On the theory of the relaxation matrix and its application to microwave transient phenomena*

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The phenomenological relaxation times T_1 and T_2 measured in microwave transient experiments are expressed in terms of specific molecular relaxation matrix elements. Conditions for this simple T_1, T_2 description are also given. The system is described in terms of a kinetic equation for the density matrix, which provides a unified treatment of the microwave transient behavior, spectral line shapes, and double resonance phenomena. Spatial degeneracy of the states and m dependence of T_1 and T_2 are discussed in detail. The recently developed semiclassical theory of molecular collisions is then applied to obtain expressions for the relevant relaxation times.

I. INTRODUCTION

The rotational relaxation of molecules in the gaseous state has been studied quite intensively recently, both theoretically and experimentally (cf. reviews[1-4]). A new approach developed recently in the infrared[5,6] and in the microwave regions[7-11] is the observation of transient phenomena. Several authors[9,11] have employed the electric field analogues of the Bloch equations of NMR to analyze their results, and have introduced phenomenological longitudinal (T_1) and transverse (T_2) relaxation times into the equations. They were able to determine T_1 and/or T_2 from the experiments. A detailed and informative description of the phenomena has been given by McGurk *et al.*[11a]

In the present paper, these relaxation times are related to the detailed collisional processes which are primarily responsible for the relaxation mechanism. The translational motion of the absorbing (emitting) molecule also gives rise to a Doppler effect which is important only at higher frequencies or much lower pressures. For the experiments described in the present paper, this effect is very small and will be neglected. A detailed treatment of Doppler broadening is given in Refs. 12 and 13.

The kinetic equation for the density matrix of the molecule of interest can be obtained from the Liouville equation for the molecular system (as in Appendix A). This equation is cast into a form, Eq. (2.1), whose matrix representation is analogous to the Redfield theory in NMR[14] and serves as the starting point for the analysis in Sec. II. It contains a relaxation matrix, which in turn is related to a certain combination of the scattering matrix elements of the collision process [Appendix A and Eq. (2.2)]. Description of collisional relaxation effects on atomic or molecular spectral line shapes by a relaxation matrix formalism has also been discussed by a number of investigators,[15-19] sometimes with an added "classical path"[20] approximation.

In Sec. III the equations are applied to a 2-level system, i.e., a system such that the probing electromagnetic field is near resonance to a transition between only

two levels of the system. However, radiationless transitions via collisions are *not* restricted to these two levels coupled by the electromagnetic field, but are possible to and from all levels. For such systems, relations are obtained between T_1 and the relaxation rate of the diagonal density matrix elements, and between T_2 and the relaxation rate of the off-diagonal elements of the density matrix. The Feynman–Vernon–Hellwarth representation[21] is employed and a set of equations analogous to the Bloch equations in NMR is obtained. To exclude in the present paper the phenomenon of overlapping lines common in pressure broadening experiments, only systems at low pressures are considered, a situation which corresponds to that used in the actual experiments.[9-11] The problem of spatial degeneracy is then treated in detail in Sec. IV, and an expression for the m-dependence of the observations is obtained there. In Sec. V, the relations between the various T_1's and T_2's measured in various types of transient experiments and the various relaxation matrix elements derived in Sec. IV are discussed. The experiments include those of transient absorption, transient emission, and pulses.

In Sec. VI the application of semiclassical theory[22,23] to the calculation of the collisional processes is described. (The application thereby yields expressions for the relaxation times T_1 and T_2 and for the m-dependence of T_2.) In Sec. VII, the assumptions involved in the derivation of the T_1, T_2 description in Secs. II–IV are summarized and a comparison with a study by Wang *et al.* on molecular beam maser experiments[24] is made. Applications of the present paper involve the use of a nonperturbative (semiclassical) method for calculating the relaxation matrix elements; differences from the previous work are the absence of added approximations for these elements, and the detailed inclusion of spatial degeneracy effects (Sec. IV).

The general line shape expression commonly used in pressure broadening theory and an expression for describing double resonance experiments are derived from the kinetic equation (2.1) in Appendices B and C, respectively.

II. THE RATE EQUATION AND SYMMETRY PROPERTIES OF THE RELAXATION MATRIX

A system consisting of a single radiatively active molecule immersed in a bath of perturbing molecules is considered. Under the assumptions of the impact theory, discussed in the first part of Appendix A, $\rho^{(s)}$ satisfies the following equation of motion ($\hbar$ is set equal to unity throughout):

$$i \frac{\partial}{\partial t} \rho^{(s)} = [H^s + \mathcal{K}, \rho^{(s)}] - i\Lambda \cdot \rho^{(s)}, \qquad (2.1)$$

where H^s is the Hamiltonian for the isolated active molecule and $\mathcal{K}$ describes the interaction of that molecule with the electromagnetic field. Throughout this paper, the electric field of the radiation is assumed to be plane polarized along the z-direction, with a magnitude $\mathcal{E} \cos \omega t$. For dipole absorption, $\mathcal{K}$ then becomes $-\mu \mathcal{E} \cos \omega t$, where μ is the z-component of the dipole moment operator for the active molecule. Λ is the relaxation superoperator, with relaxation matrix elements given by (2.2) (Appendix A), and is sometimes denoted by $-R$ in the literature (Redfield's relaxation matrix). The dot in (2.1) signifies that Λ is operating on $\rho^{(s)}$. As an operator in a space in which $\rho^{(s)}$ is a vector, the matrix representation of Λ has twice as many indices as does that of $\rho^{(s)}$:

$$\Lambda_{f'i',fi} = (N/2\pi) \sum_b \int dE_b \rho_b \sum_{b'} [\delta_{f'f} \delta_{i'i} \delta_{b'b} - S_{f'b';fb}(E_F) S^*_{i'b';ib}(E_I)], \qquad (2.2)$$

where the sums are over the quantum numbers of the orbital (l, m) and rotational–vibrational motion of the perturber; ρ_b is the equilibrium distribution for the perturber and includes that for the relative translational motion; S is the scattering matrix; $E_I = E_i + E_b$, $E_F = E_f + E_b$, where E_i, E_f, E_b are the unperturbed energy of the active molecule in state i, in state f, and of the perturber in state b, respectively. The energy of the perturber before collision is the same for both the spectroscopic states. N is the density of the perturbing gas. As in Ref. 25, different letters or subscripts will be assigned to the levels coupled by spectral transitions (e.g., $i \rightarrow f$ or $j_i \rightarrow j_f$) while collisional transitions between various levels will be denoted by primes (e.g., $i \rightarrow i'$ or $j_i \rightarrow j_i'$). The generalized Boltzmann equation (2.1) has been discussed in some detail by Snider and Sanctuary,[26] who noted the relation to the fundamental work of Fano[27]: Fano's $\langle m \rangle$ reduces to the $-i\Lambda$ in (2.4) in the impact approximation.

The following two properties follow from (2.2),[15] the first directly and the second from unitarity of the S-matrix:

$$\Lambda_{if,i'f'} = \Lambda^*_{fi,f'i'} \qquad (2.3)$$

$$\sum_{i'} \Lambda_{i'i',ii} = 0. \qquad (2.4)$$

Physically, the diagonal element $\Lambda_{ii,ii}$ is proportional to the total rate of collisional transfer *out of* level i while the elements $\Lambda_{i'i',ii}$ for $i \neq i'$ are proportional to the *negative* of the rate of collisional transfer from level i to i'. Thus, Eq. (2.4) is simply the statement

that a molecule that *leaves* state i must end up in some state after a collision.

The types of intermolecular potentials involved are real and it follows[28] that the S-matrix is symmetric. Then it is found from (2.2) that[15,29]

$$\Lambda_{i'i',ii} e^{-E_i/k_B T} = \Lambda_{ii,i'i'} e^{-E_i'/k_B T}, \qquad (2.5)$$

where E_i, E_i' are the energies of the active molecule in states i and i', respectively, and k_B is the Boltzmann constant.

Substituting (2.4) into (2.5) yields

$$\sum_i \Lambda_{i'i',ii} \rho_{ii}^{(0)} = 0, \qquad (2.6)$$

where $\rho_{ii}^{(0)}$ is the equilibrium Boltzmann distribution function for the active molecule:

$$\rho_{ii}^{(0)} = \exp(-E_i/k_B T) \Big/ \sum_j \exp(-E_j/k_B T). \qquad (2.7)$$

Writing Eq. (2.1) in terms of the matrix representatives, the equations of motion for the diagonal and off-diagonal density matrix elements for a particular $i \rightarrow f$ line can be written as

$$i \frac{\partial}{\partial t} \rho_{fi}^{(s)} = \omega_{fi} \rho_{fi}^{(s)} + \mathcal{K}_{fi} (\rho_{ii}^{(s)} - \rho_{ff}^{(s)}) - i \sum_{f'i'} \Lambda_{fi,f'i'} \rho_{f'i'}^{(s)} \qquad (2.8)$$

$$i \frac{\partial}{\partial t} \rho_{ii}^{(s)} = (\mathcal{K}_{if} \rho_{fi}^{(s)} - \rho_{if}^{(s)} \mathcal{K}_{fi}) - i \sum_k \Lambda_{ii,kk} \rho_{kk}^{(s)}, \qquad (2.9)$$

where ω_{fi} is $E_f - E_i$, and where the tensorial properties[25] in Sec. IV have been anticipated in eliminating certain terms [cf. Eqs. (4.17) and (4.22) for a system in the absence of static fields and Eqs. (4.35)–(4.36) in the presence of those fields]. When two or more lines are coupled by the electromagnetic field, the second term in the RHS of (2.8) and the first term in the RHS of (2.9) are replaced by $\sum_k (\mathcal{K}_{fk} \rho_{ki}^{(s)} - \rho_{fk}^{(s)} \mathcal{K}_{ki})$ and $\sum_k (\mathcal{K}_{ik} \rho_{ki}^{(s)} - \rho_{ik}^{(s)} \mathcal{K}_{ki})$, respectively.

The case where transients are observed is the one being principally investigated here. However, other experiments can be interpreted from the steady-state solutions of Eqs. (2.1) or (2.8)–(2.9), an example of which is the solution appropriate for spectral line shapes (Appendix B) and another example of which is that appropriate for modulated microwave double resonance experiments (MMDR). In Appendix C it is shown that Eq. (2.9) reduces to the same form as that used by Gordon[30] to analyze the MMDR experiments.

III. THE 2-LEVEL SYSTEM

The behavior of a 2-level system under radiative excitation and radiationless relaxation can be conveniently described by an equation analogous to the Bloch equation in NMR. The concept was first introduced by Feynman, Vernon, and Hellwarth[21] and has been used in the interpretation of optical[5d] and microwave[9,11] transient phenomena and of molecular beam maser experiments.[24] In most cases, phenomenological relaxation times T_1 and T_2 are introduced.

For a 2-level system, the dynamics are conveniently described by the Feynman–Vernon–Hellwarth (FVH) representation,[21] where one defines[9,11,24] a vector

$$\mathbf{r} = \begin{bmatrix} r_1 \\ r_2 \\ r_3 \end{bmatrix} = \begin{bmatrix} \rho_{fi}^{(s)} + \rho_{if}^{(s)} \\ i(\rho_{fi}^{(s)} - \rho_{if}^{(s)}) \\ \rho_{ff}^{(s)} - \rho_{ii}^{(s)} \end{bmatrix} . \tag{3.1}$$

The energy of interaction of the active molecule with radiation is

$$\mathcal{H} = -\mu \mathcal{E} \cos \omega t. \tag{3.2}$$

Consistent with the assumption of a 2-level system for a transition $i \to f$, the only nonvanishing matrix elements of μ are μ_{if} and μ_{fi}.

We consider first the case in the absence of collisions. From Eq. (2.4) with the term $\Lambda \cdot \rho$ omitted, the equations of motion for the density matrix elements are

$$i \frac{\partial}{\partial t} \rho_{fi} = \omega_{fi} \rho_{fi} + \mu_{fi} \mathcal{E} \cos \omega t (\rho_{ff} - \rho_{ii}) \tag{3.3a}$$

$$i \frac{\partial}{\partial t} \rho_{ii} = - (\mu_{if} \rho_{fi} - \rho_{if} \mu_{fi}) \mathcal{E} \cos \omega t, \tag{3.3b}$$

where the superscript (s) is omitted for brevity. These equations can readily be converted into a vector equation for $\mathbf{r}$[21,24b]:

$$\frac{d}{dt} \mathbf{r} = \Omega \times \mathbf{r}, \quad \text{(no collisions)} \tag{3.4}$$

where the components of Ω are given by

$$\Omega_1 = - (\mu_{if} + \mu_{fi}) \mathcal{E} \cos \omega t \tag{3.5a}$$

$$\Omega_2 = - i(\mu_{fi} - \mu_{if}) \mathcal{E} \cos \omega t \tag{3.5b}$$

$$\Omega_3 = \omega_{fi}. \tag{3.5c}$$

With proper choice of the phase of the wavefunctions, μ_{if} can be made real and then Ω becomes

$$\Omega = \begin{bmatrix} \omega_1 \cos \omega t \\ 0 \\ \omega_{fi} \end{bmatrix}, \tag{3.6a}$$

where ω_1 is defined as

$$\omega_1 = -2\mu_{if} \mathcal{E}. \tag{3.6b}$$

The effect of collisions alone is considered next. To account for the relaxation of linear molecules such as OCS, collisional transitions to levels other than those coupled by the electromagnetic field (i.e., i and f) must be taken into account. However, for the case of an isolated line where the radiation field is near resonance to a line $i \to f$, the only important off-diagonal density matrix elements are ρ_{if} and ρ_{fi}. Hence from the kinetic equation (2.2), the rate of change of ρ due to collisional relaxation is given by

$$-\left(\frac{\partial}{\partial t} \rho_{fi}\right)_{\text{coll}} = \Lambda_{fi,fi} \rho_{fi} + \Lambda_{fi,if} \rho_{if} \tag{3.7}$$

and a similar expression obtains for ρ_{if}. Adding and subtracting, one obtains

$$-\left(\frac{d}{dt} r_1\right)_{\text{coll}} = \Gamma_+ r_1 + \delta_+ r_2 \tag{3.8a}$$

$$-\left(\frac{d}{dt} r_2\right)_{\text{coll}} = -\delta_- r_1 + \Gamma_- r_2, \tag{3.8b}$$

with $\Gamma_\pm$ and $\delta_\pm$ given by

$$\Gamma_\pm = \text{Re}(\Lambda_{fi,fi} \pm \Lambda_{if,fi}) \tag{3.9a}$$

$$\delta_\pm = \text{Im}(\Lambda_{fi,fi} \pm \Lambda_{if,fi}). \tag{3.9b}$$

We note that in (3.7) and (3.8), the relaxation matrix elements like $\Lambda_{if,ii}$ do not appear since they are zero by symmetry considerations, an aspect discussed in Sec. IV.

