long path transmission of laser signals is the so-called continuum absorption in the window spectral regions. This structureless absorption has been studied experimentally by Bignell[2] and by Burch[3-5] and collaborators; it has been treated phenomenologically by Clough, et al.[6]. For self-broadening of H_2O in the 1000 cm^{-1} window region, the absorption is characterized by a strong negative temperature dependence.

Theoretical models advanced to explain the absorption include far-wing absorption from distant strong lines, dimer (or cluster) absorption, collision-induced absorption, or some combination of the above.

The far-wing theory and calculations presented in this Report contain the following features:

- The primary approximation is the single-perturber approximation. This assumes that the far-wing absorption can be obtained by calculating the absorption due to a single radiator-perturber pair, and then multiplying by the total number of pairs. This is consistent with the observed density dependence of the absorption coefficient. The single-perturber approximation for absorption in window regions seems to have first been discussed by Baranger.[7] The approximation can also be obtained as a limiting case from the dipole autocorrelation function in the time domain.[8] One of the present Authors has also discussed this approach using a T-matrix formalism[9] directly in the frequency domain.

- The present treatment considers absorption arising only from <u>unbound</u> states of the two-body system.

- Line coupling contributions, although formally contained in the theory, have not been included in the present calculations.

- It is assumed that the anisotropic interaction can be treated using a multipole expansion. For strong, close collisions this assumption may break down.

- Perturbation theory in the anisotropic potential is also assumed. An isotropic, Lennard-Jones, potential is included and is treated exactly.

- A unitarity cutoff (analogous to Anderson's well-known S_2 cutoff) is employed in the strong collision limit. A rigorous justification of this cutoff procedure is lacking and remains a problem in terms of interpretation of results.

- The theory rigorously satisfies the fluctuation-dissipation theorem (FDT)[8-10] if the unitarity cutoff is ignored. If such a cutoff is applied, the validity of the FDT depends on the manner in which the cutoff procedure is employed. In the past, failure to satisfy the FDT has lead to ambigious interpretations of far-wing absorption.

In Sections 2, 3, and 4 we present the general theoretical approach used in the calculations of far-wing absorption. In Section 5 we present results from these calculations.

2.0 GENERAL THEORY - THE SINGLE-PERTURBER APPROXIMATION

In the problem of line broadening in plasmas, Baranger[7] has discussed application of the "one-electron" approximation to the far-wing and window spectral regions. For the case of molecular collisional broadening we shall employ the term "single-perturber" approximation.

The justification given by Baranger for the single-perturber approximation is essentially that the far-wing absorption will be governed by the behavior of the dipole autocorrelation function at very short times. This statement must be regarded with some caution because the approximation is as much an expansion in density as in small times.

The general statement of the approximation is as follows:

"At sufficiently low densities one may calculate the far-wing spectrum by computing the absorption due to a single pair consisting of one radiator and perturber, and then multiplying by the total number of pairs."

It should be noted that this is distinct from the binary collision approximation which assumes the absorption can be computed by calculating the absorption arising from a single radiator and N_{per} perturbers which it may interact, and then multiplying by the number of radiating molecules, N_{rad}. The binary collision approximation envisions that the radiator interacts with one perturber at a time, however, over the time scale of interest for the radiative process, the radiator interacts with many perturbers. At low densities, the binary-collision approximation leads to the well-known Lorentzian (impact) lineshape for isolated lines near the linecenter. As pointed out by Baranger,[7] the rounding of the Lorentzian at the line center is always a many-body effect. The single-perturber approximation is actually a special case of the binary collision approximation in which multiple scattering can be ignored over the time scale of interest.

Baranger has also noted that, although the single-perturber approximation is not valid at the line center (it contains singularities), there is generally a range of frequencies for which the impact and single-perturber approximations overlap. Schematically, for an isolated line, the single perturber lineshape function assumes the form

$$\phi_{if}(\omega) = \frac{1}{\pi} \frac{\Gamma(\omega - \omega_{fi})}{(\omega - \omega_{fi})^2} \tag{1}$$

where ω_{fi} is the line center frequency. Equation (1) is also the approximate form of a Lorentzian several halfwidths away from resonance, i.e. for $(\omega-\omega_{fi})>>\Gamma$, except, in the case of a simple Lorentzian, the halfwidth function, $\Gamma(\omega-\omega_{fi})$, is usually replaced by its value at line center, $\Gamma(0)$. To the extent that the halfwidth function varies slowly over a frequency range of several halfwidths, there will clearly be some overlap of the two approximations.

Our mathematical discussion of the single-perturber approximation will proceed via the frequency domain analysis of Ref. 9. In Appendix A we indicate how these same results can be obtained from a small-time, low-density limit of the dipole autocorrelation function in the time-domain.

From Section 2 of Ref. 9 the absorption coefficient (cm^{-1}) can be computed as

$$\alpha(\omega) = \frac{4\pi^2\omega}{3C} X''(\omega) \quad , \tag{2}$$

where $x''(\omega)$ can be written (consistent with the FDT)

$$X''(\omega) = \tanh\left(\frac{\beta\hbar\omega}{2}\right)[\phi(\omega) + \phi(-\omega)] \tag{3a}$$

$$= (1 - e^{-\beta\hbar\omega})\phi(\omega) \, , \tag{3b}$$

$$= [\phi(\omega) - \phi(-\omega)] \, , \tag{3c}$$

with $\beta = 1/k_BT$, and where $\phi(\omega)$ is the Fourier transform of the dipole autocorrelation function $\phi(t)$.[8,10] (The definitions of x'' in Refs. 8 and 9 differ by a factor of n_{rad}, the radiator density.)

An exact many-body formula for $\phi(\omega)$ is

$$\phi(\omega) = \frac{1}{\Omega} \sum_{IF} \varrho(\xi_I) | < I | \mu | F > |^2 \, \delta(\xi_F - \xi_I - \hbar\omega) \tag{4}$$

Here Ω denotes the system volume, I, F refer to exact eigenstates of the many-body system, and

$$\varrho(\xi_I) = e^{-\beta\xi_I} / \mathrm{Tr}(e^{-\beta H}) \tag{5}$$

is the equilibrium canonical density matrix.

Now in the single-perturber approximation, we replace Eq. (4) by

$$\phi(\omega) = \frac{N_{pairs}}{\Omega} \sum_{IF} \varrho(E_I) | < I | \mu | F > |^2 \delta(E_F - E_I - \hbar\omega) \tag{6}$$

where |I>, |F> denote exact eigenstates of a <u>two-body</u> Hamiltonian consisting of a single radiator and perturber. Also in Eq. (6), N_{pairs} is the number of pairs given for foreign broadening by

$$N_{pairs} = N_{rad} N_{per} , \qquad (7)$$

and for self-broadening by

$$N_{pairs} = \frac{N_{rad}}{2} (N_{rad} - 1) \quad , \qquad (8)$$

$$\cong \frac{N_{rad}^2}{2} \qquad (9)$$

The eigenstates |I>, |F> are <u>not</u> simply product states consisting of a radiator state, a perturber state, and a state describing the relative translational motion. That is, in general the internal states of the two molecules are coupled, true bound states of the pair are admissible, and $\vec{\mu}$ is the dipole moment for the <u>composite</u> two-body system.

In the analysis which follows, we carry out a perturbative treatment in the anisotropic interaction, considering absorptive contributions associated only with <u>unbound</u> states of the system. In this case, the basis states, can be taken as product states (including an isotropic interaction which is treated exactly), and for $\vec{\mu}$, we can write, for foreign broadening,

$$\vec{\mu} = \vec{\mu}_{rad} , \qquad (10)$$

and for self-broadening

$$\vec{\mu} = \vec{\mu}_{rad} + \vec{\mu}_{per} \quad . \qquad (11)$$

The difference between Eq. (10) and Eq. (11) essentially makes up for the factor of 2 difference between Eq. (7) and Eq. (9) and has the consequence that self-broadening can be treated in basically the same fashion as foreign broadening.

In carrying out the analysis, we write the two-body Hamiltonian as

$$H = H_0 + V , \tag{12}$$

where any purely isotropic interaction is contained in H_0, and where V denotes the anisotropic interaction between the two molecules. Here, anisotropic means that V is angle-dependent and couples the internal states of the two molecules with the relative translational vector connecting the molecules.

The eigenstates of H_0 are product states of the form

$$H_0|i\rangle = \epsilon_i|i\rangle , \tag{13}$$

$$|i\rangle = |j_i m_i\rangle|J_i M_i\rangle|k_i\rangle \tag{14}$$

where j_i denotes a radiator state, J_i denotes a perturber state, and k_i denotes a state of relative translational motion; the m's and M's are magnetic quantum numbers for the internal states. The state $k_i\rangle$ is an eigenstate of the Hamiltonian

$$-\left[\frac{\hbar^2\nabla_{\vec{r}}^2}{2m} + V_0(r)\right]|k_i\rangle = \epsilon_{k_i}|k_i\rangle \tag{15}$$

where $\vec{r}$ is the relative coordinate, $r=\vec{r}$, $V_0(r)$ is the isotropic potential, and $\varepsilon_k=\hbar^2k^2/2m$, with m the reduced two-body mass. For the basis states above, the energy ε_i can be written as the sum $\varepsilon_i=\varepsilon_{j_i}+\varepsilon_{J_i}+\varepsilon_{k_i}$, and the unperturbed density matrix factors according to

$$\varrho(\epsilon_i) = \varrho(\epsilon_{ji})\,\varrho(\epsilon_{J_i})\,\varrho(\epsilon_{ki}) \qquad (16)$$

The T-matrix formulation in Ref. 9 rigorously includes line coupling contributions. However, our initial calculations have ignored this complication. In this regard, we also remark that some of the equations presented in Section 2.4 of Ref. 9 are actually a slight oversimplification of the uncoupled line approximation. The essence of the uncoupled line approximation is that when one encounters a matrix element product of the form

$$<j_i m_i|\overline{\mu}|j_f m_f><j_{f'} m_{f'}|\overline{\mu}|j_{i'} m_{i'}> \qquad (17)$$

one sets $j'=j_i$ and $j'=j_f$, however one does <u>not</u> set $m_{i'}=m_i$ or $m_{f'}=m_f$ for the magnetic quantum numbers.

For $\phi(\omega)$, we obtain

$$\phi(\omega) = r \sum_{j_i j_f} \varrho(\epsilon_{ji})(2j_i + 1)|<j_i||\mu||j_f>|^2 \cdot \Psi_{if}(\omega - \omega_{fi}) \,. \qquad (18)$$

In the above equation:

1. The prefactor r is the same renormalization factor discussed in Eq. (2.13) of Ref. 8, and in Ref. 9, i.e.

$$r = \mathrm{Tr}(e^{-\beta H_0}) / \mathrm{Tr}(e^{-\beta H}) \,. \qquad (19)$$

   In all of our calculations, we have approximated this factor by unity.

2. The reduced matrix element is defined by the Wigner-Eckhart[11] theorem in the form

$$<j_i m_i|\vec{\mu}|j_f m_f> = <j_i||\mu||j_f> \cdot \sum_{m=0,\pm 1} \hat{\epsilon}_m (j_f 1 m_f m|j_f 1 j_i m_i) \qquad (20)$$

   The reduced matrix element satisfies the symmetry relation

$$(2j_i + 1)|<j_i||\mu||j_f>|^2 = (2j_f + 1)|<j_f||\mu||j_i>|^2 . \qquad (21)$$

3. The radiator's density matrix is given by

$$\varrho(\epsilon j_i) = \frac{e^{-\beta\epsilon_{j_i}}}{\sum_{j_i} e^{-\beta\epsilon_{j_i}}(2j_i + 1)} , \qquad (22)$$

so that

$$\sum_{j_i} \varrho(\epsilon j_i)\,(2j_i + 1) = 1 . \qquad (23)$$

If the various j_i states carry different nuclear statistical weights, factors of $(2j_i+1)$ are to be replaced everywhere, e.g. Eqs. (21) through (23), by $(2j_i+1)g(j_i)$.

While discussing statistics, the perturber density matrix, $\rho(\epsilon_{J_i})$, in Eq. (16) is given by an expression identical in form to Eq. (22); the density matrix for the relative translation motion is simply given by

$$\varrho(\epsilon_k) = \frac{e^{-\beta\epsilon_k}}{\sum_k e^{-\beta\epsilon_k}} \qquad (24)$$

so that

$$\sum_k \varrho(\epsilon_k) = 1 . \qquad (25)$$

4. The function Ψ in Eq. (18) satisfies the symmetry relation[9]

$$\Psi_{fi}(-Z) = e^{-\beta\hbar Z}\,\Psi_{if}(Z) , \qquad (26)$$

for arbitrary frequency z. In particular,

$$\Psi_{fi}(-\omega + \omega_{fi}) = e^{-\beta\hbar(\omega-\omega_{fi})}\,\Psi_{if}(\omega-\omega_{fi}) \qquad (27)$$

From Eq. (22) we can note that

$$\varrho(\epsilon j_f)\, e^{\beta\hbar\omega_{fi}} = \varrho(\epsilon j_i)\,, \tag{28}$$

where $\hbar\omega_{fi}=(\varepsilon_f-\varepsilon_i)$. By letting $\omega\to-\omega$ in Eq. (18), interchanging names of dummy summations $j_i \rightleftarrows j_f$, and by making use of symmetry properties (21), (27), and (28), one may readily show

$$\phi(-\omega) = e^{-\beta\hbar\omega}\,\phi(\omega) \tag{29}$$

Equations (27) and (29) are the fundamental relations which guarantee that the FDT is satisfied and that Eqs. (3a) through (3c) are equivalent. We caution, however, that the proof of Eq. (27) in Ref. 9 did not include a unitarity cutoff for strong collisions. One must be careful in the application of a cutoff if the FDT is still to be satisfied (see Section 5).

By using symmetry relations (21), (28), and Eq. (26) in the form

$$\Psi_{fi}(\omega + \omega_{fi}) = e^{\beta\hbar(\omega+\omega_{fi})}\,\Psi_{if}(-\omega - \omega_{fi}) \tag{30}$$

one may rewrite Eq. (18) as a restricted sum over pairs of states with $\varepsilon_{fi}=\varepsilon_f-\varepsilon_i>0$, i.e. with $\omega_{fi}>0$; the result is

$$\phi(\omega) = \nu \sum_{\substack{j_i j_f \\ \epsilon_f > \epsilon_i}} \varrho(\epsilon j_i)(2j_i + 1)\,|<j_i||\mu||j_f>|^2\, \Psi_{tot}(\omega) \tag{31}$$

with

$$\Psi_{tot}(\omega) = \Psi_{if}(\omega - \omega_{fi}) + e^{\beta\hbar\omega}\,\Psi_{if}(-\omega - \omega_{fi}) \tag{32}$$

The above result has the nice advantage that we can consider a total contribution to absorption for the pair of state ε_i, ε_f. We shall refer to the first term in Eq. (32) as the positive oscillator term, and the second term will be referred to as the negative oscillator term, i.e. it is resonant for $\omega=-\omega_{fi}<0$. Note that computation of the negative oscillator term only involves the simple replacement of arguments $(\omega-\omega_{fi})\rightarrow(-\omega-\omega_{fi})$. Therefore, for the most part, our discussion will concentrate on the positive oscillator term.

The positive oscillator term can be put into the form of an off-resonance Lorentzian with a frequency dependent halfwidth,

$$\Psi_{if}(\omega - \omega_{fi}) = n_{rad} \frac{1}{\pi} \frac{\Gamma(\omega - \omega_{fi})}{(\hbar\omega - \epsilon_{fi})^2} \tag{33}$$

where $n_{rad}=N_{rad}/\Omega$ is the radiator density, and where the perturber density $n_{per}=N_{per}/\Omega$ is contained in the halfwidth function $\Gamma(\omega-\omega_{fi})$, which has units ergs.

We now write down the equations which determine the halfwidth function Γ. First, we do this in a simplified, schematic fashion which suppresses magnetic quantum numbers, Clebsch-Gordan coefficients, and m-summations. At the conclusion of this section, we shall present the general formulas for Γ which require Clebsch-Gordan reduction (see Appendix C).

The simplified equation for $\Gamma(\omega-\omega_{fi})$ is

$$\begin{aligned}\Gamma(\omega - \omega_{fi}) = N_{per} \sum_{Jk} \varrho(\epsilon_J)\varrho(\epsilon_k) \sum_{j_f J'k'} |<\alpha|V|\beta>|^2 \cdot \pi\delta(\epsilon_{\alpha\beta} + \hbar\omega - \hbar\omega_{fi}) \\ + e^{\beta\hbar(\omega-\omega_{fi})} \cdot N_{per} \sum_{Jk} \varrho(\epsilon_J)\varrho(\epsilon_k) \\ \cdot \sum_{j_f J'k'} |<\alpha'|V|\beta'>|^2 \pi \delta(\epsilon_{\alpha'\beta'} - \hbar\omega + \hbar\omega_{fi})\end{aligned} \tag{34}$$

where for simplicity,

$$|\alpha> = |j_f J k> , \tag{35a}$$

$$|\beta> = |j_f J' k'> , \tag{35b}$$

$$|\alpha'> = |j_i J k> , \tag{35c}$$

$$|\beta'> = |j_i J' k'> , \tag{35d}$$

and $\varepsilon_{\alpha\beta}=\varepsilon_\alpha-\varepsilon_\beta$, $\varepsilon_{\alpha'\beta'}=\varepsilon_{\alpha'}-\varepsilon_{\beta'}$.

With regard to Eq. (34) we note that the contributions from the initial and final states (i,f) of the radiative transition do not enter in a symmetric fashion. It is precisely this asymmetry which causes the FDT to be satisfied. At line center, $(\omega-\omega_{fi})=0$, this asymmetry disappears. The halfwidth function satisfies the same symmetry relation as Ψ in Eq. (26), namely (at the risk of introducing more indices), if we define $\Gamma_{if}(z)=\Gamma(z)$, then

$$\Gamma_{fi}(-Z) = e^{-\beta\hbar Z} \cdot \Gamma_{if}(Z) \tag{36}$$

for general frequency z (which is to be substituted for $(\omega-\omega_{fi})$ in Eq. (34)).

The first (final state) contribution to the halfwidth function has a simple interpretation, namely it is essentially Fermi's golden rule averaged over initial states and summed over final states. The interpretation of the second term in Eq. (34) is complicated by the FDT asymmetry. Note that the asymmetry involves two things:

1. the temperature dependenct factor $\exp[\beta\hbar(\omega-\omega_{fi})]$ in the second term of Eq. (34); and
2. the off-resonance energy $\hbar(\omega-\omega_{fi})$ enters the delta functions with a different <u>sign</u> in the two terms of Eq. (34).

General Results: We close this section by writing down the general expression for the halfwidth function, including Clebsch-Gordan coefficients and magnetic quantum numbers. As a preliminary to listing the relevant equation, we note from Eq. (34) that we will eventually have to consider a summation over translational states of the form

$$\text{sum} = N_{per} \sum_{kk'} \varrho(\epsilon_k) <k|V|k'><k'|V|k> \qquad (37)$$

where k denotes any complete set of relative translational states.

In Appendix B we show that this sum can be rewritten as (the sum is still an operator in the space of the internal molecular coordinates)

$$\text{sum} = \frac{n_{per}}{z}\left(\frac{2}{\pi}\right)^2 \sum_{\ell m_\ell} \sum_{\ell' m_{\ell'}}$$

$$\cdot \int_0^\infty dk e^{-\beta\epsilon_k} \int_0^\infty dk' <R_{k\ell m_\ell}|V|R_{k'\ell' m_{\ell'}}><R_{k'\ell' m_{\ell'}}|V|R_{k'\ell' m_{\ell'}}> \qquad (38)$$

In the above equation:

1.
$$R_{k\ell m_\ell}(r) \equiv <\vec{r}|R_{k\ell m_\ell}>$$
$$= Y_{\ell m_\ell}(\theta, \varphi) \frac{1}{r} \phi_\ell(k;r), \qquad (39)$$

where the radial wavefunction (r is the magnitude of the relative coordinate) has the asymptotic normalization

$$\phi_\ell(k;r) \xrightarrow[r \to \infty]{} \sin[kr - ½ \ell\pi + \delta_\ell(k)] \qquad (40)$$

2. The meaning of the matrix element is

$$<R_k\ell m_\ell|V|R_{k'\ell' m_{\ell'}}>$$
$$= \int_0^\infty d\varphi \int_{-1}^1 d(\cos\theta) \int_0^\infty r^2 dr R_{k\ell m_\ell}(\vec{r})\, V(\vec{r}) R_{k'\ell' m_{\ell'}}(\vec{r}) \qquad (41)$$

3. The quantity z is a translational partition sum given by

$$z = \frac{1}{\Omega} \sum_{\vec{k}} e^{-\beta \epsilon_{\vec{k}}}$$

$$= \frac{1}{(2\pi)^3} \int d^3k \, e^{-\beta \epsilon_{\vec{k}}}$$

$$= \left(\frac{m}{2\pi\beta\hbar^2} \right)^{3/2} \tag{42}$$

For the halfwidth function we obtain

$$\Gamma(\omega - \omega_{fi}) = \left(\frac{n_{per}}{z} \right) \left(\frac{2}{\pi} \right)^2 \sum_{J} \varrho(\epsilon_J) \int_0^\infty dke^{-\beta \epsilon_k}$$

$$\int_0^\infty dk' \sum_{J'} \sum_{\ell\ell'} \{ \text{sum}\,(j_i) + \text{sum}\,(j_f) \} \tag{43}$$

Here, including all m-summations which must be reduced using Clebsch-Gordan algebra,

$$\text{sum}\,(j_f) = \sum_{j_{f''}} \pi\delta(\epsilon_{ff''} + \hbar\omega - \hbar\omega_{fi})$$

$$\cdot \frac{1}{(2j_i + 1)} \sum_{m_i m_{i'} m} \sum_{m_f m_{f'} m_{f''}} \sum_{MM'} \sum_{m_\ell m_{\ell'}}$$

$$\cdot\, \delta m_{i},m_{i'} \, (j_f\; 1 m_f m \,|\, j_f\; 1 j_i m_i)(j_f\; 1 m_{f'} m \,|\, j_f\; 1 j_i m_{i'})$$

$$\cdot <j_f m_{f'};\, JM;\, R_{k\ell m_\ell} | V | j_{f''} m_{f''};\, J'M';\, R_{k'\ell' m_{\ell'}}>$$

$$\cdot <j_{f''} m_{f''};\, J'M';\, R_{k'\ell' m_{\ell'}} | V | j_f m_f;\, JM;\, R_{k\ell m_\ell}> \tag{44}$$

$$\text{sum}\,(j_i) = e^{\beta\hbar(\omega-\omega_{fi})} \sum_{j_{i''}} \pi\, \delta(\epsilon_{ii''} - \hbar\omega + \hbar\omega_{fi})$$

$$\cdot \frac{1}{(2j_i + 1)} \sum_{m_f m_{f'} m} \sum_{m_i m_{i'} m_{i''}} \sum_{MM'} \sum_{m_\ell m_{\ell'}}$$

$$\cdot\, \delta_{m_{f'}, m_{f'}} (j_f\ 1 m_f m | j_f\ 1 j_i m_i)(j_f\ 1 m_{f'} m | j_f\ 1 j_i m_{i'})$$

$$\cdot < j_i m_{i'};\ JM;\ R_{k\ell m_\ell} | V | j_{i''} m_{i''};\ J'M';\ R_{k'\ell' m_{\ell'}} >$$

$$\cdot < j_{i''} m_{i''};\ J'M';\ R_{k'\ell' m_{\ell'}} | V | j_i m_i;\ JM;\ R_{k\ell m_\ell} > . \tag{45}$$

In the delta function expressions above, we have defined

$$\epsilon_{ff''} = (\epsilon_{j_f} - \epsilon_{j_{f''}}) + (\epsilon_J - \epsilon_{J'}) + (\epsilon_k - \epsilon_{k'}) , \tag{46}$$

$$\epsilon_{ii''} = (\epsilon_{j_i} - \epsilon_{j_{i''}}) + (\epsilon_J - \epsilon_J') + (\epsilon_k - \epsilon_{k'}) . \tag{47}$$

The three terms on the right hand side of Eqs. (46) and (47) are, respectively, change in energy of the radiator (internal energy), the perturber (internal energy), and relative translational motion in a collision where f→f" or i→i".