The rate of relaxation for the diagonal density matrix elements is similarly given from (2.9) by

$$-\left(\frac{\partial}{\partial t} \rho_{ii}\right)_{\text{coll}} = \Lambda_{ii,ii} \rho_{ii} + \Lambda_{ii,ff} \rho_{ff} + \sum_k{}' \Lambda_{ii,kk} \rho_{kk} \tag{3.10}$$

and a similar equation obtains for ρ_{ff}. Here, the prime over the summation implies that levels i and f are not summed. Equation (2.6) now gives

$$\Lambda_{ii,ii} \rho_{ii}^{(0)} + \Lambda_{ii,ff} \rho_{ff}^{(0)} + \sum_k{}' \Lambda_{ii,kk} \rho_{kk}^{(0)} = 0. \tag{3.11}$$

Since only levels i and f are disturbed by the electromagnetic field, for $k \neq i, f$, ρ_{kk} is approximately equal to its equilibrium value $\rho_{kk}^{(0)}$. When this approximation is substituted into (3.10), and (3.11) is used, one finds

$$-\left(\frac{\partial}{\partial t} \rho_{ii}\right)_{\text{coll}} = \Lambda_{ii,ii}(\rho_{ii} - \rho_{ii}^{(0)}) + \Lambda_{ii,ff}(\rho_{ff} - \rho_{ff}^{(0)}) \tag{3.12}$$

and a similar equation applies for ρ_{ff}.

With the following definitions,

$$r_3 \equiv \rho_{ff} - \rho_{ii} \tag{3.13}$$

$$r_3^{(0)} \equiv \rho_{ff}^{(0)} - \rho_{ii}^{(0)} \tag{3.14}$$

$$r_4 \equiv \rho_{ff} + \rho_{ii} \tag{3.15}$$

$$r_4^{(0)} \equiv \rho_{ff}^{(0)} + \rho_{ii}^{(0)}, \tag{3.16}$$

one may deduce from (3.12) that

$$-\left(\frac{d}{dt} r_3\right)_{\text{coll}} = -\tfrac{1}{2}(\Lambda_{ff,ii} - \Lambda_{ii,ii} + \Lambda_{ii,ff} - \Lambda_{ff,ff})(r_3 - r_3^{(0)})$$
$$+ \tfrac{1}{2}(\Lambda_{ff,ii} - \Lambda_{ii,ii} + \Lambda_{ff,ff} - \Lambda_{ii,ff})(r_4 - r_4^{(0)}) \tag{3.17}$$

$$-\left(\frac{d}{dt} r_4\right)_{\text{coll}} = \tfrac{1}{2}(\Lambda_{ff,ff} + \Lambda_{ii,ff} - \Lambda_{ii,ii} - \Lambda_{ff,ii})(r_3 - r_3^{(0)})$$
$$+ \tfrac{1}{2}(\Lambda_{ff,ff} + \Lambda_{ii,ff} + \Lambda_{ii,ii} + \Lambda_{ff,ii})(r_4 - r_4^{(0)}). \tag{3.18}$$

The coefficient of r_4 in (3.17) can be written as a sum of two terms,

$$\tfrac{1}{2}[(\Lambda_{ff,ff} + \Lambda_{ff,ii}) - (\Lambda_{ii,ii} + \Lambda_{ii,ff})]. \tag{3.19}$$

Using Eq. (2.2), the first term in (3.19) can be written explicitly as

$$\Lambda_{ff,ff} + \Lambda_{ff,ii} = \frac{N}{2\pi} \sum_b \int dE_b \rho(b) \sum_{b'} \left(\delta_{bb'} - |S_{fb',fb}|^2 - |S_{fb',ib}|^2 \right)$$

$$= \frac{N}{2\pi} \sum_b \int dE_b \rho(b) \left[1 - \sum_{b'} \left(|S_{fb',fb}|^2 + |S_{fb',ib}|^2 \right) \right]. \qquad (3.20)$$

From the unitary property of the S-matrix, one has

$$\sum_{k,b} |S_{fb',kb}|^2 = 1. \qquad (3.21)$$

Substituting (3.21) into (3.20), one obtains

$$\Lambda_{ff,ff} + \Lambda_{ff,ii} = -\frac{N}{2\pi} \sum_b \int dE_b \rho(b) \sum_{b'} \sum_{k \neq i,f} |S_{fb',kb}|^2. \qquad (3.22)$$

Similarly, the second term in (3.18) can be written as

$$\Lambda_{ii,ii} + \Lambda_{ii,ff} = -\frac{N}{2\pi} \sum_b \int dE_b \rho(b) \sum_{b'} \sum_{k \neq i,f} |S_{ib',kb}|^2. \qquad (3.23)$$

Now, if the scattering dynamics at levels i and f are not very different, the right hand sides of Eqs. (3.22) and (3.23) will be approximately equal, whence the coefficient of r_4 in Eq. (3.17) is approximately zero. Then, the relaxation equation for r_3 can be written as

$$-\left(\frac{d}{dt} r_3 \right)_{coll} = \zeta (r_3 - r_3^{(0)}), \qquad (3.24)$$

where

$$\zeta = \frac{1}{2}(\Lambda_{ii,ii} - \Lambda_{ff,ii} + \Lambda_{ff,ff} - \Lambda_{ii,ff}). \qquad (3.25)$$

Combining Eqs. (3.4), (3.8), and (3.24), one obtains the complete equation of motion for $\mathbf{r}$:

$$\frac{d}{dt} \mathbf{r} = \mathbf{\Omega} \times \mathbf{r} - \mathbf{\Gamma} \cdot (\mathbf{r} - \mathbf{r}^{(0)}), \qquad (3.26)$$

where $\mathbf{\Omega}$ is given by Eq. (3.6), and $\mathbf{r}^{(0)}$ and $\mathbf{\Gamma}$ by

$$\mathbf{r}^{(0)} = \begin{bmatrix} 0 \\ 0 \\ r_3^{(0)} \end{bmatrix}, \qquad (3.27)$$

$$\mathbf{\Gamma} = \begin{bmatrix} \Gamma_+ & \delta_+ & 0 \\ -\delta_- & \Gamma_- & 0 \\ 0 & 0 & \zeta \end{bmatrix}, \qquad (3.28)$$

with $\Gamma_\pm$, $\delta_\pm$ given by Eq. (3.9) and ζ by Eq. (3.25).

$\mathbf{\Omega}$ in Eq. (3.26) is time-dependent, as in (3.6a). Following the usual practice in NMR, a transformation into a rotating frame is made[31]:

$$\mathbf{r}' = C(\omega t) \cdot \mathbf{r}, \qquad (3.29)$$

where

$$C(\omega t) = \begin{bmatrix} \cos\omega t & \sin\omega t & 0 \\ -\sin\omega t & \cos\omega t & 0 \\ 0 & 0 & 1 \end{bmatrix}. \qquad (3.30)$$

In this rotating frame, the equation of motion is

$$\frac{d\mathbf{r}'}{dt} = \mathbf{\Omega}' \times \mathbf{r}' - \mathbf{\Gamma}' \cdot (\mathbf{r}' - \mathbf{r}^{(0)}), \qquad (3.31)$$

where

$$\mathbf{\Omega}' = \begin{bmatrix} \frac{1}{2}\omega_1(1 + \cos 2\omega t) \\ -\frac{1}{2}\omega_1 \sin 2\omega t \\ \omega_{fi} - \omega \end{bmatrix} \qquad (3.32)$$

and

$$\mathbf{\Gamma}' = C(\omega t) \cdot \mathbf{\Gamma} \cdot C(\omega t)^{-1}. \qquad (3.33)$$

For microwave (or infrared) absorption at low pressure, the rapidly varying terms $\cos 2\omega t$ and $\sin 2\omega t$ in $\mathbf{\Omega}'$ can be neglected. Equation (3.32) then becomes

$$\mathbf{\Omega}' = \begin{bmatrix} \frac{1}{2}\omega_1 \\ 0 \\ \omega_{fi} - \omega \end{bmatrix}. \qquad (3.34)$$

In the absence of relaxation effect, $\mathbf{\Gamma}$ vanishes and so Eq. (3.31) indicates that $\mathbf{r}'$ would precess as in Fig. 1 about axis OA with constant angular velocity $|\mathbf{\Omega}'| = [\frac{1}{4}\omega_1^2 + (\omega_{fi} - \omega)^2]^{1/2}$.

Similarly, when the rapidly varying terms of frequency 2ω are ignored in $\mathbf{\Gamma}'$, one has

$$\mathbf{\Gamma}' = \begin{bmatrix} \frac{1}{2}(\Gamma_+ + \Gamma_-) & \delta & 0 \\ -\delta & \frac{1}{2}(\Gamma_+ + \Gamma_-) & 0 \\ 0 & 0 & \zeta \end{bmatrix}$$

$$= \begin{bmatrix} 1/T_2 & 0 & 0 \\ 0 & 1/T_2 & 0 \\ 0 & 0 & 1/T_1 \end{bmatrix} - \begin{bmatrix} 0 & \delta & 0 \\ -\delta & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \qquad (3.35)$$
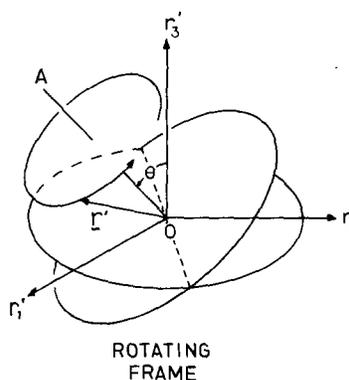

ROTATING FRAME

FIG. 1. Geometric representation of the interaction of the electromagnetic field $\delta \cos\omega t$ with the two-level system in the rotating frame. $\text{Tan}\theta$ equals $\frac{1}{2}\omega_1/(\omega_{fi} - \omega)$. OA lies in the (r_1', r_2') plane.

where the relaxation times T_1 and T_2 are given by (3.36) and (3.37) and δ is given by (3.38):

$$1/T_2 = \tfrac{1}{2}(\Gamma_+ + \Gamma_-) = \mathrm{Re}(\Lambda_{fi,fi}) \tag{3.36}$$

$$1/T_1 = \zeta = \tfrac{1}{2}(\Lambda_{ii,ii} - \Lambda_{ff,ii} + \Lambda_{ff,ff} - \Lambda_{ii,ff}) \tag{3.37}$$

$$\delta = \tfrac{1}{2}(\delta_+ + \delta_-) = \mathrm{Im}\Lambda_{fi,fi} \, . \tag{3.38}$$

Noting that

$$\begin{bmatrix} 0 & -\delta & 0 \\ \delta & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \cdot \mathbf{r}' = \mathbf{e}_3' \delta \times \mathbf{r}' , \tag{3.39}$$

where $\mathbf{e}_3'$ is a unit vector along the r_3'-axis of the rotating frame, Eq. (3.31) can be written finally as

$$\frac{d\mathbf{r}'}{dt} = \boldsymbol{\Omega}'' \times \mathbf{r}' - \begin{bmatrix} 1/T_2 & 0 & 0 \\ 0 & 1/T_2 & 0 \\ 0 & 0 & 1/T_1 \end{bmatrix} \cdot \mathbf{r}' , \tag{3.40}$$

where

$$\boldsymbol{\Omega}'' = \boldsymbol{\Omega}' + \mathbf{e}_3' \delta = \begin{bmatrix} \tfrac{1}{2}\omega_1 \\ 0 \\ \omega_{fi} - \omega + \delta \end{bmatrix} , \tag{3.41}$$

$\boldsymbol{\Omega}'$ is given by (3.34), and δ defined by Eq. (3.38) provides a shift in resonant frequency due to collisions.