Some details of the Clebsch-Gordan reduction of Eqs. (44) and (45) are presented in Appendix C for an anisotropic potential corresponding to a dipole-dipole or dipole-quadrupole interaction. From Appendix C, the result for Eqs. (44) and (45) becomes (for dipole-dipole case)

$$\text{sum}\,(j_f) = \sum_{j_{f'}} \pi\delta(\epsilon_{ff'} + \hbar\omega - \hbar\omega_{fi})$$

$$\cdot\ \frac{2}{3}\,(2\ell + 1)\,(2J + 1)\,(\ell 2\ 00|\ell 2\ell' 0)^2$$

$$|<R_{k\ell}|\ \frac{1}{r^3}\ |R_{k'\ell'}>|^2$$

$$\cdot\ |<j_f||\mu_1||j_{f'}>|^2\ |<J||\mu_2||J'>|^2\,. \tag{48}$$

$$\text{sum}\,(j_i) = e^{\beta\hbar(\omega-\omega_{fi})} \sum_{j_{i'}} \pi\ \delta(\epsilon_{ii'} - \hbar\omega + \hbar\omega_{fi})$$

$$\cdot\ \frac{2}{3}\,(2\ell + 1)\,(2J + 1)\,(\ell 2\ 00|\ell 2\ell' 0)^2$$

$$\cdot\ |<R_{k\ell}|\ \frac{1}{r^3}\ |R_{k'\ell'}>|^2$$

$$\cdot\ |<j_i||\mu_1||j_{i'}>|^2\ |<J||\mu_2||J'>|^2\,. \tag{49}$$

In the above equations

$$R_{k\ell}(r) = \frac{1}{r}\ \phi_\ell(k;\, r)\,, \tag{50}$$

and the meaning of the radial matrix element in the above equations is

$$<R_{k\ell}|\ \frac{1}{r^3}\ |R_{k'\ell'}>$$

$$= \int_0^\infty r^2 dr\ R_{k\ell}(r)\ \frac{1}{r^3}\ R_{k'\ell'}(r)$$

$$= \int_0^\infty \phi_{k\ell}(r)\ \frac{1}{r^3}\ \phi_{k'\ell'}(r)\,dr$$

$$= <\phi_{k\ell}|\ \frac{1}{r^3}\ |\phi_{k'\ell'}>\,, \tag{51}$$

At a convenient point, in going between Eqs. (44) and (45) and Eqs. (48) and (49), we have changed names of dummy variables $j_{f''} \rightarrow j_{f'}$, $j_{i''} \rightarrow j_{i'}$.

Finally, we remark that the two terms in Eq. (43) correspond to Anderson's S_2(outer) terms. In certain problems, one has to also worry about Anderson's S_2(inner).[12,13] This term obtains from an uncoupled line approximation to Eq. (51) in Ref. 9. This term has been ignored for the problem of primary interest here (H_2O self-broadening) because it involves diagonal matrix elements of the dipole moment operator, for the case of dipole-dipole interactions.

In the next section we discuss the above equations further in terms of quantities manipulated by our computer codes. In doing this, we also identify the analog of Anderson's S_2 functions. This is important for considerations of an Anderson cutoff scheme in the strong collision limit.

3.0 REDUCTION TO COMPUTATIONAL FORM

The Schroedinger Eq. (15) which determines the eigenstates $\phi_l(k;r)$ in Eqs. (39), (40), (50), and (51) has been solved numerically for the case of a Lennard-Jones potential with well minimum energy E_s, occuring at radius r_s. Some details of the matrix element calculations will be presented in the next section. The parameter r_s is used as the length scale unit in these calculations. In particular, for the dipole-dipole case, matrix elements of r^{-3} are computed as

$$I(\ell k; \ell' k') = \int_0^\infty dZ \phi_\ell(k; Z) \frac{1}{Z^3} \phi_{\ell'}(k'; Z) \tag{52}$$

where the reduced length is $z=r/r_s$. We may also denote the above matrix element by $I(l\varepsilon;l'\varepsilon')$, where $\varepsilon=\hbar^2k^2/2m$ is the energy associated with wavevector k. We define dipole line strengths by

$$|\langle j||\mu||j'\rangle|^2 = \mu^2 S_{jj'} . \qquad (53)$$

Here μ is the scalar dipole moment ($\mu=1.85\mathrm{x}10^{-18}$ esu-cm is the permanent moment for H_2O), and the line strengths satisfy the sum rule

$$\sum_{j'} S_{jj'} = 1 . \qquad (54)$$

For programming convenience we will eventually (but not immediately) convert all energies from ergs to cm^{-1} using

$$\epsilon(\mathrm{ergs}) = hc\epsilon(\mathrm{cm}^{-1}) . \qquad (55)$$

For the case of self-broadening through dipole-dipole interactions, we compute and store the following dimensionless (squared) matrix element

$$M_\ell(\epsilon;\epsilon') = \left(\frac{\mu^2}{hcr_s^3}\right)^2 \varrho(\epsilon)\varrho(\epsilon')$$
$$\bullet \sum_{\ell'} (\ell 200|\ell 2\ell' 0)^2 |I(\ell\epsilon;\ell'\epsilon')|^2 \qquad (56)$$

In this expression, with ε in cm^{-1}

$$\varrho(\epsilon) = \left(\frac{8mcr_s^2}{h\epsilon}\right)^{1/2} , \qquad (57)$$

is a density of states factor with units=cm. That the M-matrix element above is dimensionless follows from the fact that

$$\left(\frac{\mu^2}{hcr_s^{\,3}}\right)^2 \text{ has units cm}^{-2},$$

while $\rho(\varepsilon)\rho(\varepsilon')$ has units cm^2, and everything else is dimensionless.

We next introduce a function which plays a role analogous to Anderson's s_2 function.[12,13] We write the function in the form

$$s_2^{tot}(\epsilon, J, \ell; \omega - \omega_{fi}) = s_2^f(\epsilon, J, \ell; \omega - \omega_{fi}) + e^{\beta\hbar(\omega-\omega_{fi})} s_2^i(\epsilon, J, \ell; \omega - \omega_{fi}) \tag{58}$$

For the dipole-dipole case the (dimensionless) functions s_2^f and s_2^i are given by

$$s_2^f(\epsilon, J, \ell; \omega - \omega_{fi}) = \frac{4\pi^2}{3} \sum_{j_{f'}} \sum_{J'} S_{j_f j_f'}\, S_{JJ'}\, M_\ell[\epsilon; \epsilon + \epsilon^f_{rot} + \hbar(\omega - \omega_{fi})] \,, \tag{59}$$

$$s_2^i(\epsilon, J, \ell; \omega - \omega_{fi}) = \frac{4\pi^2}{3} \sum_{j_{i'}} \sum_{J'} S_{j_i j_i'}\, S_{JJ'}\, M_\ell[\epsilon; \epsilon + \epsilon^i_{rot} - \hbar(\omega - \omega_{fi})] \,, \tag{60}$$

with

$$\epsilon^f_{rot} \equiv (\epsilon_{j_f} - \epsilon_{j_{f'}}) + (\epsilon_J - \epsilon_{J'}) \,, \tag{61}$$

$$\epsilon^i_{rot} \equiv (\epsilon_{j_i} - \epsilon_{j_{i'}}) + (\epsilon_J - \epsilon_{J'}) \,. \tag{62}$$

That the above s_2 plays the role of Anderson's s_2-function (at least in the line center limit $\omega-\omega_{fi} \to 0$) will presently be demonstrated. The FDT asymmetry between the final and initial state contributions is again evident in Eqs. (58) through (60).

For the halfwidth function of Eq. (45), we may now write

$$\Gamma(\omega - \omega_{fi}) = \frac{n_{per}}{4\pi^2} \left(\frac{2\pi}{z}\right) \int_0^\infty d\epsilon \left(\frac{2m\epsilon}{\pi\hbar^2}\right) e^{-\beta\epsilon} \cdot \sum_J \varrho(\epsilon_J)\, (2J + 1)\, \sigma(\epsilon, J) \,. \tag{63}$$

In the above expression, $\sigma(\varepsilon,J)$ is a cross section (cm^2) given by

$$\sigma(\epsilon, J) = \left(\frac{\pi\hbar^2}{2m\epsilon}\right) \sum_{\ell} (2\ell + 1)\, s_2^{tot}(\epsilon, J, \ell; \omega - \omega_{fi}) \,. \tag{64}$$

Before going on, we note, if Eqs. (63) and (64) are combined, that the factors $(\pi\hbar^2/2m\varepsilon)$ cancel. This is useful in terms of writing the results in alternative forms.

Next, in the limit of large l, and using $l=kb$, where b is the classical impact parameter, with $\varepsilon=\hbar^2k^2/2m$, one can see that σ in Eq. (70) takes the approximate form

$$\sigma(\epsilon, J) \equiv \int_0^{\infty} 2\pi\, b db\, s_2^{tot}(\epsilon, J, b; \omega - \omega_{fi}) \tag{65}$$

This is the usual form which relates the s_2 function to the cross section in Anderson's formalism.

To complete the analogy with Anderson's theory we rewrite the average over energy in Eq. (63) in terms of a Maxwell-Boltzmann velocity average. We use

$$\epsilon = \frac{1}{2} mv^2 \,, \tag{66}$$

and for the partition function (Eq. (42)) we can write

$$\frac{1}{2\pi^2 z} = \left(\frac{\hbar}{m}\right)^3 \frac{1}{\int_0^{\infty} v^2 dv\, e^{-\beta \frac{1}{2} m v^2}} \tag{67}$$

Using the above results, and defining

$$\overline{\Gamma}\,(\omega - \omega_{fi}) = \frac{1}{\hbar}\,\Gamma(\omega - \omega_{fi})\,, \tag{68}$$

where $\bar{\Gamma}$ is the halfwidth function in rad/sec, we obtain

$$\overline{\Gamma}[\omega - \omega_{fi}) = n_{per} \int_0^\infty v dv f(v) \cdot \sum_J \varrho(\epsilon_J)(2J + 1)\,\sigma(v, J) \tag{69}$$

with

$$f(v) = \frac{v^2\, e^{-\beta \frac{1}{2} mv^2}}{\int_0^\infty v^2\, e^{-\beta \frac{1}{2} mv^2}\, dv} \tag{70}$$

the Maxwell-Boltzmann distribution function. We can rewrite this

$$\overline{\Gamma}(\omega - \omega_{fi}) = n_{per} \sum_J \varrho(\epsilon_J)(2J + 1) < v\,\sigma(v, J) > \,. \tag{71}$$

In the line-center limit this has the form of an Anderson[12,13] type theory, including velocity averaging. With an appropriate definition of the average cross section, Eq. (71) can be expressed as

$$\overline{\Gamma} = n_{per}\, \overline{v}(T)\, \overline{\sigma}(T)\,, \tag{72}$$

where $\bar{v}$ is the mean thermal velocity.

This essentially completes the analogy of the present theory with Anderson's formalism. Certain questions remain as to whether Anderson's cutoff procedures for s_2 can be taken directly over for the far-wing problem.

Finally, we wish to write down the previous equations in the form in which they were actually programmed for calculation. This basically involves combining Eqs. (63) and (64), cancelling the factors of ($\pi\hbar^2/2m\varepsilon$), and converting all energies to cm^{-1}, including the partition sum denominator integral, which can be written

$$\frac{2\pi}{z} = \frac{\overline{\lambda}^{3}\,\overline{\epsilon}}{\int_0^\infty d\epsilon' \sqrt{\frac{\epsilon'}{\overline{\epsilon}}}\; e^{-\beta hc\epsilon'}} \; . \tag{73}$$

here ε', ε are in cm^{-1} and we have defined some average thermal quantities as follows: the basic definition is the mean thermal velocity

$$\overline{v} = \left(\frac{8}{\pi}\,\frac{k_B T}{m}\right)^{1/2} , \tag{74}$$

In terms of $\bar{v}$ we also define

$$\overline{\epsilon}(\mathrm{ergs}) = \frac{1}{2}\, m\overline{v}^{2} = hc\,\overline{\epsilon}(\mathrm{cm}^{-1}) \, , \tag{75}$$

$$\text{i.e., } \overline{\epsilon}(\mathrm{cm}^{-1}) = \left(\frac{4}{\pi}\,\frac{k_B T}{hc}\right) . \tag{76}$$

We caution that Eq. (75) is simply a <u>definition</u> of $\bar{\varepsilon}$, and $\bar{\varepsilon}$ is not the average energy in a thermodynamic sense. Finally, we define an average DeBroglie wavelength by

$$\overline{\lambda} = \frac{h}{m\overline{v}} = \left(\frac{h}{2mc\,\overline{\epsilon}(\mathrm{cm}^{-1})}\right)^{1/2} . \tag{77}$$

Equations (33), (63), and (64) can now be re-expressed as

$$\Psi_{if}(\omega - \omega_{fi}) = n_{rad}\,\frac{1}{hc}\,\frac{1}{\pi}\,\frac{\tilde{\Gamma}(\omega - \omega_{fi})}{(\omega - \omega_{fi})^{2}} \quad , \tag{78}$$

with

$$\tilde{\Gamma}(\omega - \omega_{fi}) = \frac{n_{per}}{4\pi^{2}}\;\frac{\overline{\lambda}^{3}\,\overline{\epsilon}\int_0^\infty d\epsilon\; e^{-\beta hc\epsilon}}{\int_0^\infty d\epsilon' \sqrt{\frac{\epsilon'}{\overline{\epsilon}}}\; e^{-\beta hc\epsilon'}}$$

$$\cdot \sum_J \varrho(\epsilon_J)\,(2J + 1) \sum_{\ell} (2\ell + 1)\; s_2^{tot}(\epsilon, J, \ell; \omega - \omega_{fi}) \; . \tag{79}$$

In the above equations, all ε's, ω's, and Γ are now in cm^{-1}. The units of Γ are manifest, namely everything is dimensionless, except

$$(n_{per}\,\overline{\lambda}^3)\,\overline{\epsilon} \sim \overline{\epsilon} = \text{cm}^{-1}\,.$$

To conclude this section, since it would be totally prohibitive to actually calculate the absorption coefficient (by summing the contribution from all lines), we have to proceed in a different fashion. For certain experimental cases it is known what the simple impact approximation predicts for absorption. This is subject to the difficulty that the impact approximation does not satisfy the FDT, so that the impact results depend on which formula (Eqs. (3a) through (3c)) one starts from.