P_r and P_i in Ref. 11 are related to the macroscopic polarization $P(t)$ induced in the sample by

$$P(t) \equiv (P_r + iP_i) e^{i\omega t} + (P_r - iP_i) e^{-i\omega t} . \tag{3.42}$$

On the other hand, $P(t)$ for a 2-level system can be calculated from

$$P(t) = N_a \mathrm{Tr}\, \mu \rho(t) = N_a(\mu_{if}\rho_{fi} + \mu_{fi}\rho_{if})$$
$$= N_a \mu_{if} r_1 = N_a \mu_{if}(r_1' \cos\omega t - r_2' \sin\omega t) , \tag{3.43}$$

where the real valuedness of μ_{if} was used and N_a is the number of molecules present. Comparing Eqs. (3.42) and (3.43), one can identify P_r and P_i with $\tfrac{1}{2}N_a \mu_{if} r_1'$ and $\tfrac{1}{2}N_a \mu_{if} r_2'$, respectively. Furthermore, ΔN in Ref. 11 corresponds to $-N_a r_3'$. Thus, apart from the inclusion of the shift δ, Eq. (3.40) is of the same form as the phenomenological equations (46) proposed by McGurk et al.[11a] The general method of solution for the Bloch equation by Laplace transform[32] is summaried there, and the relation between P_r, P_i, ΔN, and the signals measured in various transient experiments are discussed in detail.

IV. SPATIAL DEGENERACY AND *m*-DEPENDENCE

The formalism in Sec. III applies to a 2-level system of nonoverlapping lines. However, in actual cases, the levels i and f may both be degenerate and one may wonder whether the system could still be described by the Bloch equations of Sec. III, since interference between the degenerate levels may occur. This degeneracy situation is considered in this section. Furthermore, certain symmetry considerations involved in writing (2.8) and (2.9) are given. Finally, we wish to obtain an expression for the m-dependence of T_2 and T_1.

Throughout the rest of this paper, only rotational transitions of a linear molecule will be considered. Then the level i can be described by eigenvectors $|j_i m_i\rangle$, where j_i is the rotational angular momentum quantum number and m_i is the magnetic quantum number which describes the projection of the angular momentum along a fixed axis in space. For plane polarized radiation, one has the spectral transition selection rules $\Delta j = j_f - j_i = \pm 1$, $\Delta m = m_f - m_i = 0$. In the $|jm\rangle$ basis, the kinetic equation (2.1) yields for a particular $j_f \rightarrow j_i$ line,

$$i\frac{\partial}{\partial t}\rho(j_f m_f, j_i m_i) = \omega_{fi}\rho(j_f m_f, j_i m_i) - \mathcal{E}\cos\omega t\left[\sum_{m_r}\langle j_f m_f|\mu_z|j_i m_r\rangle\rho(j_i m_r, j_i m_i)\right.$$
$$\left. - \sum_{m_s}\rho(j_f m_f, j_f m_s)\langle j_f m_s|\mu_z|j_i m_i\rangle\right] - i\sum_{j_f' m_f'}\sum_{j_i' m_i'}\langle\langle j_f m_f, j_i m_i|\Lambda|j_f' m_f', j_i' m_i'\rangle\rangle\rho(j_f' m_f', j_i' m_i') \tag{4.1}$$

and

$$i\frac{\partial}{\partial t}\rho(j_i m_i, j_i m_i) = -\mathcal{E}\cos\omega t\sum_{m_s}[\langle j_i m_i|\mu_z|j_f m_s\rangle\rho(j_f m_s, j_i m_i) - \rho(j_i m_i, j_f m_s)\langle j_f m_s|\mu_z|j_i m_i\rangle]$$
$$- i\sum_{j_f m_f}\sum_{j_f' m_f'}\langle\langle j_i m_i, j_i m_i|\Lambda|j_f m_f, j_f' m_f'\rangle\rangle\rho(j_f m_f, j_f' m_f') , \tag{4.2}$$

where ω_{fi} denotes $E(j_f m_f) - E(j_i m_i)$ and so equals the difference in energy between levels f and i, and $\rho(j_f m_f, j_i m_i)$ denotes $\langle j_f m_f|\rho^{(s)}|j_i m_i\rangle$. In Eq. (4.1), the sums over j_f' and j_i' are confined to $j_f' = j_f$, j_i and $j_i' = j_i$, j_f. In the general case where two or more lines are excited by the electromagnetic field, j_f' and j_i' in Eq. (4.1) are to be summed over all values and not merely over the above two. Also, the second term on the RHS of Eq. (4.1) and

the first term on the RHS of Eq. (4.2) are to be replaced by

$$-\mathcal{E}\cos\omega t\sum_{j_r m_r}[\langle j_f m_f|\mu_z|j_r m_r\rangle\rho(j_r m_r, j_i m_i)$$
$$- \rho(j_f m_f, j_r m_r)\langle j_r m_r|\mu_z|j_i m_i\rangle]$$

and

$$\mathcal{E}\cos\omega t\sum_{j_r m_r}[\langle j_i m_i|\mu_z|j_r m_r\rangle\rho(j_r m_r, j_i m_i)$$

$$-\rho(j_i m_i, j_r m_r)\langle j_r m_r | \mu_z | j_i m_i\rangle],$$

respectively, where j_r, m_r are summed over all values.

In (4.1) and (4.2), the relaxation matrix element is written as $\langle\langle j_f' m_i', j_f' m_f' | \Lambda | j_i m_i, j_f m_f\rangle\rangle$ instead of the $\Lambda_{i,f',if}$ in Sec. II. In this notation, $|j_f m_f, j_i m_i\rangle\rangle$ is a vector in the Liouville space,[25,27] which is a Hilbert space of operators [a summary of Liouville space notation is given in Appendix A of Ref. 221)]:

$$|j_f m_f, j_i m_i\rangle\rangle \equiv |j_f m_f\rangle\langle j_i m_i|. \tag{4.3}$$

Ben-Reuven[25] has considered in detail the symmetry properties of the relaxation matrix based on rotational invariance of the collision process and the isotropy of the environment of the system. For a 2^K-pole spectral transition, one may construct the following Liouville vector of tensorial character $KQ(K, Q$ are integers)[25,33,221]:

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

$$\times |j_f m_f, j_i m_i\rangle\rangle. \tag{4.4}$$

An identical relation obtains between $\langle\langle j_f j_i, KQ|$ and $\langle\langle j_f m_f, j_i m_i|$, which are the Hermitian conjugates of $|j_f j_i, KQ\rangle\rangle$ and $|j_f m_f, j_i m_i\rangle\rangle$, respectively. A matrix element $\langle\langle j_f' j_i'; KQ| \Lambda |j_f j_i; KQ\rangle\rangle$, denoted by $\Lambda^K_{f'i',fi}$, can be defined using the matrix elements

$$\langle\langle j_f' m_f', j_i' m_i' | \Lambda | j_f m_f, j_i m_i\rangle\rangle$$

and Eq. (4.4), and it has been shown that[27]

$$\langle\langle j_f' j_i'; K'Q' | \Lambda | j_f j_i; KQ\rangle\rangle = \Lambda^K_{f'i',fi}\delta_{KK'}\delta_{QQ'}, \tag{4.5}$$

where $\Lambda^K_{f'i',fi}$ is a "reduced" relaxation matrix element independent of Q. A summary of the derivation of Eq. (4.5) is given at the end of Appendix A. Although not explicitly stated in (4.5), Λ is also parity invariant.[25] For example, the parity for dipole transition $j_i \to j_f$ is -1 while a spectral transition $j_i \to j_i$ (if allowed) would be of parity +1. Parity consideration requires that $\langle\langle j_f j_i | \Lambda | j_i j_i\rangle\rangle$ vanish.

From (4.4) and an orthogonality relation for the 3-j symbols,[34a]

$$\sum_{j_3=|j_1-j_2|}^{j_1+j_2} \sum_{m_3=-j_3}^{j_3} (2j_3+1)\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1' & m_2' & m_3 \end{pmatrix}\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$$

$$= \delta_{m_1 m_1'}\delta_{m_2 m_2'}, \tag{4.6}$$

one obtains

$$|j_f m_f, j_i m_i\rangle\rangle$$

$$= \sum_{K,Q} (-1)^{j_f-m_f}(2K+1)^{1/2}\begin{pmatrix} j_f & j_i & K \\ m_f & -m_i & -Q \end{pmatrix}|j_f j_i, KQ\rangle\rangle \tag{4.7}$$

and an identical relation between $\langle\langle j_f m_f, j_i m_i|$ and $\langle\langle j_f j_i, KQ|$. Then, using Eqs. (4.5) and (4.7), the relaxation matrix elements in the uncoupled basis can be expressed as

$$\langle\langle j_f' m_f', j_i' m_i' | \Lambda | j_f m_f, j_i m_i\rangle\rangle = \sum_{K,Q} (2K+1)(-1)^{j_f'-m_f'+j_f-m_f}\begin{pmatrix} j_f' & j_i' & K \\ m_f' & -m_i' & -Q \end{pmatrix}\begin{pmatrix} j_f & j_i & K \\ m_f & -m_i & -Q \end{pmatrix}\Lambda^K_{f'i',fi}. \tag{4.8}$$

In Eq. (4.8), only those values of K which satisfy $|j_i - j_f| \le K \le j_i + j_f$ and $|j_i' - j_f'| \le K \le j_i' + j_f'$ simultaneously are summed and Q is summed from $-K$ to K. Because of the properties of the 3-j symbols,[33] one has a selection rule for the m's:

$$m_i - m_f = m_i' - m_f'. \tag{4.9}$$

A. Case where static fields are absent

When no static field is present, the $(2j_i+1)$ m-sublevels for level i are degenerate. Using the Wigner-Eckart theorem,[34b] if T^K_Q is an irreducible tensorial operator, then

$$\langle j_i m_i | T^K_Q | j_f m_f\rangle = (-1)^{j_i-m_i}\begin{pmatrix} j_i & j_f & K \\ m_i & -m_f & -Q \end{pmatrix} T^K_{if}, \tag{4.10}$$

where T^K_{if} is independent of Q and is termed the "reduced matrix element." Since μ is the z-component of the dipole moment operator, it is of tensional character $K=1$, $Q=0$. Hence,

$$\langle j_i m_i | \mu | j_f m_f\rangle = (-1)^{j_i-m_i}\begin{pmatrix} j_i & j_f & 1 \\ m_i & -m_f & 0 \end{pmatrix}\bar{\mu}_{if}, \tag{4.11}$$

where $\bar{\mu}_{if}$ stands for the reduced dipole moment matrix element defined by Eq. (4.10) with K equal to unity.

It is convenient to expand the density matrix in an irreducible tensorial basis whose matrix elements are given by the following linear combinations[33] (cf. Refs. 13 and 15):

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

$$\times \rho(j_f m_f, j_i m_i). \tag{4.12}$$

For dipole absorption, we have $K=1$, $Q=0$ and define $\bar{\rho}_{fi}$ by

$$\bar{\rho}_{fi} \equiv \rho_{fi}(1,0)/\sqrt{3}$$

$$= \sum_m (-1)^{j_f-m}\begin{pmatrix} j_f & j_i & 1 \\ m & -m & 0 \end{pmatrix}\rho(j_f m, j_i m). \tag{4.13}$$

Considering an absorption experiment, one now sets in the kinetic equation (4.1) $m_f = m_i = m$ for this case of $Q=0$. Because of the property of the 3-j symbol, only the $m_r = m$ and $m_s = m$ terms in the sums of the second term on the RHS of Eq. (4.1) are nonvanishing. Equation (4.1) then reads

$$i\frac{\partial}{\partial t}\rho(j_f m, j_i m)$$

$$= \omega_{fi}\rho(j_f m, j_i m) - \mathcal{E}\cos\omega t \langle j_f m | \mu | j_i m \rangle [\rho(j_i m, j_i m)$$

$$- \rho(j_f m, j_f m)] - i \sum_{j'_f m'_f} \sum_{j'_i m'_i}$$

$$\times \langle\langle j_f m, j_i m | \Lambda | j'_f m'_f, j'_i m'_i \rangle\rangle \rho(j'_f m'_f, j'_i m'_i). \quad (4.14)$$

Both sides of Eq. (4.14) are multiplied by

$$(-1)^{j_f - m} \begin{pmatrix} j_f & j_i & 1 \\ m & -m & 0 \end{pmatrix}$$

and summed over m. One then obtains, using (4.5), (4.7), (4.11), (4.13), and an orthogonality relation for the 3-j symbols,[34a]

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

$$\times [\rho(j_i m, j_i m) - \rho(j_f m, j_f m)] - i \sum_{f' i'} \Lambda^1_{fi, f' i'} \bar{\rho}_{f' i'}. \quad (4.15)$$

For the diagonal elements of the density matrix, Eq. (4.2) gives

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

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

$$- i \sum_{j_f m_f} \sum_{j'_f m'_f} \langle\langle j_i m, j_i m | \Lambda | j_f m_f, j'_f m'_f \rangle\rangle \rho(j_f m_f, j'_f m'_f). \quad (4.16)$$

Summing both sides of (4.16) over m and dividing by $(2j_i + 1)$, Eqs. (4.5), (4.7), (4.11), and (4.13) may be used to obtain

$$i \frac{\partial}{\partial t}\bar{\rho}_i = \frac{\mathcal{E}\cos\omega t}{2j_i + 1}(\bar{\mu}_{if}\bar{\rho}_{fi} - \bar{\rho}_{if}\bar{\mu}_{fi}) - i \sum_k \lambda^0_{ii,kk}\bar{\rho}_k, \quad (4.17)$$

where

$$\bar{\rho}_i = \sum_m \rho(j_i m, j_i m)/(2j_i + 1) = \rho_{ii}(0,0)/\sqrt{2j_i + 1} \quad (4.18)$$

and

$$\lambda^0_{ii, kk} = [(2j_k + 1)/(2j_i + 1)]^{1/2} \Lambda^0_{ii, kk}. \quad (4.19)$$

The definition given in (4.12) and the following equation were used:

$$\begin{pmatrix} j & j & 0 \\ m & -m & 0 \end{pmatrix} = (-1)^{j-m}(2j+1)^{-1/2}. \quad (4.20)$$

Next we make the assumption that the $\rho(j_i m, j_i m)$ and $\rho(j_f m, j_f m)$ in the second term of (4.15) can be replaced by their average values $\bar{\rho}_i$ and $\bar{\rho}_f$ defined by (4.18).[35] Noting that

$$\sum_m \begin{pmatrix} j_f & j_i & 1 \\ m & -m & 0 \end{pmatrix}^2 = \frac{1}{3}, \quad (4.21)$$

one has

$$i \frac{\partial}{\partial t}\bar{\rho}_{fi} = \omega_{fi}\bar{\rho}_{fi} - \frac{1}{3}(\bar{\rho}_f - \bar{\rho}_i)\bar{\mu}_{fi}\cos\omega t$$

$$- i \sum_{f' i'} \Lambda^1_{fi, f' i'}\bar{\rho}_{f' i'}. \quad (4.22)$$

The above approximation amounts to replacing

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

by an average, $\frac{1}{3}(\bar{\rho}_i - \bar{\rho}_f)$. A similar assumption has been made before.[11a] Simple numerical tests support this approximation.[36] This assumption is needed only for absorption experiments performed in the absence of static field. For absorption experiments performed in the presence of static field (Sec. IVB) and for emission experiments where no resonant external field is present, the above assumption is not needed: In the case of of the emission experiments both the second term on the RHS of (4.15) and the first term on the RHS of (4.16) are absent, and so the motion of diagonal density matrix elements is uncoupled from that of the off-diagonal ones.

Equation (2.9) can be written in the $|jm\rangle$ basis as

$$\sum_{j_k, m_k} \langle\langle j_i m, j_i m | \Lambda | j_k m_k, j_k m_k \rangle\rangle \rho^{(0)}(j_k m_k, j_k m_k) = 0. \quad (4.23)$$

However, for a rigid rotor, the Boltzmann distribution function $\rho^{(0)}(j_k m_k, j_k m_k)$, which equals

$$\exp(-E_k/k_B T)\Big/\sum_k (2j_k + 1)\exp(-E_k/k_B T),$$

is independent of m_k and will be denoted by ρ^0_k. Summing both sides of Eq. (4.23) over m, dividing throughout by $(2j_i + 1)$, and using Eqs. (4.5), (4.7), (4.19), and (4.20), one obtains

$$\sum_k \lambda^0_{ii, kk}\rho^0_k = 0, \quad (4.24)$$

where

$$\rho^0_k = \exp(-E_k/k_B T)\Big/\sum_k (2j_k + 1)\exp(-E_k/k_B T). \quad (4.25)$$

Finally, $\bar{\mu}_{if}$ can be chosen to be real, with suitable choice of the phase of the wavefunctions.

As in Sec. III, only $\bar{\rho}_i$, $\bar{\rho}_f$, $\bar{\rho}_{if}$, and $\bar{\rho}_{fi}$ may be taken to be different from their equilibrium values in this study of the $i \to f$ line. Comparing Eqs. (4.17), (4.19), and (4.22), their counterparts for $\bar{\rho}_{if}$ and $\bar{\rho}_f$, and (4.24) with Eqs. (3.3), (3.7), (3.10), and (3.11), one sees that the former can be recast into a form which satisfies the Bloch equation (3.40). To this end we set

$$\mathbf{r} = \begin{bmatrix} r_1 \\ r_2 \\ r_3 \end{bmatrix} = \begin{bmatrix} A(\bar{\rho}_{fi} + \bar{\rho}_{if}) \\ iA(\bar{\rho}_{fi} - \bar{\rho}_{if}) \\ (\bar{\rho}_f - \bar{\rho}_i)/\sqrt{3} \end{bmatrix}, \quad (4.26)$$

where

$$A = [(j_f + j_i + 1)/(2j_f + 1)(2j_i + 1)]^{1/2} \quad (4.27)$$

and

$$\mathbf{r}^{(0)} = \begin{bmatrix} 0 \\ 0 \\ (\rho^0_f - \rho^0_i)/\sqrt{3} \end{bmatrix}, \quad (4.28)$$

where ρ^0_f is the Boltzmann distribution of the rotational

level f, exclusive of the degeneracy factor, and is defined by (4.25). When r is transformed into $\mathbf{r}'$ in the rotating frame as defined by Eqs. (3.29) and (3.30), $\mathbf{r}'$ again satisfies the Bloch equation (3.40). In the present case of absorption in the absence of external fields, ω_1 and δ in Eq. (3.41) become

$$\omega_1 = 2\bar{\mu}_{if}\mathcal{E}A/\sqrt{3} \tag{4.29}$$

$$\delta = \operatorname{Im}\Lambda^1_{fi,fi} \tag{4.30}$$

and the relaxation times are given by [cf. Eqs. (3.36) and (3.37)]

$$1/T_2 = \operatorname{Re}\Lambda^1_{fi,fi} \tag{4.31}$$

$$1/T_1 = \tfrac{1}{2}(\lambda^0_{ii,ii} - \lambda^0_{ff,ii} + \lambda^0_{ff,ff} - \lambda^0_{ii,ff}) . \tag{4.32}$$

B. Case of static fields

When a static field is present, the interaction of the molecule with the field will be assumed to be so small that the rotational invariance of the collision process is not affected. Expressions for the m-dependence of linewidths have been developed in Ref. 15. For the case of a strong static *magnetic* field when all m-states are well separated and the experiment is performed at low enough pressure that the lines are not overlapping as a result of collision, all the coupling terms for which $m'_i \neq m_i$ can be neglected in (4.1) and (4.2). Hence, the system can then be approximated by a 2-level system and T_1 and T_2 are given by Eqs. (3.36) and (3.37).

The case of a static *electric* field is more complicated. For linear molecules, the energy now depends only on j and $|m|$, and the $\pm m$ states are degenerate even in the limit of a strong field. For the $\Delta m = \pm 1$ transition, because of the selection rule (4.9),

$$\langle\langle j_i m_i,\ j_f m_f |\Lambda| j_i(-m_i),\ j_f(-m_f)\rangle\rangle$$

vanishes and so the $m_i \to m_f$ and $m_i \to -m_f$ lines are not coupled. Therefore, Eqs. (4.8), (3.36), and (3.37) are still applicable for calculating the relaxation times. However, for the $\Delta m = 0\ (m \neq 0)$ transition, elements such as $\langle\langle j_i m,\ j_f m |\Lambda| j_i(-m),\ j_f(-m)\rangle\rangle$ are nonzero and so the $(j_i, m) \to (j_f, m)$ and $(j_i, -m) \to (j_f, -m)$ lines are coupled. However, one can define the following linear combination of ρ to uncouple the kinetic equation[15]:

$$\rho_\pm(j_i j_f) \equiv \rho(j_i m, j_f m) \pm \rho(j_i(-m), j_f(-m)), \tag{4.33}$$

where the dependence of $\rho_\pm$ on m is suppressed in the notation. A similar equation is introduced for $\rho_\pm(j_i j_i)$ where f in (4.33) is replaced by i. Using the Wigner-Eckart theorem [Eq. (4.10)] and the selection rule $j_f - j_i = 1$, one can show that

$$\langle j_i m \mid \mu \mid j_f m\rangle = \langle j_i(-m) \mid \mu \mid j_f(-m)\rangle . \tag{4.34}$$

Then the equation of motion for the off-diagonal elements of the density matrix is

$$i\frac{\partial}{\partial t}\rho_\pm(j_f, j_i) = \omega_{fi}\rho_\pm(j_f j_i) - \langle j_f m \mid \mu \mid j_i m\rangle$$
$$\times \mathcal{E}\cos\omega t[\rho_\pm(j_i j_i) - \rho_\pm(j_f j_f)]$$
$$- i\lambda^\pm_{fi,fi}\rho_\pm(j_f j_i) - i\lambda^\pm_{fi,if}\rho_\pm(j_i j_f) \tag{4.35}$$

and that for the diagonal elements is

$$i\frac{\partial}{\partial t}\rho_\pm(j_i j_i) = -\mathcal{E}\cos\omega t[\langle j_i m \mid \mu \mid j_f m\rangle \rho_\pm(j_f j_i)$$
$$- \rho_\pm(j_i j_f)\langle j_f m \mid \mu \mid j_i m\rangle]$$
$$- i\lambda^\pm_{ii,ii}\rho_\pm(j_i j_i) - i\lambda^\pm_{ii,ff}\rho_\pm(j_f j_f), \tag{4.36}$$

where $\lambda^\pm_{fi,fi}$, $\lambda^\pm_{fi,if}$, $\lambda^\pm_{ii,ff}$, and $\lambda^\pm_{ii,ii}$ denote

$$\langle\langle j_f m, j_i m |\Lambda| j_f m, j_i m\rangle\rangle \pm \langle\langle j_f(-m),\ j_i(-m) |\Lambda| j_f m, j_i m\rangle\rangle,$$

$$\langle\langle j_f m,\ j_i m |\Lambda| j_i m,\ j_f m\rangle\rangle \pm \langle\langle j_f(-m), j_i(-m) |\Lambda| j_i m,\ j_f m\rangle\rangle,$$

$$\langle\langle j_i m,\ j_i m |\Lambda| j_f m,\ j_f m\rangle\rangle \pm \langle\langle j_i(-m),\ j_i(-m) |\Lambda| j_f m,\ j_f m\rangle\rangle,$$

and

$$\langle\langle j_i m,\ j_i m |\Lambda| j_i m,\ j_i m\rangle\rangle \pm \langle\langle j_i(-m) j_i(-m) |\Lambda| j_i m, j_i m\rangle\rangle,$$

respectively, and are found to equal

$$\lambda^\pm_{fi,fi} = -\sum_K (2K+1)\begin{pmatrix} j_f & j_i & K \\ m & -m & 0 \end{pmatrix}^2 [-1 \pm (-1)^K]\Lambda^K_{fi,fi}, \tag{4.37}$$

$$\lambda^\pm_{fi,if} = \sum_K (2K+1)\begin{pmatrix} j_f & j_i & K \\ m & -m & 0 \end{pmatrix}^2 [-1 \pm (-1)^K]\Lambda^K_{fi,if}, \tag{4.38}$$

$$\lambda^\pm_{ii,ff} = -\sum_K (2K+1)\begin{pmatrix} j_i & j_i & K \\ m & -m & 0 \end{pmatrix}\begin{pmatrix} j_f & j_f & K \\ m & -m & 0 \end{pmatrix}$$
$$\times [1 \pm (-1)^K]\Lambda^K_{ii,ff}, \tag{4.39}$$

and

$$\lambda^\pm_{ii,ii} = \sum_K (2K+1)\begin{pmatrix} j_i & j_i & K \\ m & -m & 0 \end{pmatrix}^2 [1 \pm (-1)^K]\Lambda^K_{ii,ii} . \tag{4.40}$$

Equations (4.35) and (4.36) show that ρ_+ and ρ_- are decoupled. Since the induced dipole moment in this case is given by

$$p(t) = \langle j_f m \mid \mu \mid j_i m\rangle \rho_+(j_i j_f) + \langle j_i m \mid \mu \mid j_f m\rangle\rho_+(j_f j_i), \tag{4.41}$$

only the equations for ρ_+ are needed. Thus, from the equation of motion for ρ_+ in (4.35) and (4.36) and from a comparison with Sec. III, the system can still be described by a Bloch equation, in which the relaxation times are given by

$$1/T_2 = \operatorname{Re}\lambda^+_{fi,fi} \tag{4.42}$$

$$1/T_1 = \tfrac{1}{2}(\lambda^+_{ii,ii} - \lambda^+_{ff,ii} + \lambda^+_{ff,ff} - \lambda^+_{ii,ff}), \tag{4.43}$$

where the λ's are given by (4.37)–(4.40).

V. RELATIONS TO TRANSIENT EXPERIMENTS

Since a variety of transient methods are now available and different types of T_1's and T_2's are thereby possible, the relation of the preceding equations to those methods is considered in this section. In various transient experiments, a convenient method of switching the molecular system on and off resonance is by a Stark switching technique.[5,7-11] It is important to identify which relaxation times are measured in each case.