We shall make comparison with the so-called "hyperbolic tangent" impact formula. This formula has some advantages, and certain predictions from the formula are available.

Before writing out the impact formula, we combine Eqs. (3b), (31), (32), and (78) to deduce that the contribution to χ'' associated with the pair of energy levels $\varepsilon_f > \varepsilon_i$ is proportional to

$$\chi''(\omega)_{FDT} = (1 - e^{-\beta hc\omega}) \left[\frac{\tilde{\Gamma}(\omega - \omega_{fi})}{(\omega - \omega_{fi})^2} + e^{\beta hc\omega} \frac{\tilde{\Gamma}(-\omega - \omega_{fi})}{(-\omega - \omega_{fi})^2} \right], \quad (80)$$

where the two terms in the bracket are the positive and negative oscillator terms, respectively.

The corresponding "hyperbolic tangent" impact formula is

$$X''(\omega)_{\text{impact}} = \tanh\left(\frac{\beta hc\omega}{2}\right)\left(1 + e^{-\beta hc\omega_{fi}}\right)$$

$$\cdot \left[\frac{\tilde{\Gamma}(0)}{(\omega - \omega_{fi})^2} + \frac{\tilde{\Gamma}(0)}{(-\omega - \omega_{fi})^2}\right] . \tag{81}$$

In writing down the above results we have dropped some constant factors which will cancel in the ratio

$$R(\omega) = X''(\omega)_{FDT} / X''(\omega)_{\text{impact}} . \tag{82}$$

One of the constant factors which has been dropped is the radiator density, n_{rad}. As a matter of fact, the perturber density, n_{per}, also cancels in the ratio because all of the halfwidth functions in Eqs. (80) and (81) are linear in n_{per}. Thus $R(\omega)$ is independent of both radiator and perturber density.

The only remaining density dependence of interest is in the halfwidth function itself. We have done all calculations at a fixed density corresponding to the density at one atmosphere pressure and room temperature, i.e. we take for the perturber density the fixed value

$$n_{per} = n_0(273/296) , \tag{83}$$

with n_0=Loschmidts number. R.H. Tipping has referred to the quantity above as a "hot Loschmidt".

To conclude this section, we note as $\omega \to \omega_{fi}$, where the negative oscillator terms in Eqs. (80) and (81) become negligible, that the two formulas approach each other. Similarly, the formulas coalesce at the negative oscillator resonance $\omega \to -\omega_{fi}$. Of course, both formulas are divergent at the line center.

4.0 CALCULATION OF MATRIX ELEMENTS

In terms of computation time, calculation of the M-matrix elements in Eq. (56) is basically governed by the speed with which the simple I-matrix elements in Eq. (52) can be generated. We have attempted to make this process as efficient as possible.

To discuss simplifications, we begin by rewriting Eq. (52) as

$$I(\ell\epsilon;\ell'\epsilon') = \int_0^\infty dZ\, \phi_\ell(\epsilon;Z)\, \frac{1}{Z^3}\, \phi_{\ell'}(\epsilon';Z)\,, \tag{84}$$

where ε, ε' are the energies. In considering the above integral we remark, for most cases of interest, that l, l' and $\varepsilon, \varepsilon'$ are "not all that different".

To be more precise: for the dipole-dipole case, the Clebsch-Gordan coefficient $(l200\ l2l'0)$ in Eq. (56) leads to the selection rules $(l'-l)=0,\pm2$. The statement in regard to ε,ε' is simply that if $\varepsilon-\varepsilon'$ is large, the matrix elements tend to be small. The point of the above comment is simply that, for most cases of interest, the wavefunctions in the integrand are such that they can generally be calculated using the <u>same</u> approximations.

With the above remark in mind, there are essentially three situations of interest which depend on l, ε, and the total isotropic potential

$$V_0(r;\ell) = V_{LJ}(r) + \frac{\ell(\ell+1)\hbar^2}{2mr^2}\,. \tag{85}$$

In the above expression the first term is the Lennard-Jones potential and the second term is the repulsive centripetal potential, which is clearly l-dependent.

In Fig. 1 we show a schematic $V_0(r,l)$ potential, along with three energy levels ε_1, ε_2, and ε_3. We will provide a few details at the end of this section, but briefly the wavefunctions associated with the above energies are calculated as follows:

Case (1). Energy level ε_1 (sufficiently low ε, sufficiently high l). We call this the centripetal regime. Classically, the turning point is such that the wavefunction never gets in to "see" the Lennard-Jones potential. The wavefunctions are then approximately eigenstates of a Hamiltonian with $V_{LJ}=0$. The approximate eigenstates are Bessel functions and the integral in Eq. (84) can be expressed in terms of the hypergeometric function.

Case (2). Energy level ε_2. We call this the intermediate region. In this case the wavefunctions ϕ are obtained numerically, as is the integral (84).

Case (3). Energy level ε_3 (sufficiently high ε, low l). We call this the hard core regime. Here the wavefunctions relatively quickly assume their asymptotic form (Eq. (40)) close to the turning point. The procedure in this case is to use numerical solutions out to a radius $Z_{max}=R_{max}/r_s$ where it has been determined that both ϕ's have assumed (to a good approximation) their asymptotic forms. Beyond this radius, the asymptotic form (40) is employed, and the resulting integral can be integrated in terms of sine and cosine integrals.

We close this section with a few details of the calculations.

Case (1). Centripetal Regime. The approximate wavefunctions are

$$\phi_\ell(\epsilon; Z) = (KZ)\, j_\ell\,(KZ)\,, \tag{86}$$

$$= \left(\frac{\pi}{2}\right)^{1/2} (KZ)^{1/2}\, J_{\ell+1/2}\,(KZ)\,. \tag{87}$$

$$(87)$$

where $K=kr_s$, and where j, J are spherical and ordinary Bessel functions, respectively. The integral (52) becomes

$$I(\ell\epsilon;\ell'\epsilon') = \frac{\pi}{2}(KK')^{1/2}$$

$$\cdot \int_0^\infty dZ\, J_{\ell+1/2}(KZ)\,\frac{1}{Z^2}\,J_{\ell'+1/2}(K'Z) \qquad (88)$$

This is a Weber-Schafheitlin type integral (see Abramowitz and Stegun[14], page 497, Eq. 11.4.34). The result can be written

$$I = \frac{\pi}{8}(KK')^{1/2}\,\frac{K^{\ell+1/2}}{(K')^{\ell-1/2}}\,\frac{\Gamma(\ell+\frac{\Delta\ell}{2})}{\Gamma(\frac{3}{2}+\frac{\Delta\ell}{2})\,\Gamma(\ell+\frac{3}{2})}$$

$$\cdot F\left(\ell+\frac{\Delta\ell}{2}, -\frac{1}{2}-\frac{\Delta\ell}{2}; \ell+\frac{3}{2}; \frac{K^2}{K'^2}\right), \qquad (89)$$

where $\Delta l=(l'-l)=0, \pm 2$, Γ is the Gamma function, and where F is the Gauss hypergeometric function. The above formula is valid only for $K/K' <1$; however, Eq. (88) is seen to be invariant under $K \rightleftarrows K'$ and $l \rightleftarrows l'$, so matrix elements with $K/K'>1$ can easily be obtained from symmetry. We note that the function in Eq. (89) has the form $F(a,b;c;z)$ with $c=a+b+m$, and with $m=2$. For this arrangement of arguments the F-function is most conveniently calculated from Eq. 15.3.11, page 559 of Abramowitz and Stegun.[14]

Case (2). Intermediate Region. The ϕ's are solved for numerically via Numerov's method using a computer code developed by R.J. LeRoy.[15] The integral (84) is evaluated numerically.

Case (3). Hard Core Regime. We use the same procedure as in Case (2) above out to a radius Z_{max}, then

$$I = \int_{0}^{Z_{max}} + \int_{Z_{max}}^{\infty} \quad . \tag{90}$$

The second integral above, for the dipole-dipole case, is of the form

$$I_2 = \int_{Z_{max}}^{\infty} \frac{dZ}{Z^3} \sin(KZ + A)\sin(K'Z + B) \quad , \tag{91}$$

where the phases A,B have been determined from the $Z<Z_{max}$ region. By repeated integration by parts, Eq. (91) can be expressed in terms of sine-cosine integrals. We define $K_\pm=K\pm K'$ and $C_\pm=A\pm B$. Then

$$I_2 = I_- - I_+ \tag{92}$$

with

$$\begin{aligned} I_- = {} & \frac{1}{4Z_{max}^2}\cos(K_- Z_{max} + C_-) \\ & - \frac{K_-}{4Z_{max}}\sin(K_- Z_{max} + C_-) \\ & + \frac{K_-^2}{4}\{\cos(C_-)\,\mathrm{Ci}\,(|K_-|Z_{max}) \\ & - \mathrm{sign}\,(K_-)\sin(C_-)\,\mathrm{si}\,(|K_-|Z_{max})\} \end{aligned} \tag{93}$$

Here sign $(K_-)=\pm1$ depending on whether K_- is positive or negative. In Eq. (93), si and Ci are the sine, cosine integrals given by (see Ref. 14, pages 231-232)

$$\mathrm{si}(X) = -\int_{X}^{\infty} \frac{dt}{t}\sin(t) \; , \tag{94}$$

$$\mathrm{Ci}(X) = -\int_{X}^{\infty} \frac{dt}{t}\cos(t) \; . \tag{95}$$

The integral I_+ in Eq. (92) is obtained by replacing $C_- \to C_+$ and $K_- \to K_+$.

The I and M-matrix elements were computed using the above methods, and the M-matrix elements were stored in a look-up table. When M-matrix elements are required (Eqs. (59) and (60)) at nonstored $\varepsilon, \varepsilon'$ values (as is virtually always the case), interpolation from the look-up table is employed.

5.0 RESULTS AND DISCUSSION

In the previous sections we have presented a far-wing lineshape theory, assuming dipole-dipole collisions to be the dominant broadening mechanism. For close collisions one might expect the higher-order multipole interactions to become important. The selection rules, $\Delta J=0,\pm1,\pm2$, for the dipole-quadrupole interaction allow for larger changes in rotational energy in Eqs. (46) and (47) than obtained from the dipole-dipole selection rules, $\Delta J=0,\pm1$. This, in turn, makes it easier to satisfy the delta functions for conservation of energy in Eqs. (34), (44), and (45) when $(\omega-\omega_{fi})$ becomes large.

We have, in our calculations, explicitly included the dipole-quadrupole and quadrupole-dipole interactions. (The distinction being radiator-perturber and perturber-radiator, respectively.) In the case of the quadrupole-dipole interaction there is also a contribution associated with Anderson's S_2(inner).[12,13] This contribution has been ignored in the present calculations.

The essential modifications necessary to treat the dipole-quadrupole and quadrupole-dipole interactions are given in Appendix C. Somewhat more explicitly, the modifications can be simply expressed as presented below.