A. Transient absorption

We consider first transient absorption experiments.[5b,9-11] A convenient procedure[11a,b] is to apply a microwave field whose frequency is tuned to the zero Stark-field transition frequency of the molecule and then to apply a Stark field. When this Stark field is switched off, the molecular system is thus brought into resonance with the applied microwave field and on-resonance transient absorption occurs in the absence of the static field. Hence, the T_1 and T_2 measured in this type of experiment are given by (4.31) and (4.32), respectively. Off-resonance absorption experiments performed with a similar procedure gives the same T_1 and T_2.[11d]

B. Transient emission

(i) For transient emission experiments,[5c,7,8,11b,d] one may apply a microwave field in resonance with the m sublevel transition M having the largest frequency shift *in the presence of a Stark field*, either on the low or the high frequency side of the zero-field frequency. When the Stark field is switched off, this M transition is switched out of resonance with microwave field and the molecule emits radiation at the zero-field frequency. The decay of the emitted signal can be determined from the equation of motion of $\rho(j_f m, j_i m)$ for $m = 0$ or from that of $\rho_+(j_f j_i)$, defined by (4.33), for $m \neq 0$. The relaxation times for these ρ's depend on those for the $\rho_{fi}(K, 0)$'s, since Eq. (4.12) can be inverted to give

$$\rho(j_f m, j_i m) = \sum_K (2K+1)^{1/2}(-1)^{j_f - m}\begin{pmatrix} j_f & j_i & K \\ m & -m & 0 \end{pmatrix}\rho_{fi}(K0) .$$

(5.1)

Now, it is clear from the analysis in Sec. IV that the relaxation of $\rho_{fi}(K0)$ is governed by Λ^K [whose element is defined by (4.5)] and that there is no interference between different K's. Hence, in principle, because of the different K's, more than one single T_2 could be required to describe the relaxation of the emitted signal, apart from the $j = 0 \to 1$ case.[35] However, experiments performed thus far showed that only one T_2 suffices to fit the data,[11d] indicating that the K dependence of T_2 is small for the systems considered. Calculations on this point are given in the following paper.[22b] Lines with Stark-shifted frequencies smaller than that for the M one cannot be examined this way due to the complication of the phenomenon of fast passage.[11c,d]

(ii) Another procedure for transient emission involves a saturation of the system at its zero-field frequency and then a switching on of the Stark field to bring the system to off-resonance.[11b] Apart from the case of $j = 0 \to 1$,[35] more than one relaxation time would in principle be needed since then all m transitions emit at their Stark-field frequencies. However, once again, a single relaxation time T_2 might suffice when the m-dependence of T_2 is small. Calculations[22b] support this sufficiency for OCS-Ar.

(iii) One way of avoiding a problem of possible collisional mixing of degenerate levels in (i) and (ii) after the Stark field has been removed would be the following: Instead of turning off the Stark field completely as in method (i), one could switch the Stark field to a lower

value where the different m transitions are still nonoverlapping. Then the arguments of Sec. IV. B apply and a single T_2 is sufficient to describe the relaxation. The T_2 for $m \neq 0$ is given by Eq. (4.42) and that for $m = 0$ is given by

$$1/T_2 = \text{Re} \langle\langle j_i 0, j_i 0 | \Lambda | j_i 0, j_i 0 \rangle\rangle ,$$

(5.2)

using Eq. (3.36). This method has not yet been used.

C. Pulse method

Another interesting example is the determination of T_1 by pulse method.[11e] At time $t = 0$, the system is brought into resonance with a microwave for a time t_r after which a near population inversion occurs and r_2' goes to zero (π pulse). Then the system is switched off resonance and allowed to emit for a time τ. Subsequently, the system is brought back into resonance with the microwave again and observations are made. If $S(t')$ and $S(t'')$ are the signals detected at times $t'(0 < t' < t_r)$ and $t''(t'' = t' + t_r + \tau)$, respectively, it has been shown that the fractional change in signal, $[S(t'') - S(t')]/S(t')$, varies with τ as $\exp(-\tau/T_1)$.[11e] If the π pulse is applied in the presence of a Stark field in resonance with a particular m transition, and if the system is switched off resonance by turning off the Stark field, only this particular m level emits and hence the T_1 measured is given by Eq. (4.42) for $m \neq 0$ and by the following equation for $m = 0$ [Eq. (3.37) was used]:

$$1/T_1 = \frac{1}{2}(\langle\langle j_i 0, j_i 0 | \Lambda | j_i 0, j_i 0 \rangle\rangle - \langle\langle j_f 0, j_f 0 | \Lambda | j_i 0, j_i 0 \rangle\rangle$$
$$+ \langle\langle j_f 0, j_f 0 | \Lambda | j_f 0, j_f 0 \rangle\rangle - \langle\langle j_i 0, j_i 0 | \Lambda | j_f 0, j_f 0 \rangle\rangle)$$

(5.3)

Thus, in principle, the T_1 obtained by pulse method [Eq. (4.42) or Eq. (5.3)] differs from that obtained by transient absorption [Eq. (4.32)]. Also, in principle, the T_2 measured from transient emission [method (iii), Eq. (5.2)] is different from that measured from transient absorption [Eq. (4.31)]. One thus sees that different experiments can give different relaxation times and it is important to apply the appropriate equations for T_1 or T_2 in making any detailed comparisons with the experimental data.

VI. SEMICLASSICAL EXPRESSIONS FOR THE RELAXATION MATRIX ELEMENTS

It has been shown in Sec. IV that to account for relaxation of various experiments, only the corresponding reduced relaxation elements $\Lambda^K_{f'i',fi}$ of Eq. (4.5) need to be calculated. It is convenient to define a complex-valued cross section by

$$\Lambda^K_{f'i',fi} = N \langle v\sigma^K_{f'i',fi}\rangle .$$

(6.1)

For the case of a linear molecule perturbed by an inert gas atom, an explicit expression is given in terms of 6-j symbols by[1b,221,22a,37] [cf. Appendix A, Eq. (A30) and following remarks]

$$\sigma^K_{f'i',fi} = \frac{\pi}{k^2} \sum_{J_f J_i} \sum_{ll'} (-)^{J_i - J_i' + l - l'}(2J_i + 1)(2J_f + 1)$$
$$\times \begin{Bmatrix} J_f & J_i & K \\ j_i & j_f & l \end{Bmatrix}\begin{Bmatrix} J_f & J_i & K \\ j_i' & j_f' & l' \end{Bmatrix}(\delta_{j_f j_f'}\delta_{j_i j_i'}\delta_{ll'}$$
$$- S^{J_f}_{j_f l', j_f l} S^{J_i *}_{j_i' l', j_i l}) ;$$

(6.2)

v is relative velocity between the active molecule and perturber, and

$$\langle v\sigma^K_{f'i',fi}\rangle = \int_0^\infty 4\pi v^2 dv\, \rho_v v\sigma^K_{f'i',fi} , \qquad (6.3)$$

with

$$\rho_v = (\mu/2\pi k_B T)^{3/2} e^{-\mu v^2/2k_B T} \qquad (6.4)$$

being the Maxwell–Boltzmann distribution of relative velocities over the initial equilibrium ensemble. Here, $j_i(j_f)$ is the rotational quantum number of the absorbing molecule in its initial (final) spectroscopic state; $l(l')$ is the orbital angular momentum of relative motion before (after) collision, and J_i, J_f are the total angular momentum quantum numbers for the angular momenta:

$$\mathbf{J}_i = \mathbf{j}_i + \mathbf{l} , \quad \mathbf{J}_f = \mathbf{j}_f + \mathbf{l} . \qquad (6.5)$$

For microwave dipole absorption of a plane-polarized radiation field, $K=1$, $Q=0$.

Full quantum mechanical calculations would be feasible only for a system with relatively few orbital–rotational states (e.g., H_2 perturbed[37] by He). Fortunately, recent advances in the semiclassical theory of molecular collisions utilizing classical trajectories[22,23] greatly simplify the calculation of the S-matrix elements for molecular systems with a large number of states, and this method will be described here. The case of a linear molecule perturbed by an inert gas atom will be considered in detail. Employing the primitive semiclassical approximation (PSC) for the S-matrix element,[22h]

$$S^J_{j'l',jl} = \frac{1}{2\pi} \sum_{\text{s.p.}} \left| -i\partial(j',l')/\partial(\overline{q}_j,\overline{q}_l) \right|^{-1/2}$$

$$\times \exp\{i[F_4(j'l'JE,jlJE) + \tfrac{1}{2}(l+l'+1)\pi]\}, \qquad (6.6)$$

where F_4 is a known phase integral over a trajectory beginning at a given $\overline{q}_j, \overline{q}_l, j, l, J,$ and E, Fitz and Marcus[22l,n] derived the following expression for the cross section of Eq. (6.2):

$$\sigma^K_{f'i',fi} = \int_0^\infty 2\pi b\, db\, S(b), \qquad (6.7)$$

where

$$S(b) = \delta_{f'f}\delta_{i'i} - \int_0^{2\pi} (d\overline{q}_l/2\pi) \int_{|\hat{j}-\hat{i}|}^{\hat{j}+\hat{i}} d\hat{J}(\hat{J}/2\hat{i}\hat{j})$$

$$\times P_{\hat{j}',\hat{j}}(\overline{q}_l, \hat{J}, b, v) \qquad (6.8)$$
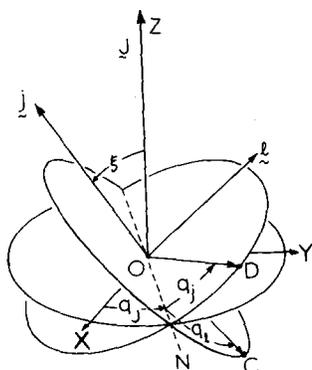

FIG. 2. Variables describing internal coordinates q_j, q_l, and q_J for the motion of an atom and a rigid rotor. The rotor axis lies along OD and the line of centers of the collision partners lies along OC, at any instant of time. XYZ are space-fixed axes.
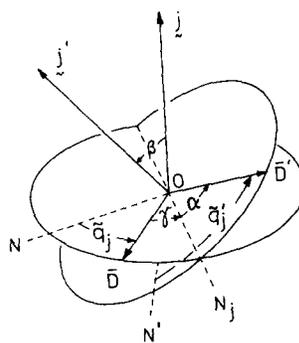

FIG. 3. Angles α, β, and γ for rotating the precollision dipole $0\overline{D}$ into the postcollision dipole $0\overline{D}'$. The $0N$ is the same as the $0N$ in Fig. 2, and $0N'$ is the corresponding quantity for the primed variables. $0N_j$ is the line of intersection of the rotational plane before collision with the one after. $\tilde{q}_j$, $\tilde{q}_{j'}$ are equal to $q_j - 2\pi\nu_j t$ and $q'_j - 2\pi\nu'_j t'$, respectively, where ν_j and ν'_j are the precollisional and postcollisional rotational frequencies.

and the impact parameter b is given by

$$b = (l + \tfrac{1}{2})/k . \qquad (6.9)$$

In Eq. (6.8), $\hat{j}$ is $\tfrac{1}{2}(\hat{j}_i + \hat{j}_f)$, where $\hat{j}_i = j_i + \tfrac{1}{2}$, etc.; $\hat{l}$ is $l_i + \tfrac{1}{2}$; $\hat{J}$ is the mean of $\hat{J}_i$ and $\hat{J}_f$, $\tfrac{1}{2}(\hat{J}_i + \hat{J}_f)$; $P_{\hat{j}',\hat{j}}(\overline{q}_l, \hat{J}, b, v)$ is a probabilitylike complex number given by

$$P_{\hat{j}',\hat{j}}(\overline{q}_l, \hat{J}, b, v) = \sum_{\text{s.p.}} \left| \partial j'/\partial(\overline{q}_j/2\pi) \right|^{-1} D^{K*}_{\delta'\delta}(\alpha, \beta, \gamma) \qquad (6.10)$$

and $D^{K*}_{\delta'\delta}(\alpha\beta\gamma)$ is the complex conjugate of $D^K_{\delta'\delta}(\alpha\beta\gamma)$ which is given by

$$D^K_{\delta'\delta}(\alpha, \beta, \gamma) = \sum_{\lambda=-K}^K \exp[i(q'_j - \omega_{f'i'}t - q_j + \omega_{fi}t + q'_j\lambda - q_j\lambda)]$$

$$\times d^K_{\delta'\lambda}(\xi')d^K_{\delta\lambda}(\xi), \qquad (6.11)$$

where ξ is the angle between $\mathbf{j}$ and $\mathbf{J}$, and ξ' is the angle between $\mathbf{j}'$ and $\mathbf{J}$. (The magnitudes of $\mathbf{j}$, $\mathbf{j}'$, and $\mathbf{J}$ are $\hat{j}$, $\hat{j}'$, and $\hat{J}$.) Here, the sum is over stationary points (s.p.), i.e., points such that the classical trajectories required are those with initial angular momentum $\hat{j} = \tfrac{1}{2}(\hat{j}_i + \hat{j}_f)$ and final angular momentum $\hat{j}' = \tfrac{1}{2}(\hat{j}'_i + \hat{j}'_f)$. $D^K_{\delta'\delta}(\alpha, \beta, \gamma)$ is a rotational matrix element defined by Edmonds.[34c] (A description[22n] of the relation of α, β, and γ to the physical rotations between the precollision dipole and postcollision dipole is given in Fig. 3.) δ' equals $j'_f - j'_i$ and δ equals $j_f - j_i$.[22n] β is the angle of reorientation of the angular momentum vector due to collision while α and γ together describe the rotational phase shift (Figs. 2 and 3).

From Eq. (4.31) and the spectral selection rule $j_f - j_i = 1$ for linear molecules, the cross section corresponding to the T_2 process involves a $D^K_{\delta'\delta}(\alpha, \beta, \gamma)$, with $\delta' = \delta = \pm 1$. From Eq. (4.32), the cross section corresponding to T_1 involves $\delta' = \delta = 0$. Since $D^K_{00}(\alpha, \beta, \gamma) = d^K_{00}(\beta)$, the T_1 process is not affected by the rotational phase shifts. For the case of Eq. (4.32) when the spectral transition occurs in the absence of static fields, K equals zero and neither rotational phase shift nor reorientation affects the T_1 process.