For the dipole-quadrupole case, for the S_2 functions in Eqs. (59) and (60), the following substitution is to be made:

$$\frac{4\pi^2}{3} S_{j_f j_f'} S_{JJ'} \rightarrow \left(\frac{15}{7}\right)^2 (2\pi^2) S_{j_f j_f'} G_{JJ'}. \tag{96}$$

In this substitution, the difference in numerical factors arises precisely from Eq. (C30a). Also in the above equation, $G_{JJ'}$ is a quadrupole strength, defined in terms of the reduced matrix element (which appears in Eqs. (C27) and (C29)) by

$$\sum_{J'} |\langle J||Q||J'\rangle|^2 = q^2 \sum_{J'} G_{JJ'} = q^2. \tag{97}$$

That is, q^2 is the square of the scalar quadrupole moment (it is independent of J), and the quadrupole strengths satisfy the sum role

$$\sum_{J'} G_{JJ'} = 1. \tag{98}$$

For the quadrupole-dipole case, the substitution analogous to Eq. (96) is

$$\frac{4\pi^2}{3} S_{j_f j_f'} S_{JJ'} \rightarrow \left(\frac{15}{7}\right)^2 (2\pi^2)\, G_{j_f j_f'} S_{JJ'}. \tag{99}$$

The dipole strengths $S_{JJ'}$ were computed using the asymmetric rotor codes developed at AFGL. The quadrupole strengths $G_{JJ'}$ were computed using a program developed by one of the present Authors,[16] which can be attached as an update to the AFGL package.

The remaining modifications are to the translational matrix elements and these are identical for the dipole-quadrupole and quadrupole-dipole cases: first, the factor z^{-3} in the I-matrix element (Eqs. (52) and (84)) gets replaced by z^{-4}; then in Eq. (56) for the M-matrix element, the following substitution is necessary:

$$\left(\frac{\mu^2}{hcr_s^3}\right)^2 (\ell 200|\ell 2\ell'0)^2 \rightarrow \left(\frac{\mu^2}{hcr_s^3}\right)\left(\frac{q^2}{hcr_s^5}\right)(\ell 300|\ell 3\ell'0)^2. \qquad (100)$$

Finally, for the hypergeometric (Eqs. (86) through (89)) and sine-cosine integral (Eqs. (90) through (95)) calculations discussed in Section 4 there is an obvious modification due to $z^{-3} \rightarrow z^{-4}$ in the I-matrix element.

We now quote the specific parameters upon which our present calculations are based. For the Lennard-Jones potential we have chosen the parameter values,[17] E_s=243 cm^{-1}=potential minimum, and r_s=3.059 cm=radius at well minimum. For the H_2O permanent dipole moment we have used the well-known value μ=1.85x10^{-18} esu-cm=1.85 Debye. For the H_2O permanent quadrupole moment we have employed the review article of Strogryn and Strogryn[18] to infer an average measured value of q=1.158x10^{26} esu-cm^2.

The only remaining adjustable "parameter" in the theory is the manner in which a unitarity cutoff is employed in the strong collision (small impact parameters, classically) limit. For sufficiently small $(\omega-\omega_{fi})$, there is no doubt that such a cutoff is necessary, because, if the cutoff is eliminated, the resulting halfwidths at the line center are large by a factor of order 40 compared to experiment. Sufficiently far in the wings the cutoff can be dropped. However, exactly how one should interpolate between these two limits remains somewhat of an open question.

Anderson's simplest cutoff procedure as applied to S_2^{tot} is to reset S_2^{tot}=1, if S_2^{tot} (as calculated by Eq. (58)) is such that it exceeds unity. An alternative (and somewhat smoother) exponential form of the cutoff is to replace S_2^{tot} by

$$(S_2^{tot})_{eff} = 1 - e^{-S_2^{tot}} . \qquad (101)$$

Theoretical justification for this type of cutoff may be found in the literature[19-22]. From Eq. (101), if $S_2^{tot} \ll 1$, we obtain $(S_2^{tot})_{eff} \approx S_2^{tot}$. If, on the other hand, $S_2^{tot} \gg 1$, Eq. (101) reduces to $(S_2^{tot})_{eff} \approx 1$.

The above cutoff schemes, based on S_2^{tot}, suffer from a major problem in the far-wing case. Due to the exponential factor in the second term of Eq. (58), the FDT cannot be satisfied unless the cutoff is applied separately to S_2^f and S_2^i in Eq. (58).

In the absence of a rigorous prescription for cutoff, we have employed the following methods which satisfy FTD and yield an S_2 which is bounded by unity as in Anderson's theory. The first method is simply to reset S_2^f (or S_2^i) equal to 1/2 if S_2^f (or S_2^i) exceeds 1/2. An exponential form of this cutoff scheme is

$$(S_2^f)_{eff} = \tfrac{1}{2}(1 - e^{-2S_2^f}). \tag{102}$$

Again for $S_2^f \gg 1$ this yields $(S_2^f)_{eff} \approx S_2^f$, while for $S_2^f \ll 1$, we obtain $S_2^f \approx$ 1/2.

In Tables 1 through 4 we present the results of our calculations of H_2O far-wing absorption. The calculations have been carried out using the exponential form (Eq. (102)) for the separate cutoffs on S_2^f and S_2^i.

The calculations have been carried out for the strong pure rotational transition 4,1,4→5,0,5 with line center frequency at ω_{fi}=100.51 cm^{-1}. In Tables 1 and 2 we present results for a photon energy ω=500 cm^{-1}. This means that the positive and negative oscillators are "off resonance" by approximately 400 cm^{-1} and 600 cm^{-1}, respectively. The columns in the tables are as follows:

Column 1 = temperature °K.

Column 2 = $\tilde{\Gamma}(0)$, the line center halfwidth in cm^{-1} as given by Eq. (79) with $(\omega-\omega_{fi})$ set to zero.

Column 3 = $\tilde{\Gamma}(\omega-\omega_{fi})$=the positive oscillator halfwidth as computed from Eq. (79).

Column 4 = $\tilde{\Gamma}(-\omega-\omega_{fi})$=negative oscillator halfwidth computed from Eq. (79).

Column 5 = $\chi''(\omega)_{FD^-}$ as computed from Eq. (80).

Column 6 = $\chi''(\omega)_{Impact}$ as computed from Eq. (81).

Column 7 = $\chi''(\omega)_{FD^-}/\chi''(\omega)_{Impact}$ as computed from Eq. (82).

Table 1 presents results for ω=500 cm^{-1} in which only dipole-dipole contributions are included. Table 2 is for ω=500 cm^{-1}, but including dipole-dipole, dipole-quadrupole, and quadrupole-dipole interactions. From the line center halfwidths in Tables 1 and 2 we note that the addition of the dipole-quadrupole interaction represents about a 2% effect, so that the dipole-dipole interaction is strongly dominant. For fixed density, the increase in the halfwidth with temperature is mainly associated with the increase in v which appears in Eq. (72). (See Fig. 2 for a plot of the temperature dependence.) The values for the halfwidths are approximately what one would expect from Anderson's theory for self broadening of low-J H_2O transitions.

The positive and negative oscillator halfwidths are seen to be reduced relative to the line center halfwidth (the impact halfwidth) due to the difficulty of conserving energy far off resonance. This also accounts for the fact that the negative oscillator halfwidth is small compared to the positive oscillator halfwidth.

It is very interesting to note that the addition of the dipole-quadrupole and quadrupole-dipole interactions in Table 2 increases the positive oscillator halfwidths by a factor of order 2 and increases the negative oscillator halfwidths by an order of magnitude! This emphasizes the importance of the higher-order multipole interactions for the far-wing problem. The origin of this can be rather simply stated: the translational matrix elements (Eq. (56)) tend to be small unless the difference in translational energies, $\epsilon-\epsilon'$, is small, typically less than 20 cm^{-1}. This being the case, when $\hbar(\omega-\omega_{fi})$ is large, the only thing left to conserve energy is the change in rotational energy. Because the selection rules on ΔJ for the dipole-quadruple and higher-order multipole interactions allow for progressively larger changes in rotational energy, these collisions are more effective in broadening the wings.

For some fixed value of $\hbar(\omega-\omega_{fi})$, there may be some particular order of multipole interaction which dominates; however, the convergence of the multipole series cannot be assured. Since the higher-order multipole interactions are progressively more effective at close separations, this also emphasizes the point that the far wings are dominated by strong, short-ranged collisions.

The results for the ratio $R(\omega)$ (Eq. (82)) in Column 7 indicate too low a level of absorption. At 1000 cm^{-1} it is known that the impact formula, Eq. (81), yields an absorption which is high compared to experiment by a factor of approximately two. Thus at ω=1000 cm^{-1}, one would like to find the ratio $R(\omega) \approx 1/2$. However, at ω=500 cm^{-1}, $R(\omega)$ is already small of order, $R(\omega)$=.20.

The results for ω=1000 cm^{-1} are presented in Tables 3 and 4. These tables show the same general trends as discussed for Tables 1 and 2. The effect of adding the dipole-quadrupole interactions is even more pronounced, the ratio $R(\omega)$ is raised by two orders of magnitude upon inclusion of the dipole-quadrupole interactions. In Tables 1 and 4, Column 7 shows little indication of the negative temperature dependence observed experimentally.

Future Work.

Although our present calculations indicate a level of far-wing absorption which is too small to account for experimental observations, these calculations have shed light on a number of important issues which remain to be addressed.

1. A more rigorous approach to the far-wing unitarity cutoff procedure should be sought. A more relaxed cutoff procedure would certainly enhance the far-wing absorption.
2. The sensitivity of the far-wing absorption to the Lennard-Jones parameters should be investigated. In particular, a deeper LJ potential should enhance the translational matrix elements.
3. It would be desirable to extend the present calculation to include quadrupole-quadrupole collisions. This should give some indication of the convergence of the multipole expansion. If divergence is indicated, some more realistic formulation of the short-ranged anisotropic interaction will be required.
4. It would be extremely interesting to apply the present formalism to the problem of N_2 broadening of H_2O in the far wings. It is known, experimentally, that N_2 broadening leads to a greatly reduced continuum ab-

sorption. From our present point of view it is tempting to speculate that this reduction is related to the small rotational constant (2 cm^{-1}) for N_2, which in turn implies much smaller changes in rotational energy in the collision processes.

5. Deep resonant and true bound states may be important, including transitions from bound to continuum states. The present formulation is not applicable to the bound state problem; however, the single-perturber approximation which concentrates on the interaction between a single radiator and perturber should remain valid.

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We are also grateful to R.J. LeRoy for kindly providing us with his Numerov method computer codes.

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TABLE 4: Summary of absorption for $\omega=1000$ cm^{-1} for various temperatures. All three interactions (dipole-dipole, dipole-quadrupole, quadrupole-dipole) are included.

FIGURE 1: A schematic of the total isotropic potential, $V_0(r,1)$, for $1>0$. Three values of the translational energy ε are indicated.

FIGURE 2: Temperature dependence of the linecenter (impact) halfwidths. It is assumed that a power low of the form

$$\Gamma(T)/\Gamma(296) = (T/296)^m$$

is approximately valid so that the quantities plotted are

$$\ln\left[\Gamma(T)/\Gamma(296)\right] \text{ vs } \ln\left[T/296\right] .$$

The slope, m, from the figure is found to be m = .365.