In Eq. (6.10), it was assumed that any stationary points are real, i.e., have real values of the initial angles $\overline{q}_j$ such that at the end of the trajectory, the angular momentum equals $\hat{j}'$. There may be cases, however, where although there are no *real* stationary points (clas-

sically inaccessible case) the final angular momentum may actually come so close to $\hat{j}'$ that imaginary stationary phase points do contribute to the cross sections. Then in analogy to the one-dimensional case,[22b,n,23c] $\sum_{s.p.} |\partial j/\partial \overline{q}_j|^{-1}$ in the above expressions is replaced by

$$2\pi |\partial j'/\partial \overline{q}_j|^{-1} \rho^{1/2} \, \mathrm{Ai}^2(\rho),$$

where $\frac{4}{3}\rho^{3/2}$ equals $\mathrm{Im}[\Delta(\overline{q}_c) - \Delta(\overline{q}_c^*)]$, $\overline{q}_c$ is the complex stationary phase point, and Ai is the Airy function. Here, $\Delta(\overline{q}_j)$ behaves like the phase of an individual S-matrix element, having the property

$$\partial \Delta/\partial \overline{q}_j' = \hat{j}^f - \hat{j}', \qquad (6.12)$$

where $\overline{q}_j'$ and $\hat{j}^f$ are the values of the angle and action variables at the end of a trajectory.

For use in this $\mathrm{Ai}(\rho)$, Δ as a function of $\overline{q}_j$ (the initial angle variable) is found by integrating the following expression[22o]:

$$\partial \Delta/\partial \overline{q}_j = (\partial \Delta/\partial \overline{q}_j')(\partial \overline{q}_j'/\partial \overline{q}_j) + (\partial \Delta/\partial \overline{q}_l')(\partial \overline{q}_l'/\partial \overline{q}_j)$$
$$= (\hat{j}^f - \hat{j}')(\partial \overline{q}_j'/\partial \overline{q}_j) + (\hat{l}^f - \hat{l}')(\partial \overline{q}_l'/\partial \overline{q}_j), \qquad (6.13)$$

and $\hat{j}^f$ as a function of $\overline{q}_j$ is approximated by a parabola near $\hat{j}'$.[38] The complex root $\overline{q}_c$ is obtained from the solution of $\hat{j}^f(\overline{q}_j) - \hat{j}' = 0$.

In calculating the cross section of T_2 for the classically inaccessible case, $D_{6',6}^K(\alpha, \beta, \gamma)$ can be approximated by the value calculated on the real trajectory of closest approach.

VII. DISCUSSION

The longitudinal and transverse relaxation times T_1 and T_2 have been related to various scattering processes and semiclassical expressions have been developed. One thus sees how the phenomenological equations can be systematically obtained from the molecular level with the introduction of *ab initio* expressions for various relaxation parameters. It is appropriate at this point to summarize the approximations used and the limitations of categorizing the relaxation process by two simple relaxation times.

The most important assumption is the impact approximation, which is described in Appendix A. Since the experiments are generally performed at room temperature and low pressure with frequencies of the radiation nearly resonant with that of the spectral line of interest, this assumption is generally satisfied.

The second assumption involves that of employing a single relaxation time T_1 for the description of the decay of the population difference towards its equilibrium value. From the discussion following Eq. (3.17), this assumption is valid if the collision dynamics of the two spectroscopic states is about the same, i.e., if Expressions (3.22) and (3.23) are equated. If this condition is not fulfilled, there is no reason to expect that a single relaxation time T_1 would be adequate to describe the relaxation of the population difference. Instead, one would have to solve simultaneously the following four equations: (3.8a), (3.8b), (3.17), and (3.18) (with the addition of the effect of the radiation field).

In the case of particular experiments—absorption experiments in the absence of a static field—the assumption following (4.22) is made, an assumption which we tested numerically.[36]

The early part of the derivation in Sec. III [up to Eq. (3.6)] parallels that given by Wang *et al.*[24b] At that point the latter authors introduced specific assumptions regarding the relaxation matrix elements to facilitate the interpretation of their molecular beam maser experimental results. For example, in applying their results to the inversion doublet of ammonia in which *both* the collision and the spectral transitions were confined to the two levels of interest, they assumed that the collision dynamics for the two levels are nearly identical, so that

$$S_{ii} \simeq S_{ff}$$
$$S_{i\alpha} = S_{f\beta} = 0, \quad \alpha \neq i,f \text{ and } \beta \neq i,f. \qquad (7.1)$$

The symmetry and unitarity of the S-matrix then yielded the following relations[24b]:

$$\Lambda_{fi,fi} = \Lambda_{ii,ii} \qquad (7.2)$$

$$\Lambda_{ii,ii} - \Lambda_{ii,ff} = \Lambda_{ff,ff} - \Lambda_{ff,ii} = 2\Lambda_{ii,ii}. \qquad (7.3)$$

It follows from Eqs. (3.36) and (3.37) that the value of $1/T_1$ is then twice that of $1/T_2$. This result was in agreement with the molecular beam maser experimental data.[24]

Wang *et al.*[24b] also discussed the relaxation of the linear molecule OCS where the microwave transition $j = 1 \leftrightarrow 2$ was observed in the molecular beam maser experiments. They assumed that (a) the system can be approximated by a four-level collisional system, two levels of which were coupled by the radiation field; (b) the population of the $j = 1$ state selected in the beam experiment is much larger than that of the remainder; and (c) all relaxation matrix elements had the same magnitude. These approximations are not used in the present analysis, and in addition the analysis of the effect of static fields is considered, and semiclassical expressions for the relaxation matrix elements are given.

A comparison of Eq. (3.36) with Eq. (B13) in Appendix B permits one to identify the $1/T_2$ measured in transient experiments with the halfwidth of the corresponding isolated line measured in low pressure steady-state experiments. Such an equivalence has been recognized and demonstrated experimentally.[11]

In a subsequent paper,[22p] calculations of T_1 and T_2 are performed for systems consisting of OCS and various collision partners. Comparison is made with available experimental results in the presence and absence of static fields.

APPENDIX A: DERIVATION OF EQS. (2.4) AND (2.5) AND SYMMETRY CONSIDERATIONS

In this appendix, the derivation of a kinetic equation is summarized for use in the text. In its initial part the procedure follows one used by Snider to derive the Waldmann–Snider equation[39] under the impact approximation, but now including the presence of the radiation field.

The physical system consists of a molecule designated as molecule 1 which interacts with the probing radiation field, and $N-1$ perturbing molecules which are radiatively inert. Boltzmann statistics are employed throughout the discussion. The system may be described by a density matrix $\rho^{(N)}$ which satisfies the Liouville equation,

$$i\frac{\partial}{\partial t}\rho^{(N)} = [H^{(N)} + \mathcal{H}, \rho^{(N)}]. \tag{A1}$$

The N-particle Hamiltonian $H^{(N)}$ is assumed to be given by

$$H^{(N)} = H^{s}(1) + \sum_{i=2}^{N}[H^{b}(i) + V_{1i}], \tag{A2}$$

where $H^{s}(1)$ is the Hamiltonian for the isolated active molecule, H^{b} is the Hamiltonian for a single perturber, V_{1i} is the interaction between the active molecule and the perturber, and $\mathcal{H}$ is the interaction of molecule 1 with the electromagnetic field (hence it operates only on the coordinates of molecule 1). Interaction between perturbers is neglected. The following reduced density matrices are defined:

$$\rho^{(s)} \equiv \mathrm{Tr}^{(2,\dots,N)}\rho^{(N)}, \tag{A3}$$

where the trace is taken over all the perturbers, and

$$\rho^{(n)}(1, 2, \dots, n) = \mathrm{Tr}^{(n+1,\dots,N)}\rho^{(N)}, \tag{A4}$$

where the trace is taken over $N-n$ perturbers. Similarly, $\rho^{(2)}(1, i)$ is defined:

$$\rho^{(2)}(1, i) = \mathrm{Tr}^{(2,\dots,i-1,i+1\dots N)}\rho^{(N)}, \tag{A4'}$$

and so

$$\rho^{(s)} = \mathrm{Tr}^{(i)}\rho^{(2)}(1, i), \tag{A3'}$$

where $\mathrm{Tr}^{(i)}$ denotes the trace taken over the ith perturber. The following equations of motion (BBGKY hierarchy) are obtained by taking suitable trace over Eq. (A1):

$$i\frac{\partial}{\partial t}\rho^{(s)} = [H^{s}(1) + \mathcal{H}, \rho^{(s)}] + \sum_{i=2}^{N}\mathrm{Tr}^{(i)}[V_{1i}, \rho^{(2)}(1, i)] \tag{A5}$$

$$i\frac{\partial}{\partial t}\rho^{(2)}(1, 2) = [H^{s}(1) + H^{b}(2) + V_{12} + \mathcal{H}, \rho^{(2)}(1, 2)]$$
$$+ \sum_{j=3}^{N}\mathrm{Tr}^{(j)}[V_{1j} + V_{2j}, \rho^{(3)}(1, 2, j)]. \tag{A6}$$

The form of V_{1i} is the same for all perturbers and hence (A5) can be simplified to

$$i\frac{\partial}{\partial t}\rho^{(s)} = [H^{s}(1) + \mathcal{H}, \rho^{(s)}] + (N-1)\,\mathrm{Tr}^{(2)}[V_{12}, \rho^{(2)}(1, 2)]. \tag{A7}$$

Equations (A6) and (A7) are not closed equations and the following assumptions are next introduced to convert them into a soluble closed form:

(1). *The impact approximation*: (a) The perturbers are statistically independent so that only binary collisions between a perturber and the active molecules are important, and (b) the time during collision is much shorter than the time between collisions so that all collisions are assumed complete;

(2). *The Boltzmann property*: The pair density ma-

trix $\rho^{(2)}(1, 2)$ factors outside the region of interaction, i.e.,

$$\rho^{(2)}(1, 2) = \rho^{(s)}(1)\rho_2 \tag{A8}$$

for most of the time when the absorber and perturbers are not interacting. Here ρ_2 denotes $\mathrm{Tr}^{(1)}\rho^{(2)}(1, 2)$, the singlet density matrix for a perturber. The weak coupling approximation in (A8) has been discussed in detail by Smith *et al.*[40]

Since the second term in the RHS of Eq. (A7) vanishes when 1 and 2 are far apart, the $\rho^{(2)}(1, 2)$ in (A7) needs to be calculated only during a collision. To this end, Eq. (A6) is solved for the behavior of $\rho^{(2)}(1, 2)$ only during a binary collision. Thus, the sum over j in (A6) can be neglected, giving

$$i\frac{\partial}{\partial t}\rho^{(2)}(1, 2) = [\,\mathcal{K}, \rho^{(2)}(1, 2)] + [V_{12}, \rho^{(2)}(1, 2)], \tag{A9}$$

where

$$\mathcal{K} = H^{s} + H^{b}(2) + \mathcal{H}. \tag{A10}$$

Assumption (2) supplies the initial condition for (A7),

$$\rho^{(2)}(1, 2)(t_0) = \rho^{(s)}(t_0)\rho_2(t_0), \tag{A11}$$

for $t_0 \to -\infty$ in a "collisional sense," i.e., where $|t_0|$ is still macroscopically small. Equation (A9), together with initial condition (A11), resembles the Schrödinger equation for a scattering problem. Under the approximations of the impact theory, the formal theory of scattering is then used to yield a solution for $\rho^{(2)}(1, 2)$[39]:

$$\rho^{(2)}(1, 2) = \Omega\rho^{(s)}(t)\rho_2(t)\Omega^{\dagger}, \tag{A12}$$

where Ω is the Møller operator.[41] Substituting (A12) into (A8), a closed equation for $\rho^{(s)}$ is obtained:

$$i\frac{\partial}{\partial t}\rho^{(s)} = [H^{s} + \mathcal{H}, \rho^{(s)}] + \mathrm{Tr}^{(2)}(N-1)[V_{12}, \Omega\rho^{(s)}\rho_2\Omega^{\dagger}]. \tag{A13}$$

Equilibrium for the translational states of the absorber and for those of the perturber is assumed, and so $\rho^{(s)}$ and ρ_2 are both diagonal in the translational states of those molecules. Thus, $\rho^{(s)}$ and the translational part of H^{s} commute. The trace (denoted by $\mathrm{Tr}_t^{(1)}$) of (A13) is next taken over the translational states of the absorber. The last term of (A13) now involves a $\mathrm{Tr}_t^{(1)}\,\mathrm{Tr}^{(2)}$. One may now transform the translational basis functions in this $\mathrm{Tr}_t^{(1)}\mathrm{Tr}^{(2)}$ to those involving the velocity of the center of mass of molecules 1 and 2, and to those involving their relative velocity. Since the operators V_{12} and Ω are diagonal in the total translational momentum of the absorber plus perturber pair, one may integrate in this trace over the translational states of the center of mass of the absorber and perturber. One then obtains an equation identical with (A13), but now $\rho^{(s)}$ and $H^{(s)}$ denote the singlet density matrix and Hamiltonian of the internal states of the absorber and $\mathrm{Tr}^{(2)}$ denotes a trace over the internal states of the perturber and over the translational states of relative translational motion of the absorber and the perturber.