TABLE 1

CASE DESCRIPTION : ONLY CONTRIBUTIONS DUE TO DIPOLE-DIPOLE INTERACTIONS CONSIDERED

TRANSITION : 414 - 505
PHOTON ENERGY (W) : 500.0000
LINECENTER (WFI) : 100.5100

TEMP	G(0)	G(W-WFI)	G(-W-WFI)	X(W)	X1(W)	X(W)/X1(W)
225.00	0.42843E+00	0.10388E+00	0.96789E-04	0.63054E-06	0.54448E-05	0.11581E+00
250.00	0.44740E+00	0.10978E+00	0.19812E-03	0.65830E-06	0.56389E-05	0.11674E+00
296.00	0.47722E+00	0.12124E+00	0.53394E-03	0.70806E-06	0.58333E-05	0.12138E+00
350.00	0.50573E+00	0.13515E+00	0.12396E-02	0.76166E-06	0.58699E-05	0.12976E+00
400.00	0.52756E+00	0.14806E+00	0.22368E-02	0.80522E-06	0.57906E-05	0.13905E+00

TABLE 2

CASE DESCRIPTION : CONTRIBUTIONS FROM BOTH INTERACTIONS ARE CONSIDERED

TRANSITION : 414 - 505
PHOTON ENERGY (W) : 500.0000
LINECENTER (WFI) : 100.5100

TEMP	G(0)	G(W-WFI)	G(-W-WFI)	X(W)	X1(W)	X(W)/X1(W)
225.00	0.43890E+00	0.18798E+00	0.15342E-02	0.12293E-05	0.55779E-05	0.22039E+00
250.00	0.45732E+00	0.19043E+00	0.23653E-02	0.12358E-05	0.57640E-05	0.21440E+00
296.00	0.48631E+00	0.19727E+00	0.43921E-02	0.12532E-05	0.59444E-05	0.21082E+00
350.00	0.51412E+00	0.20733E+00	0.75056E-02	0.12741E-05	0.59673E-05	0.21352E+00
400.00	0.53553E+00	0.21751E+00	0.10977E-01	0.12903E-05	0.58781E-05	0.21951E+00

TABLE 3

CASE DESCRIPTION : ONLY CONTRIBUTIONS DUE TO DIPOLE-DIPOLE INTERACTIONS CONSIDERED

TRANSITION : 414 - 505
PHOTON ENERGY (W) : 1000.0000
LINECENTER (WE) : 100.5100

TEMP	G(0)	G(W-WE)	G(-W-WE)	X(W)	X1(W)	X(W)+X1(W)
225.00	0.42843E+00	0.25387E-04	0.54539E-08	0.34006E-10	0.13434E-05	0.25313E-04
250.00	0.44740E+00	0.41222E-04	0.13891E-07	0.54386E-10	0.14307E-05	0.38014E-04
296.00	0.47722E+00	0.91279E-04	0.73278E-07	0.11967E-09	0.15634E-05	0.76557E-04
350.00	0.50573E+00	0.44267E-04	0.39169E-06	0.73170E-10	0.16765E-05	0.43644E-04
400.00	0.52756E+00	0.27458E-03	0.14635E-05	0.37284E-09	0.17468E-05	0.21344E-03

TABLE 4

CASE DESCRIPTION : CONTRIBUTIONS FROM BOTH INTERACTIONS ARE CONSIDERED

TRANSITION : 414 - 505
PHOTON ENERGY (W) : 1000.0000
LINECENTER (WE) : 100.5100

TEMP	G(0)	G(W-WE)	G(-W-WE)	X(W)	X1(W)	X(W)+X1(W)
225.00	0.43890E+00	0.37276E-02	0.79546E-07	0.46386E-08	0.13762E-05	0.33705E-02
250.00	0.45732E+00	0.48694E-02	0.28038E-06	0.60719E-08	0.14629E-05	0.41550E-02
296.00	0.48631E+00	0.73190E-02	0.17389E-05	0.91592E-08	0.15929E-05	0.57499E-02
350.00	0.51412E+00	0.39169E-01	0.85232E-05	0.48037E-07	0.17043E-05	0.28185E-01
400.00	0.53553E+00	0.14635E-01	0.26146E-04	0.18356E-07	0.17732E-05	0.10357E-01

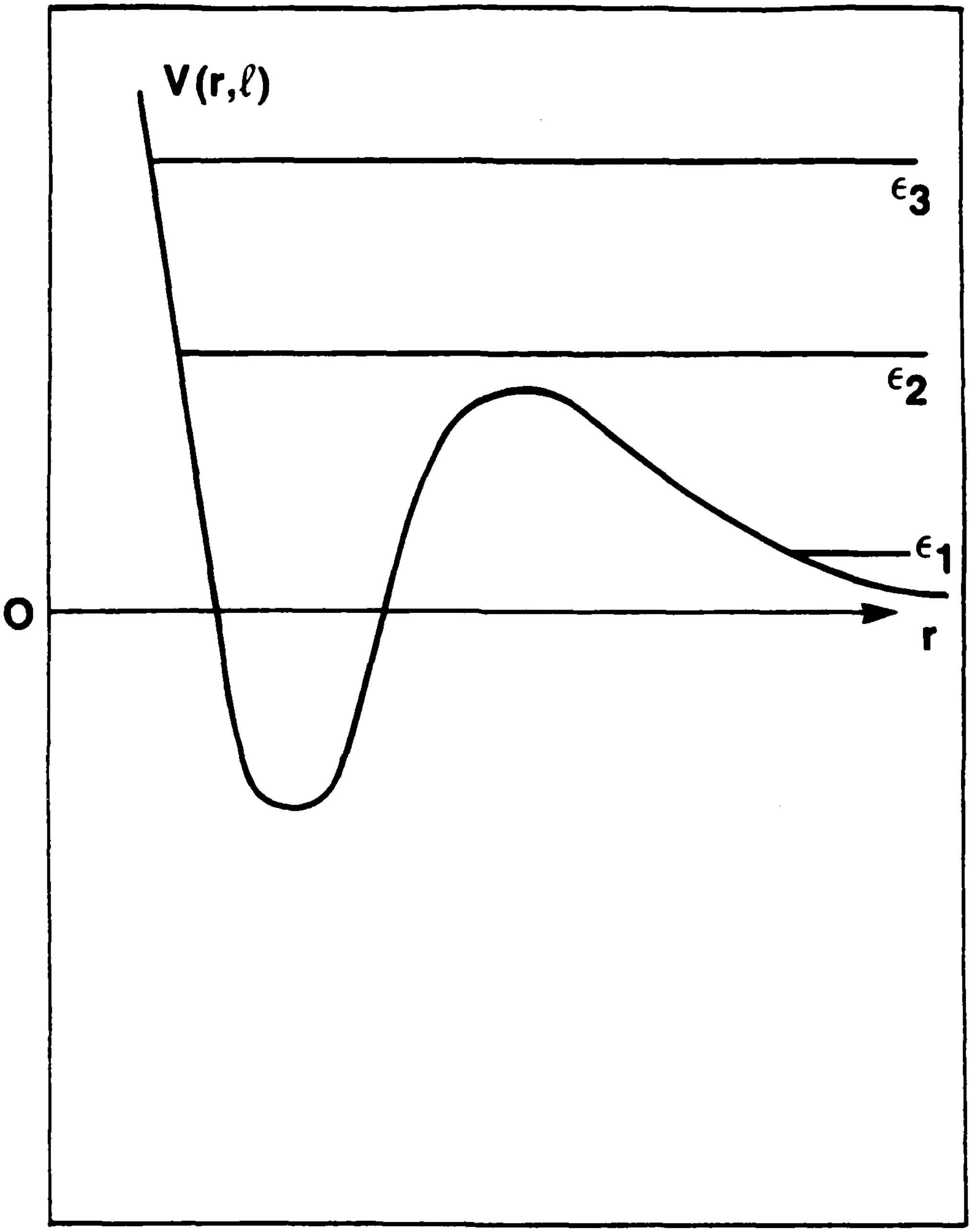
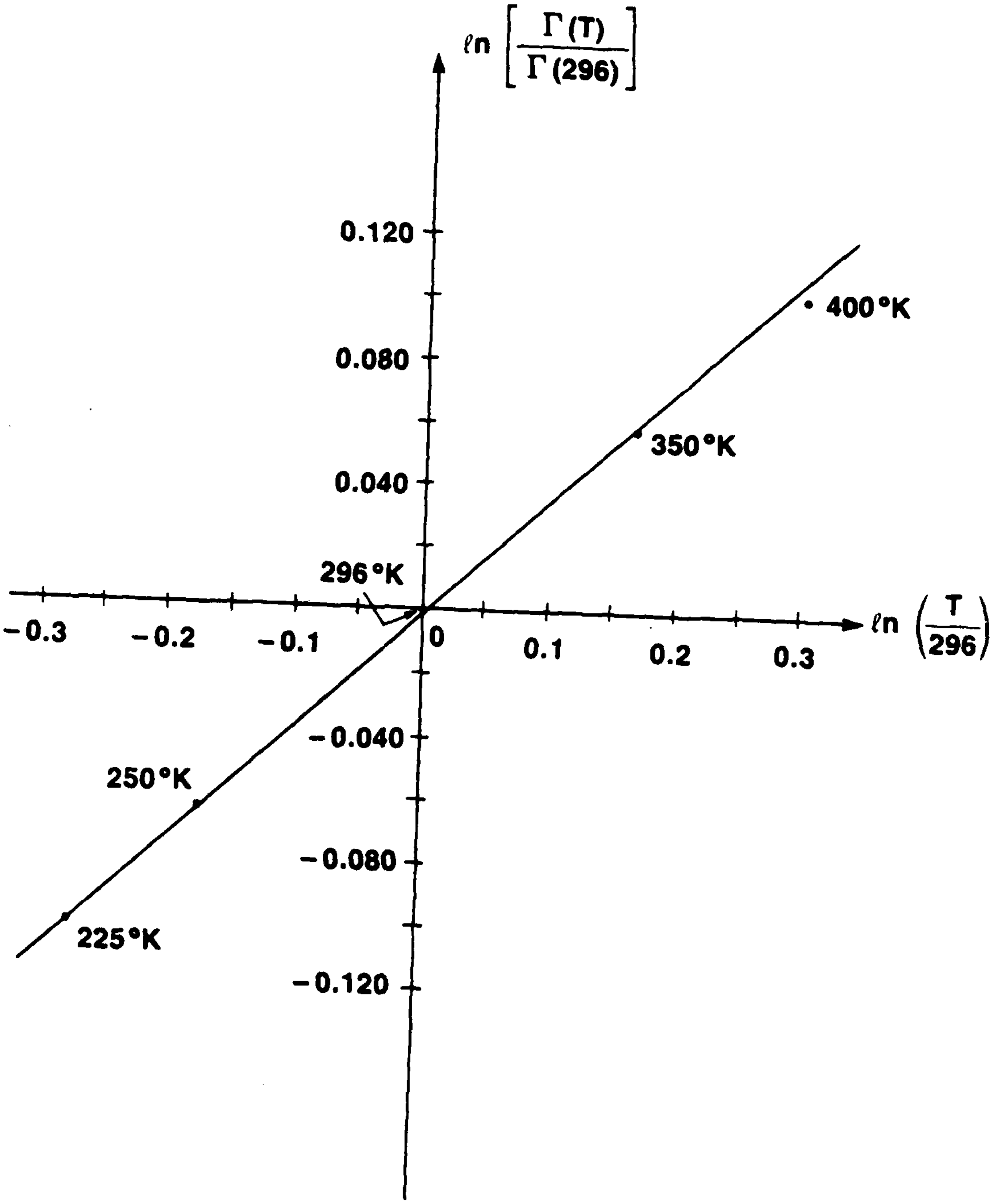


FIGURE 1



$\ell n \left[\frac{\Gamma(T)}{\Gamma(296)} \right]$
0.120
0.080
0.040
−0.040
−0.080
−0.120
−0.3
−0.2
−0.1
0
0.1
0.2
0.3
$\ell n \left(\frac{T}{296} \right)$
400°K
350°K
296°K
250°K
225°K

FIGURE 2

APPENDIX A

Derivation of The Single-Perturber Approximation from the Autocorrelation Function in the Time Domain

In this Appendix we derive the single-perturber approximation from the time-domain treatment of the dipole autocorrelation function, as presented in Ref. 8. From Ref. 8 we make use of Eqs. (3.20b), (3.25), (4.13) through (4.15), and (4.27), (4.28). These equations ignore M-sums and Clebsch-Gordan coefficients, and, for simplicity, we continue this omission.

In second order perturbation theory in the anisotropic interaction, the dipole autocorrelation function can be written

$$\phi_{if}(t) = \exp\{N_{per}[K_f(t) + K_i(t) + K_{if}(t)]\} . \qquad (A1)$$

The terms $K_f(t)$, $K_i(t)$ correspond to Anderson's s_2(outer) terms, while $K_{if}(t)$ corresponds to s_2(inner). We shall ignore $K_{if}(t)$ for the reasons given at the end of Section 2.

The expressions for K_f, K_i are

$$K_f(t) = -\frac{1}{\hbar^2}\sum_{Jk} \varrho(\epsilon_J)\,\varrho(\epsilon_k) \sum_{j_{f'}J'k'} |<\alpha|V|\beta>|^2 f(t) , \qquad (A2)$$

$$K_f(t) = -\frac{1}{\hbar^2}\sum_{Jk} \varrho(\epsilon_J)\,\varrho(\epsilon_k) \sum_{j_{i'}J'k'} |<\alpha'|V|\beta'>|^2 \tilde{f}(t) , \qquad (A3)$$

where, for simplicity,

$\alpha> \;=\; j_f Jk>$

$\beta> \;=\; j_{f'} J'k'>$

$\alpha'> \;=\; j_i Jk>$

$\beta'> \;=\; j_{i'} J'k'>$

We also define $\hbar\omega_{\alpha\beta}=\varepsilon_\alpha-\varepsilon_\beta$ and $\hbar\omega_{\alpha'\beta'}=\varepsilon_{\alpha'}-\varepsilon_{\beta'}$.