Since it is convenient to describe the effect of collision by a relaxation matrix Λ defined by

$$i \frac{\partial}{\partial t} \rho^{(s)} = [H^s + \mathcal{K}, \rho^{(s)}] - i \Lambda \cdot \rho^{(s)} ,$$ (A14)

the following matrix element of the last term of the modified (A13) must be evaluated:

$$\langle f | \mathrm{Tr}^{(2)} [V_{12}, \Omega \rho^{(s)} \rho_2 \Omega^\dagger] | i \rangle ,$$

where $|i\rangle$, $|f\rangle$ can be chosen[26a] to be eigenstates of the internal state Hamiltonian H^s with energy eigenvalues E_i, E_f. It will be assumed that $\mathcal{K}$ does not affect the collision dynamics.[42] Let the eigenstates of H^b (for a single perturber) be $|a\rangle$, $|b\rangle$, ... with energy eigenvalues E_a, E_b, etc. The eigenvectors are assumed to have the normalization

$$\langle i'a' | ia \rangle = \delta_{ii'} \delta_{aa'} \delta (E_{ia} - E_{i'a'}) ,$$ (A15)

where E_{ia} stands for $E_i + E_a$, etc. Thereby, the "sums" in Eqs. (A20), (A23), and (A25) below include an integral over the energies E_{ia}, etc. The commutator can be expressed as

$$[V_{12}, \Omega \rho^{(s)} \rho_2 \Omega^\dagger] = V_{12} \Omega \rho^{(s)} \rho_2 \Omega^\dagger - \Omega \rho^{(s)} \rho_2 \Omega^\dagger V_{12}^\dagger$$
$$= t \rho^{(s)} \rho_2 \Omega^\dagger - \Omega \rho^{(s)} \rho_2 t^\dagger$$
$$= t \rho^{(s)} \rho_2 - \rho^{(s)} \rho_2 t^\dagger + t \rho^{(s)} \rho_2 t^\dagger G^\dagger$$
$$- G t \rho^{(s)} \rho_2 t^\dagger ,$$ (A16)

where the t-matrix and the Green's function G are defined by[41]

$$t = V_{12} \Omega , \quad G(E) = \lim_{\epsilon \to 0^+} \frac{1}{E - \mathcal{K} + i\epsilon} ,$$ (A17)

and the Møller operator can be expressed in terms of t and G by[41]

$$\Omega = I + G(E) t ,$$ (A18)

where I is the identity operator.

The distribution of perturbers among the eigenstates of $H^{(b)}$ can be considered to be stationary,[27] i.e.,

$$\langle a | \rho_2 | b \rangle = \rho_a \langle a | b \rangle .$$ (A19)

Thus, from (A16),

$$\langle f'a' | [V_{12}, \Omega \rho^{(s)} \rho_2 \Omega^\dagger] | i'b' \rangle = \sum_{fa} \langle f'a' | t | fa \rangle \rho_{fi}^{(s)} \rho_a \langle a | b' \rangle - \sum_{ia} \rho_{f'i}^{(s)} \rho_{a'} \langle a' | a \rangle \langle ia | t^\dagger | i'b' \rangle$$
$$+ \sum_{ifa} \left[\langle f'a' | t | fa \rangle \langle ia | t^\dagger | i'b' \rangle \rho_a \rho_{fi}^{(s)} \left(\frac{1}{E_{ia} - E_{i'b'} - i\epsilon} - \frac{1}{E_{fa} - E_{f'a'} + i\epsilon} \right) \right] .$$ (A20)

However, in the impact approximation, only complete collisions are considered, and this means that only on-the-energy-shell t-matrix elements are involved. Thus

$$E_{ia} - E_{i'b'} \simeq E_{fa} - E_{f'a'} \simeq 0$$ (A21)

and

$$\lim_{\epsilon \to 0^+} \left(\frac{1}{E_{ia} - E_{i'b'} - i\epsilon} - \frac{1}{E_{fa} - E_{f'b'} + i\epsilon} \right) = 2\pi i \delta (E_{ia} - E_{i'b'}).$$ (A22)

Hence,

$$\langle f' | \mathrm{Tr}^{(2)} [V_{12}, \Omega \rho^{(s)} \rho_2 \Omega^\dagger] | i' \rangle$$
$$= \sum_{a'} \langle f'a' | [V_{12}, \Omega \rho^{(s)} \rho_2 \Omega^\dagger] | ia \rangle$$
$$= \sum_{fi} \sum_{aa'} \rho_a \rho_{fi}^{(s)} [\langle f'a' | t | fa \rangle \langle a'i' | ai \rangle - \langle i'a' | t | ia \rangle^*$$
$$\times \langle af | a'f' \rangle + 2\pi i \delta (E_{ia} - E_{i'a'}) \langle f'a' | t | fa \rangle$$
$$\times \langle i'a' | t | ia \rangle^*] .$$ (A23)

Comparing (A23) with the definition of the matrix elements,

$$\langle f' | \Lambda \cdot \rho^{(s)} | i' \rangle = \sum_{fi} \Lambda_{f'i', fi} \rho_{fi}^{(s)} ,$$ (A24)

it is clear that

$$-i \Lambda_{f'i', fi} = N_2 \sum_{aa'} \rho_a [\langle f'a' | t | fa \rangle \langle a'i' | ai \rangle$$

$$- \langle i'a' | t | ia \rangle^* \langle af | a'f' \rangle + 2\pi i \delta (E_{ia} - E_{i'a'})$$
$$\times \langle f'a' | t | fa \rangle \langle i'a' | t | ia \rangle^*] ,$$ (A25)

where N_2 is defined by $N - 1$ and equals the number of perturbers present. (N_2 is termed N in the text.) Equation (A25) is the same as Eq. (30) of Ben-Reuven,[25b] apart from a notational difference: Our $-i\Lambda$ is his Λ.

It is noted that each of the elements $\langle f'a' | t | fa \rangle$, $\langle i'a' | t | ia \rangle$ contains products of two wavefunctions in the volume V and hence is of order V^{-1}. $\sum_a \langle f'a' | t | fa \rangle \times \langle i'a' | t | ia \rangle^*$ is of order V^{-1} also, because $\sum_a$ implies a phase space integration, yielding a factor V. Thus, the term with bracket in the RHS of (A25) is of order V^{-1}. Since the eigenstates $|ia\rangle$, etc., are normalized to δ-functions, N_2 is interpreted as the density of the perturbing gas. Employing the relation between the S- and T-matrices,[43]

$$S_{i'a', ia} = \delta_{ii'} \delta_{aa'} - 2\pi i \langle i'a' | t | ia \rangle ,$$ (A26)

(A25) can be converted into the following convenient form:

$$\Lambda_{f'i', fi}$$
$$= \frac{N_2}{2\pi} \sum_{aa'} \int dE_a \rho_a (\delta_{f'f} \delta_{i'i} \delta_{a'a} - S_{f'a', fa} S_{i'a', ia}^*) ,$$ (A27)

where now, the *sum* is interpreted as over all relevant *quantum numbers* for the perturber ($lm\beta$, below), and the "sum" over the energy is written explicitly as an integral. ρ_a denotes the equilibrium distribution function

for the perturber and includes as one factor the Maxwell–Boltzmann distribution function for the relative velocity v,

$$(\mu/2\pi k_B T)^{3/2} \exp(-\mu v^2/2k_B T) ,$$

and as another the distribution function for the internal states β of the perturber; a denotes β and the two orbital quantum numbers, l and m.

It is useful to sketch how Eq. (A27) can be transformed to the relevant equation of Ref. 22(1), namely Eqs. (5.1) and (5.2) of the present paper. One introduces for $|a\rangle$ the vector $|klm\rangle$ with the normalization

$$\langle a'|a\rangle \equiv \langle k'l'm'|klm\rangle = \delta(E_k - E_{k'})\delta_{ll'}\delta_{mm'} \quad (A28)$$

(i.e., for purpose of brevity and notation in this discussion we omit, as in Ref. 22(1), $|\beta\rangle$). The ρ_a in (A19) was defined via

$$\langle a'|\rho_2|b\rangle = \rho_{a'}\langle a'|b\rangle = \rho_a \delta_{a'b}\delta(E_{a'} - E_b) . \quad (A29)$$

Since ρ_2 equals $\exp(-H^b/k_B T)/Z$, where Z is $\mathrm{Tr}\exp(-H^b/k_B T)$, one obtains $\exp(-k^2/2\mu k_b T)/Z$ for ρ_2. Z equals $\sum_k \langle k|\exp(-H^b/k_B T)|k\rangle$, i.e., $\sum_k \exp(k^2/2\mu k_B T)$. Using the relation[221]

$$\sum_k \equiv \int_0^\infty d^3k/(2\pi)^3 ,$$

one finds $(\mu k_B T/2\pi)^{3/2}$ for Z. The resulting value for ρ_a, i.e., for ρ_{klm}, proves to be the same as Eq. (B13) of Ref. 22(1). We shall call it $\rho(k)$.

Equation (A27) can be rewritten in terms of the basis set (A28) as

$$\Lambda_{f'i',fi}$$

$$= \frac{N}{2\pi} \int dE_k \rho(k) \sum_{\substack{lm \\ l'm'}} [\delta_{j'_f j_f}\delta_{m'_f m_f}\delta_{j'_i j_i}\delta_{m'_i m_i}\delta_{l'l}\delta_{m'm}$$

$$- \langle j'_f m'_f, l'm'|S|j_f m_f, lm\rangle \langle j'_i m'_i, l'm'|S|j_i m_i, lm\rangle^*] .$$

$$(A30)$$

Introducing such relations as $dE_k = d(k^2/2\mu) = k\,dk/\mu = \mu v\,dv$, $\rho(k) = (2\pi/\mu)^3\rho_v$, where ρ_v denotes $(\mu/2\pi k_B T)^{3/2}$ $\times \exp(-\mu v^2/2k_B T)$, one finds that

$$(1/2\pi)\int_{-0}^\infty dE_k \rho(k)(\cdots)$$

becomes

$$\int_0^\infty 4\pi v^3 \rho_v dv(\pi/k)^2(\cdots) .$$

Using the relations such as (4.4) and the related arguments in the latter half of Appendix B of Ref. 22(1), one then obtains the desired equations, Eqs. (5.1) and (5.2).

In the rest of Appendix A, the symmetry properties of Λ due to rotational invariance are summarized. This discussion follows that of Ref. 27(a) and is included because of the importance of this property and in order to make the present paper relatively self-contained.

In Fano's notation,[27] the LHS of Eq. (A15) can be written as

$$[V_{12}, \Omega\rho^{(s)}\rho_2\Omega^\dagger] = \mathbf{m}(0) \cdot (\rho^{(s)}\rho_2) \quad (A31)$$

and the present Λ is related to $\mathbf{m}(0)$ by

$$-i\Lambda = \mathrm{Tr}_2 \rho_2 \mathbf{m}(0) . \quad (A32)$$

From the RHS of Eq. (A16), one sees that $\mathbf{m}(0)$ is composed of combinations of t-matrices and hence is diagonal in J_i and J_f, the total angular momenta of the two spectroscopic states. Thus, it is also diagonal in K, which is defined by

$$\mathbf{K} = \mathbf{J}_f - \mathbf{J}_i , \quad (A33)$$

where

$$\mathbf{J}_i = \mathbf{j}_i + \mathbf{l}_i$$

$$\mathbf{J}_f = \mathbf{j}_f + \mathbf{l}_f , \quad (A34)$$

and whose eigenvector in Liouville space is given by[44]

$$|(j_i l_i)J_i[(j_f l_f)J_f]^* ; KQ\rangle\rangle .$$

On the other hand, one has the following scheme to obtain K which would bring out the tensorial character of the spectral transition:

$$\mathbf{K} = \mathbf{K}_s + \mathbf{K}_b , \quad (A35)$$

where

$$\mathbf{K}_s = \mathbf{j}_f - \mathbf{j}_i$$

$$\mathbf{K}_b = \mathbf{l}_f - \mathbf{l}_i , \quad (A36)$$

with eigenvectors in Liouville space given by

$$|(j_f j_i^*)K_s, (l_f l_i^*)K_b; KQ\rangle\rangle .$$

These two coupling schemes are related by[25a]

$$|(j_f j_i^*)K_s, (l_f l_i^*)K_b; KQ\rangle\rangle = \sum_{J_f, J_i} [(2J_f+1)(2J_i+1)(2K_s+1)(2K_b+1)]^{1/2}\begin{Bmatrix} j_f & l_f & J_f \\ j_i & l_i & J_i \\ K_s & K_b & K \end{Bmatrix} |(j_f l_f)J_f, [(j_i l_i)J_i]^*; KQ\rangle\rangle , \quad (A37)$$

where the expression in braces is a $9\text{-}j$ symbol.[34]

In general, $\mathbf{m}(0)$ is *not* diagonal in K_s and K_b. However, only the matrix elements of Λ are needed, and so only a thermal average over the bath variables is needed. In an *isotropic* environment in which ρ_2 is spherically symmetric, taking a trace over the perturber coordinates involves only the $K_b = 0$ subspace. Hence K_s equals K and the required eigenvectors are given by

$$|(j_f j_i^*)K, (ll^*)0; KQ\rangle\rangle = \sum_{J_f, J_i} (-1)^{j_f + J_f + l + K}[(2J_f+1)(2J_i+1)]^{1/2}(2l+1)^{-1/2}\begin{Bmatrix} J_f & J_i & K \\ j_i & j_f & l \end{Bmatrix}|(j_f l)J_f[(j_i l)J_i]^*; KQ\rangle\rangle , \quad (A38)$$

where the relation[34]

$$\begin{Bmatrix} j_f & l_f & J_f \\ j_i & l_i & J_i \\ K_s & 0 & K \end{Bmatrix} = (-1)^{j_f + J_i + l_i + K} \delta_{l_f l_i} \delta_{K_s K} \begin{Bmatrix} J_f & J_i & K \\ j_i & j_f & l \end{Bmatrix} / [(2l_i + 1)(2K + 1)]^{1/2}$$

(A39)

has been used.