The time dependence is contained in the functions

$$f(t) = \frac{1}{\omega^2_{\alpha\beta}} [1 - \cos(\omega_{\alpha\beta}t)]$$

$$- \frac{i}{\omega_{\alpha\beta^2}} [\omega_{\omega\beta}t - \sin(\omega_{\alpha\beta}t)] \,. \qquad (A4)$$

$$\tilde{f}(t) = \frac{1}{\omega_{\alpha'\beta'^2}} [1 - e^{\beta\hbar\omega_{\alpha'\beta'}} \cos(\omega_{\alpha'\beta'}t)]$$

$$+ \frac{i}{\omega_{\alpha'\beta'}} [\omega_{\alpha'\beta'}(t - i\beta\hbar) - e^{\beta\hbar\omega_{\alpha'\beta'}} \sin(\omega_{\alpha'\beta'}t)] \,. \qquad (A5)$$

The FDT asymmetry between the final Eq. (A4) and initial Eq. (A5) is contained in the temperature dependent $\beta\hbar\omega_{\alpha'\beta'}$ factors in Eq. (A5).

The single perturber approximation assumes that the far-wings will be governed by times sufficiently small, and densities sufficiently low that Eq. (A1) may be approximated by

$$\phi_{if}(t) \cong 1 + N_pK_f(t) + N_pK_i(t) \qquad (A6)$$

That this is as much an expansion in density as in small time can be appreciated by noting that one obtains nonsense if $K_f(t),K_i(t)$ are expanded in power series - that is one obtains nonsense if one attempts to Fourier transform the power series expansions.

When we take the Fourier transform of Eq. (A6), the first term leads to a delta function singularity at the line center, $\omega=\omega_{fi}$. This has been noted in Baranger's discussion of the single-perturber approximation. Moreover, $K_f(t),K_i(t)$ also contain additional singular contributions at the line center.

The singular contributions are connected with the nonoscillatory terms in Eqs. (A4) and (A5), i.e. the terms which do not contain a sine or cosine variation. These singular terms contribute only at the line center and are to be discarded in the wings. As discussed by Baranger, the single-perturber approximation is not valid at the line center.

If we now discard the nonoscillatory terms in Eqs. (A4) and (A5), we obtain

$$f(t) \cong - \frac{1}{\omega^2_{\alpha\beta}} \, e^{-i\omega_{\alpha\beta}t} \, , \tag{A7}$$

$$\tilde{f}(t) = - \frac{1}{\omega_{\alpha'\beta'}} \, e^{\beta\hbar\omega_{\alpha'\beta'}} e^{i\omega_{\alpha'\beta'}t} \, , \tag{A8}$$

where we note the difference in sign in the arguments of the time-dependent exponential factors.

With the above simplifications, the Fourier transform

$$\phi_{if}(\omega) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt \, e^{-i(\omega-\omega_{fi})t} \, \phi_{if}(t) \tag{A9}$$

can be performed trivially using

$$\frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt \, e^{-i(\omega-\omega_{fi}+\omega_{\alpha\beta})t}$$

$$= \delta[\epsilon_{\alpha\beta} + \hbar(\omega - \omega_{fi})] \, , \tag{A10}$$

$$\frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt \, e^{-i(\omega-\omega_{fi}-\omega_{\alpha'\beta'})t}$$

$$= \delta[\epsilon_{\alpha'\beta'} - \hbar(\omega - \omega_{fi})] \, , \tag{A11}$$

For $\phi_{if}(\omega)$, we obtain

$$\phi_{if}(\omega) = N_p \sum_{Jk} \varrho(\epsilon_J)\, \varrho(\epsilon_k) \sum_{j_f J'k'} \frac{|<\alpha|V|\beta>|^2}{\epsilon^2_{\alpha\beta}} \cdot \delta(\epsilon_{\alpha\beta} + \hbar\omega - \hbar\omega_{fi})$$

$$+ N_p \sum_{Jk} \varrho(\epsilon_j)\, \varrho(\epsilon_k) \sum_{j_i J'k'} \frac{|<\alpha'|V|\beta'>|^2}{\epsilon^2_{\alpha'\beta'}} \cdot e^{\beta\hbar\omega_{\alpha'\beta'}}\, \delta(\epsilon_{\alpha'\beta'} - \hbar\omega + \hbar\omega_{fi}) . \qquad \text{(A12)}$$

By making use of the delta functions in this expression, we obtain

$$\phi_{if}(\omega) \quad \frac{1}{\pi} \frac{\Gamma(\omega - \omega_{fi})}{(\epsilon_{fi} - \hbar\omega)^2} \quad , \qquad \text{(A13)}$$

where the halfwidth function is given by

$$\Gamma(\omega - \omega_{fi}) = N_p \sum_{Jk} \varrho(\epsilon_J)\, \varrho(\epsilon_k) \sum_{j_f J'k'} |<\alpha|V|\beta>|^2 \cdot \pi\, \delta(\epsilon_{\alpha\beta} + \hbar\omega - \hbar\omega_{fi})$$

$$+ e^{\beta\hbar(\omega-\omega_{fi})} N_p \sum_{Jk} \varrho(\epsilon_J)\, \varrho(\epsilon_k) \sum_{j_i J'k'} |<\alpha'|V|\beta'>|^2\, \pi\, \delta(\epsilon_{\alpha'\beta'} - \hbar\omega + \hbar\omega_{fi}) \qquad \text{(A14)}$$

This is identical to Eq. (34) of the text which was obtained from the T-matrix theory of Ref. 9. Equation (A13) differs from Eq. (33) of the text by a factor of n_{rad}, the radiator density.

APPENDIX B

Miller and Poll Normalization of Translational States

We consider the quantity in Eq. (37)

$$\text{sum} = N_{per} \sum_{kk'} \varrho(\epsilon_k) <k|V|k'> <k'|V|k> , \qquad (B1)$$

$$= \frac{N_{per}}{\Omega} \frac{\sum_{kk'} e^{-\beta\epsilon_k} <k|V|k'> <k'|V|k>}{\frac{1}{\Omega}\sum_k e^{-\beta\epsilon_k}} , \qquad (B2)$$

or

$$\text{sum} = \frac{n_{per}}{z} \sum_{kk'} e^{-\beta\epsilon_k} <k|V|k'> <k'|V|k> \qquad (B3)$$

with $n_{per}=N_{per}/\Omega$ the perturber number density, and

$$z = \frac{1}{\Omega} \sum_{\vec{k}} e^{-\beta\epsilon_{\vec{k}}} \qquad (B4)$$

the translational partition sum. With $\varepsilon_k=\hbar^2k^2/2m$, this evaluates to give

$$z = \left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2} . \qquad (B5)$$

A particularly convenient set of basis states |k> for the present problem, can be written

$$\Psi_k(\vec{r}) = <\vec{r}|k> = Y_{\ell m_\ell}(\theta, \phi)\, R_\ell(k; r) , \qquad (B6)$$

where Y is a spherical harmonic, and $R_l(k;r)$ is a radial wavefunction with the Miller and Poll[23] normalization. This is a normalization to unity within a large but finite radius R_0, according to

$$\int_0^{R_0} r^2 dr\, R_\ell(k; r)^2 = 1 . \qquad (B7)$$

The asymptotic form of the radial wavefunction is[19]

$$R_\ell(k;\, r) \xrightarrow[r \to \infty]{} k \sqrt{\frac{2}{R_o}}\, \frac{\sin[kr - \tfrac{1}{2}\ell\pi + \delta_\ell(k)]}{kr}\,, \tag{B8}$$

where $\delta_l(k)$ is a phase shift.

Next, it is convenient to define new wavefunctions according to

$$R_\ell(k;\, r) = \sqrt{\frac{2}{R_o}}\, \frac{1}{r}\, \phi_\ell(k;\, r) \tag{B9}$$

From Eq. (B8) the ϕ's will have the asymptotic form of pure sine waves, i.e.

$$\phi_\ell(k;\, r) \xrightarrow[r \to \infty]{} \sin[kr - \tfrac{1}{2}\ell\pi + \delta_\ell(k)] \tag{B10}$$

Thus

$$\Psi_k(\vec{r}) = \frac{1}{r} \sqrt{\frac{2}{R_o}}\, Y_{\ell m_\ell}(\theta,\, \phi)\, \phi_\ell(k;\, r)\,, \tag{B11}$$

$$= \sqrt{\frac{2}{R_o}}\, R_{k\ell m_\ell}(\vec{r})\,. \tag{B12}$$

where we have defined

$$R_{k\ell m_\ell}(\vec{r}) = Y_{\ell m_\ell}(\theta,\, \varphi)\, \frac{1}{r}\, \phi_\ell(k;\, r) \tag{B13}$$

In Dirac notation we write this

$$|k\rangle = \sqrt{\frac{2}{R_o}}\, |R_{k\ell m}\rangle\,. \tag{B14}$$

Now Miller and Poll's prescription for computing a "short-ranged" quantity, e.g. a matrix element of a multipole interaction which vanishes as $r \to \infty$, is that sums over k can be replaced by

$$\sum_k \to \sum_{k\ell m_\ell} = \sum_{\ell m_\ell} \int_0^\infty dk\, \frac{R_o}{\pi} \tag{B15}$$

When Eq.s (B14) and (B15) are inserted into Eq. (B3), we obtain

$$\text{sum} = \frac{n_{per}}{z}\left(\frac{2}{\pi}\right)^2 \sum_{\ell m_\ell} \sum_{\ell' m_{\ell'}}$$

$$\cdot \int_0^\infty dk\, e^{-\beta\epsilon_k} \int_0^\infty dk' \, \langle R_{k\ell m_\ell} | V | R_{k'\ell' m_{\ell'}} \rangle \langle R_{k'\ell' m_{\ell'}} | V | R_{k\ell m_\ell} \rangle \qquad \text{(B16)}$$

APPENDIX C

Clebsch-Gordan Albegra

We shall consider the sum (j_f) term as given by Eq. (44). Evaluation of sum (j_i) proceeds in a similar fashion.

We begin the calculation by noting that the three magnetic quantum numbers m_i, $m_{i'}$, m do not occur in the V-matrix elements. These three sums can be performed immediately, and simply give

$$\sum_{m_i m_{i'}} \sum_{m} \delta m_i, m_{i'} \cdot (j_f 1 m_f m | j_f 1 j_i m_i)(j_f 1 m_{f'} m | j_f 1 j_i m_{i'}) = \left(\frac{2j_i + 1}{2j_f + 1} \right) \delta_{m_{f'}, m_f} . \qquad \text{(C1)}$$

We use the above Kronecher delta to perform the $m_{f'}$ sum, and then we change some names of dummy summation variables to provide a simpler notation. Specifically, we let

$$j_{f''} \rightarrow j_{f'}$$
$$m_{f''} \rightarrow m_{f'}$$
$$m_1 \rightarrow m$$
$$m_{1'} \rightarrow m'$$

This yields

$$\text{sum}\,(j_f) = \sum_{j_{f'}} \delta(\epsilon_{ff'} + \hbar\omega - \epsilon_{fi})Q , \qquad \text{(C2)}$$

where Q is the "quantity"

$$Q = \frac{1}{(2j_f + 1)} \sum_{m_f m_{f'}} \sum_{M,M'} \sum_{mm'} |\mathcal{V}|^2 , \qquad \text{(C3)}$$

with

$$\mathcal{V} = \langle j_f m_f;\ JM;\ R_{k\ell m} | V | j_{f'} m_{f'};\ J'M';\ R_{k'\ell' m'} \rangle \tag{C4}$$

Here the states involved are actually products, i.e. $|j_f m_f; JM; R_{klm}\rangle = |j_f m_f\rangle |JM\rangle |R_{klm}\rangle$.

Dipole-Dipole Case

For the dipole-dipole case

$$V = \frac{1}{r^3} (\vec{\mu}_1 \cdot \vec{\mu}_2 - 3\, \vec{\mu}_1 \cdot \hat{r}\, \vec{\mu}_2 \cdot \hat{r}) \tag{C5}$$

where $\vec{\mu}_1, \vec{\mu}_2$ are the radiator and perturber dipole moments and $\vec{r}$ is the relative coordinate.

The vector $\hat{r}$ can be written

$$\hat{r} = \sqrt{\frac{4\pi}{3}} \sum_{m_r = 0, \pm 1} Y_{1m_r}(\theta, \varphi)\, \hat{\epsilon}_{m_r} . \tag{C6}$$

Here the Y's are spherical harmonics (Condon and Shortley phases), and the ϵ's are given by

$$\hat{\epsilon}_0 = \hat{z},\ \hat{\epsilon}_{-1} = \frac{\hat{x} + i\hat{y}}{\sqrt{2}},\quad \hat{\epsilon}_{+1} = \frac{-\hat{x} + i\hat{y}}{\sqrt{2}}, \tag{C7}$$

The $\hat{\epsilon}$'s satisfy an orthogonality rule which can be written as

$$\hat{\epsilon}_{m_r} \cdot \hat{\epsilon}_{-m_{r'}} = (-1)^{m_{r'}}\, \delta_{m_{r'}, r} , \tag{C8}$$

or as

$$\hat{\epsilon}_{m_r} \cdot \hat{\epsilon}^{*}_{m_{r'}} = \delta m_{r'}, m_r . \tag{C9}$$

The dipole-dipole interaction can then be written

$$\begin{aligned} V = {} & \frac{1}{r^3}\, \vec{\mu}_1 \cdot \vec{\mu}_2 \\ & - \frac{3}{r^3}\, \frac{4\pi}{3} \sum_{m_r} \sum_{m_{r'}} Y_{1m_r}(\theta, \varphi)\, Y_{1m_{r'}}(\theta, \varphi) \\ & \cdot \vec{\mu}_1 \cdot \hat{\epsilon}_{m_r}\, \vec{\mu}_2 \cdot \hat{\epsilon}_{m_{r'}} \end{aligned} \tag{C10}$$

The basic strategy for reducing all the multipole interactions to a convenient form is to use the addition theorem for spherical harmonics:[24]

$$\begin{aligned} & Y_{\ell_1 m_1}(\theta, \varphi)\, Y_{\ell_2 m_2}(\theta, \varphi) \\ &= \left[\frac{(2\ell_1 + 1)(2\ell_2 + 1)}{4\pi\,(2\ell_3 + 1)} \right]^{1/2} \\ &\quad \cdot \sum Y_{\ell_3 m_3}(\theta, \varphi) \\ &\quad \cdot (\ell_1 \ell_2 m_1 m_2 | \ell_1 \ell_2 \ell_3 m_3) \cdot (\ell_1 \ell_2\, 00 | \ell_1 \ell_2 \ell_3 0) \,. \end{aligned} \tag{C11}$$

In the dipole-dipole case, the product $Y_1 \cdot Y_1$, via the addition theorem, produces a Y_0 (which cancels the first term in Eq. (C10)) and a Y_2. The result is

$$\begin{aligned} V &= -\frac{3\sqrt{4\pi}}{r^3}\, \frac{(1100|1120)}{\sqrt{5}} \\ &\quad \cdot \sum_{m_r m_{r'}} \sum_{m_3} (11 m_r m_{r'} | 112 m_3) Y_{2m_3}(\theta, \varphi)\, (\vec{\mu}_1 \cdot \hat{\epsilon}_{m_r})\, (\vec{\mu}_2 \cdot \hat{\epsilon}_{m_{r'}}) \,. \end{aligned} \tag{C12}$$

Now the Wigner-Eckhart theorem (Eq. (20)) can conveniently be put in an operator form

$$\vec{\mu} = \sum_{m_1 = 0, \pm 1} \mu(m_1) \hat{\epsilon}_{m_1} \,, \tag{C13}$$

where, from Eq. (20), the matrix element of the operator $\mu(m_1)$ are given by

$$\begin{aligned} & < j_f m_f | \mu(m_1) | j_{f'} m_{f'} > \\ &= < j_f || \mu || j_{f'} > (j_{f'} 1 m_{f'} m_1 , j_{f'}\, 1 j_f m_f) \end{aligned} \tag{C14}$$

From Eq. (C13) we then note

$$\begin{aligned} \vec{\mu} \cdot \hat{\epsilon}_{m_r} &= \sum_{m_1 = 0, \pm 1} \mu(m_1)\, \hat{\epsilon}_{m_1} \cdot \hat{\epsilon}_{m_r} \,, \\ &= \sum_{m_1} \mu(m_1)\, (-1)^{m_r}\, \delta_{m_1, -m_r} \,, \end{aligned}$$

$$\vec{\mu} \cdot \hat{\epsilon}_{m_r} = (-1)^{m_r}\, \mu(-m_r) \,. \tag{C15}$$

The dipole-dipole interaction then assumes its final form

$$V = -\frac{3\sqrt{4\pi}}{r^3}\,\frac{(1100|1120)}{\sqrt{5}}$$

$$\sum_{m_r m_{r'}}\sum_{m_3}(11 m_r m_{r'}|112 m_3)\,Y_{2m_3}(\theta,\varphi)$$

$$\cdot\,(-1)^{m_r+m_{r'}}\,\mu_1(-m_r)\,\mu_2(-m_{r'}) \tag{C16}$$

In this form the matrix element is easily evaluated; Y_{2m_3} operates between $R_{klm}\rangle$ states, $\mu_1(-m_r)$ operates between $j_f m_f\rangle$ radiator states, and $\mu_2(-m_{r'})$ operates between $JM\rangle$ perturber states. The complete matrix element V in Eq. (C4) can then be written

$$V = -3\sqrt{4\pi}\,\frac{(1100|1120)}{\sqrt{5}}\,\langle R_{k\ell}|\,\frac{1}{r^3}\,|R_{k'\ell'}\rangle$$

$$\sum_{m_r m_{r'}}\sum_{m_3}(-1)^{m_r+m_{r'}}(11\, m_r m_{r'}|112\, m_3)$$

$$\cdot\,\langle Y_{\ell m}|Y_{2m_3}(\theta,\varphi)|Y_{\ell' m'}\rangle$$

$$\cdot\,\langle j_f m_f|\mu_1(-m_r)|j_{f'} m_{f'}\rangle\langle JM|\mu_2(-m_{r'})|J'M'\rangle \tag{C17}$$

Matrix elements of the μ operator are obtained, in terms of reduced matrix elements, using Eq. (C14). Matrix elements of the Y operator are obtained from the formula[16]

$$\langle Y_{\ell m}|Y_{\ell_3 m_3}(\theta,\varphi)|Y_{\ell' m'}\rangle$$

$$= \left[\frac{(2\ell_3+1)(2\ell'+1)}{4\pi(2\ell+1)}\right]^{\frac{1}{2}}(\ell_3\ell' m_3 m'|\ell_3\ell'\ell m)\cdot(\ell_3\ell' 00|\ell_3\ell'\ell 0) \tag{C18}$$

The above formula obtains by combining the addition theorem, Eq. (C11), with the orthogonality relation for spherical harmonics

$$<Y_{\ell_1 m_1}|Y_{\ell_2,m_2}> = \delta_{\ell_1,\ell_2}\,\delta_{m_1,m_2}\,. \qquad (C19)$$

Upon squaring the matrix element in Eq. (C17) and inserting into Eq. (C3), the sums over the m-indices can be carried out using one of the fundamental orthogonality relations for Clebsch-Gordan coefficients, namely

$$\sum_{m_1 m_2} (j_1 j_2 m_1 m_2 | j_1 j_2 j' m')(j_1 j_2 m_1 m_2 | j_1 j_2 j m) = \delta_{j',j}\,\delta m,m' \qquad (C20)$$

or for j'=j and m'=m

$$\sum_{m_1 m_2} (j_1 j_2 m_1 m_2 | j_1 j_2 j m)^2 = 1 \qquad (C21)$$

In carrying out this exercise, one has to make use of symmetry properties of CG coefficients.[11,13]

The final results for the dipole-dipole case is

$$\begin{aligned} Q = {} & \frac{2}{3}\,(2\ell + 1)(2J + 1)(\ell 200|\ell 2\ell' 0)^2 \\ & \cdot\, |<R_{k\ell}|\,\frac{1}{r^3}\,|R_{k'\ell'}>|^2 \\ & \cdot\, |<j_f||\mu_1||j_{f'}>|^2\,|<J||\mu_2||J'>|^2 \end{aligned} \qquad (C22)$$

Upon inserting Eq. (C22) into Eq. (C2), we arrive at the result for sum (j_f) quoted in Eq. (44) of the text.

Dipole-Quadrupole Case

The basic strategy of using the addition theorem is the same as before but a good deal more complicated to carry out. We present only a few of the details here.

The dipole-quadrupole interaction can be written

$$V = \frac{3}{2}\,\frac{1}{r^4}\,[2\,\hat{r}\cdot\overleftrightarrow{Q}\cdot\vec{\mu} - 5(\hat{r}\cdot\vec{\mu})(\hat{r}\cdot\overleftrightarrow{Q}\cdot\hat{r})] \qquad (C23)$$

In this expression we shall take $\vec{\mu}$ to be the dipole moment of the radiator and $\overleftrightarrow{Q}$ to be the quadrupole moment tensor of the perturber. The reverse process also occurs and has been included in our calculations.

The traceless quadrupole moment tensor is given by

$$\overleftrightarrow{Q} = \sum_i e_i(r_i r_i - \frac{1}{3}\,|r_i|^2\,\overleftrightarrow{I})\,, \qquad (C24)$$

where $\overleftrightarrow{I}$ is the unit tensor.

In reducing Eq. (C23), we use Eq. (C6) for $\hat{r}$, the operator form of the Wigner-Eckhart theorem embodied in Eqs. (C13) through (C15) for $\vec{\mu}$, and finally, a particularly useful tensor Wigner-Eckhart theorem for $\overleftrightarrow{Q}$, namely

$$\overleftrightarrow{Q} = \sum_{m_3=0,\pm1,\pm2} Q_{op}(-m_3)\,\overleftrightarrow{T}_{-m_3} \qquad (C25)$$

Here

$$\overleftrightarrow{T}_{-m_3} = \sqrt{\frac{2}{3}} \sum_{m_1=0,\pm1}\ \sum_{m_2=0,\pm1} (11m_1m_2|112m_3)\ \hat{\epsilon}_{m_1}\,\hat{\epsilon}_{m_2} \qquad (C26)$$

where the matrix elements of the <u>operator</u> $Q_{op}(-M_3)$ are given by

$$<J_1M_1|Q_{op}(-m_3)|J_2M_2> \; = \; <J_1||Q||J_2>\,(J_2\,2 - M_2 - m_3|J_2\,2\,J_1 - M_1) \qquad (C27)$$

and where $<J_1||Q||J_2>$ is a reduced matrix element.

By repeated use of the addition theorem to Eq. (C23), the dipole-quadrupole interaction can be reduced to the form[25]

$$V = -\sqrt{\frac{4\pi}{3}}\ \frac{15}{7}\ \frac{1}{r^4}$$

$$\cdot \sum_{m_r=0,\pm 1}\ \sum_{m_3=0,\pm 1,\pm 2}\ \sum_{m''=0,\pm 1} (-1)^{m_r}\, \mu(-m_r)$$

$$\cdot (-1)^{m_3}\, Q_{op}(m_3)\,(12\ m_r\ m_3 | 12\ 3m'') \cdot Y_{3m''}(\theta,\ \varphi) \tag{C28}$$

The matrix elements of V above can now be obtained using Eqs. (C14), (C18), and (C27). Upon squaring the matrix element, inserting into Eq. (C3), and carrying out the m-summations using Eqs. (C20) and (C21), we find as the final result for the dipole-quadrupole case

$$Q = \left(\frac{15}{7}\right)^2 (2\ell + 1)(2J + 1)$$

$$\cdot (\ell 300 | \ell 3 \ell' 0)^2$$

$$\cdot \left| \left< R_{k\ell} \right| \frac{2}{r^4} \left| R_{k'\ell'} \right> \right|^2$$

$$\cdot \left| \left< j_f || \mu || j_{f'} \right> \right|^2 \left| \left< J || Q || J' \right> \right|^2 \tag{C29}$$

This can be readily be compared to Eq. (C22) for the dipole-dipole case. The differences are

$$\frac{2}{3} \longrightarrow \left(\frac{15}{7}\right)^2 \tag{C30a}$$

$$\frac{1}{r^3} \longrightarrow \frac{1}{r^4} \tag{C30b}$$

$$(\ell 200 | \ell 2 \ell' 0)^2 \longrightarrow (\ell 300 | \ell 3 \ell' 0)^2 \tag{C30c}$$

$$\left| \left< J || \mu || J' \right> \right|^2 \longrightarrow \left| \left< J || Q || J' \right> \right|^2 \tag{C30d}$$

From the CG coefficient in (C30c) above, the selection rules for the dipole-dipole case are $(l'-l)=0,\pm 2$; for the dipole-quadrupole case $(l'-l)=\pm 1,\pm 3$.

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25. It should be noted for both the dipole-dipole and dipole-quadrupole cases that the final result involves only the highest l value generated by the addition theorem. This has been demonstrated to be true for all the multipole interactions (C. Gray, unpublished notes).

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