Hence, from Eqs. (A31) and (A38),

$$\langle\langle j_f' j_i'; K'Q' | \Lambda | j_f j_i; KQ \rangle\rangle = i \sum_{ll'B} \langle\langle (j_f' j_i'^+) K', (l'l'^+)0; K'Q' | m(0) | (j_f j_i^+) K, (ll^+)0; KQ \rangle\rangle \rho_2(\beta)$$

$$= i \sum_{ll'B} \rho_2(\beta) \sum_{\substack{J_i J_f \\ J_i' J_f'}} (-1)^{j_f + J_i + l + K + j_f' + J_i' + l' + K'} [(2l + 1)(2l' + 1)]^{-1/2} [(2J_f + 1)(2J_i + 1)(2J_f' + 1)$$

$$\times (2J_i' + 1)]^{1/2} \begin{Bmatrix} J_f & J_i & K \\ j_i & j_f & l \end{Bmatrix} \begin{Bmatrix} J_f' & J_i' & K' \\ j_i' & j_f' & l' \end{Bmatrix} \langle\langle (j_f' l') J_f' [(j_i' l') J_i']^+; K'Q' | m(0) | (j_f l) J_f [(j_i l) J_i]^+; KQ \rangle\rangle ,$$

(A40)

where the eigenstates of the perturber is written as $|\beta l\rangle$. The isotropy of the environment implies that the matrix elements of ρ_2 depend on β only. The last factor of Eq. (A40) gives the following Kronecker deltas by rotational invariance: $\delta_{J_f J_f'} \delta_{J_i J_i'} \delta_{KK'} \cdot \delta_{QQ'}$. Hence, the result of Eq. (4.5) is achieved.

APPENDIX B: DERIVATION OF THE LINE SHAPE EXPRESSION

In this appendix, the line shapes expression commonly used in line-broadening theories[1,25,27] is derived from the kinetic equation (2.1). In contrast with the correlation function method, [1,25,27] the derivation shows the problem involved in applying the kinetic equation method to the case of overlapping lines.

In steady-state absorption experiments, the quantity measured is the absorption coefficient α which is related to the molecular susceptibility χ of the radiatively active molecule by the equation[45] [cf. Refs. 46 and 10(b)]

$$\alpha = (4\pi N_a \omega / c) \text{Im} \chi ,$$ (B1)

where ω and c are the frequency and group velocity of the radiation, respectively, and $\text{Im}\chi$ denotes the imaginary part of χ. The susceptibility, on the other hand, has been defined in terms of the macroscopic dipole moment $P(t)$ [given by Eq. (3.43)] which is induced by the radiation field $\mathcal{E} \cos\omega t$ by[45] [cf. Refs. 46 and 10(b)]

$$P(t) = N_a \text{Re}(\chi \mathcal{E} e^{-i\omega t}) .$$ (B2)

When $P(t)$ is found from $\rho(t)$ and (3.43), Eqs. (B1) and (B2) yield α.

To obtain the steady-state solution to Eq. (2.1), one sets

$$\rho^{(s)}(t) = A e^{-i\omega t} + A^\dagger e^{i\omega t} + B ,$$ (B3)

where B is a Hermitian operator. Then $\rho^{(s)}(t)$ is Hermitian also. From Eqs. (3.43), (B2), and (B3), one finds

$$\chi = 2 \text{Tr} \mu A / \mathcal{E}$$ (B4)

and

$$\text{Tr} \mu B = 0 .$$ (B5)

Hence, the value of A is required. Substituting Eq. (B3) into Eq. (2.1) and ignoring terms varying in time as $\exp(\pm 2i\omega t)$, one obtains

$$A = \frac{1}{2}(\omega - L_0 + i\Lambda)^{-1} \cdot [B, \mu] \mathcal{E}$$ (B6)

and

$$(L_0 - i\Lambda) \cdot B - \frac{1}{2}\{[\mu, A] + [\mu, A^\dagger]\} \mathcal{E} = 0 .$$ (B7)

From Eq. (B6), since A (and $A^\dagger$) is of the order $\mu \mathcal{E}$, the second term of Eq. (B7) is order $(\mu \mathcal{E})^2$. Under usual conditions for microwave absorption experiments, terms of second order in $(\mu \mathcal{E})$ can be neglected. Thus, B must satisfy

$$(L_0 - i\Lambda) \cdot B = 0.$$ (B8)

From Eqs. (B1), (B4), and (B6), one obtains the following expressions for the absorption coefficient:

$$\alpha(\omega) = 4\pi N_a(\omega/c) \text{Im Tr}\{\mu(\omega - L_0 + i\Lambda)^{-1} \cdot [B, \mu]\}.$$ (B9)

A solution for B which satisfies Eqs. (B4) and (B8) is the Boltzmann distribution $\exp(-\beta H^s)/\text{Tr} \exp(-\beta H^s)$, where β equals $1/k_B T$. [See Eqs. (2.6) and (2.7) and note in (B4) that this ρ^0 commutes with H^s.] If one introduces the approximation

$$\omega \simeq \omega_{fi} ,$$ (B10)

then the matrix element $[B, \mu]_{fi}$ becomes

$$[B, \mu]_{fi} = [\rho^{(0)}, \mu]_{fi}$$

$$= (\rho_{ff}^{(0)} - \rho_{ii}^{(0)}) \mu_{fi}$$

$$\simeq \rho_{ff}^{(0)} \mu_{fi} (1 - e^{-\beta\omega}).$$ (B11)

Substituting Eqs. (B11) into Eq. (B9), one obtains the familiar line shape expression[1]:

$$\alpha(\omega) = 4\pi N_a(\omega/c)(1 - e^{-\beta\omega}) \text{Im Tr}[\mu(\omega - L_0 + i\Lambda)^{-1} \cdot \rho^{(0)} \mu].$$

(B12)

While the last step, from Eq. (B11) to Eq. (B12), is quite justifiable for the case where the $i \to f$ and $f \to i$ lines do not overlap, one sees from (B10) that if they do overlap, one has $\omega_{if} \simeq \omega \simeq \omega_{fi}$ (and so $\omega \simeq 0$). However, this

approximation of $\omega_{if} \simeq \omega_{fi}$ has already appeared earlier, where two overlapping lines are treated in the impact approximation. Since the kinetic equation (2.1) uses the impact approximation at the onset, it is not surprising that a similar approximation recurs later. For this reason, the derivation of Eq. (B12) via the conventional correlation function approach[1,25,27] which introduces the impact approximation at a later stage is more satisfying.

A much lengthier derivation in which the states i, f, etc., are taken to be[42] instantaneous eigenstates of $H^s + \mathcal{K}$ instead of H^s can be given. One replaces ρ in Eq. (2.1) by $D + \hat{\rho}(t)$, where D is $\rho - \hat{\rho}(t)$ and $\hat{\rho}(t)$ is the instantaneous Boltzmann distribution appropriate to $H^s + \mathcal{K}$ (cf. Ref. 45). One can then show that $\Lambda \cdot \hat{\rho} = 0$, instead of $\Lambda \cdot \rho^{(0)} = 0$. One ultimately then obtains Eq. (B12), but with a milder assumption than (B10) and (B11), namely one that only replaces $[1 - \exp(-\beta\omega_{if})]/\omega_{if}$ by $[1 - \exp(-\beta\omega)]/\omega$.

If Eq. (B12) is applied to an isolated line $i \leftrightarrow f$, in which, at the same time, the negative resonance term and the coupling between ρ_{fi} and all other $\rho_{f'i'}$'s, including ρ_{if}, are neglected (the latter neglect corresponds to omitting terms such as $\Lambda_{if,fi}$), one obtains

$$\alpha(\omega) = 4\pi N_a(\omega/c)(1 - e^{-\beta\omega})|\mu_{fi}|^2 \rho_{ff}^{(0)}$$
$$\times \mathrm{Im}(\omega - \omega_{fi} + i\Lambda_{fi,fi})^{-1}. \qquad (B13)$$

The same result can also be obtained directly from Eq. (2.8), by setting $\rho_{fi} = A_{fi}\exp(-i\omega t)$ [instead of Eq. (B3)], and hence $\rho_{if} = A_{fi}^*\exp(i\omega t)$, replacing the diagonal elements of ρ by their equilibrium values, equating the coefficient of $\exp(-i\omega t)$ in (2.8) to zero, and evaluating A_{fi}. This method of setting ρ_{fi} equal to $A_{fi}\exp(-i\omega t)$ is used next in Appendix C to obtain the MMDR equation.

APPENDIX C: APPLICATION OF EQS. (2.8) AND (2.9) TO DOUBLE RESONANCE EXPERIMENTS

In a double resonance experiment, a sample of gas at low pressure is irradiated simultaneously with two fields, a high power field, $E_p\cos\omega_p t$, the "pump field" in resonance with a transition $i \leftrightarrow f$, and a weak field $E_s\cos\omega_s t$ called the "signal field," in resonance with another transition $i' \leftrightarrow f'$. The transfer of population from the pumped levels i,f by inelastic collision to signal levels i', f' is observed by comparing the absorption with the pump on and off. In modulated microwave double resonance spectroscopy (MMDR),[30] the pump field is modulated on and off at a frequency of about 100 KC/sec and the signal field is monitored at the modulation frequency. The modulation frequency is low enough so that steady state solutions may be used in the analysis (period of modulation is typically 10 μsec, typical relaxation time is of the order $\lesssim 0.1$ μsec).

We consider first the signal levels i', f'. Since the experiment is performed at low pressure, the phenomenon of overlapping lines does not occur and the line $i' \leftrightarrow f'$ (as well as $i \leftrightarrow f$) can be treated as an isolated line. Following the remarks made at the end of Appendix B, one sets $\rho_{f'i'}^{(s)} = A_{f'i'}\exp(-i\omega_s t)$, and the steady state solution is found from Eq. (2.8),

$$\rho_{f'i'}^{(s)} = (\rho_{f'f'}^{(s)} - \rho_{i'i'}^{(s)})\mu_{f'i'}E_s/2[(\omega_s - \omega_{f'i'}) + i\Lambda_{f'i',f'i'}], \qquad (C1)$$

where the relation

$$\mathcal{K}_{f'i'} = -\mu_{f'i'}E_s\cos\omega_s t = -\mu_{f'i'}\tfrac{1}{2}E_s(e^{i\omega_s t} + e^{-i\omega_s t}) \qquad (C2)$$

has been used and only the resonant part is retained in Eq. (C1). The absorption of the signal field, being proportional to the imaginary part of $\rho_{f'i'}^{(s)}$, is thus proportional to the population difference $\rho_{f'f'}^{(s)} - \rho_{i'i'}^{(s)}$. Hence, only the equation of motion for the diagonal density matrix element, i.e., Eq. (2.9), is required.

We consider next the half of the modulation period when the pump field is on. For the pump levels, i, f (assuming the pump field is exactly at resonance), (C1) gives

$$\rho_{fi}^{(s)} = \mu_{fi}E_p e^{-i\omega_p t}(\rho_{ff}^{(s)} - \rho_{ii}^{(s)})/2i\gamma, \qquad (C3)$$

where $\gamma = \mathrm{Re}\Lambda_{fi,fi}$ is the linewidth for the line $i \to f$. Substituting (C3) into (2.9), neglecting terms rapidly varying with time and ignoring the disturbance of the signal field on the populations of the levels i', f', one has

$$i\frac{\partial}{\partial t}\rho_{ii}^{(s)} = -(\rho_{ff}^{(s)} - \rho_{ii}^{(s)})|\mu_{fi}E_p|^2/2i\gamma - i\sum_k \Lambda_{ii,kk}\rho_{kk}^{(s)}$$

or

$$\frac{\partial}{\partial t}\rho_{ii}^{(s)} = -(\delta\pi_{ii}\rho_{ii} + \delta\pi_{if}\rho_{ff} + \sum_k \pi_{ik}\rho_{kk}), \qquad (C4)$$

where

$$\pi_{ik} = \Lambda_{ii,kk}$$
$$\delta\pi_{ii} = -\delta\pi_{if} = |\mu_{fi}E_p|^2/\Delta\omega_{1/2}.$$

$\Delta\omega_{1/2}$ denotes 2γ and is the full width at half maximum of the line $i \leftrightarrow f$ under nonsaturation conditions. Similarly,

$$\frac{\partial}{\partial t}\rho_{ff}^{(s)} = -(\delta\pi_{ff}\rho_{ff}^{(s)} + \delta\pi_{fi}\rho_{ii}^{(s)} + \sum_k \pi_{fk}\rho_{kk}^{(s)}), \qquad (C5)$$

where

$$\delta\pi_{ff} = \delta\pi_{ii} = -\delta\pi_{fi} = -\delta\pi_{if}.$$

For other levels other than i, f, the relaxation is given by

$$\frac{\partial}{\partial t}\rho_{ii}^{(s)} = -\sum_k \pi_{jk}\rho_{kk}^{(s)}, \quad j \neq i, f. \qquad (C6)$$

Putting (C4), (C5), and (C6) in matrix form and identifying $\rho_{ii}^{(s)}$ with n_i, one obtains the rate equation (21) of Ref. 32(a):

$$d\mathbf{n}/dt = -(\pi + \delta\pi) \cdot \mathbf{n}. \qquad (C7)$$

During the half period when the pump field is off, the population changes according to [Eq. (2.9) with the first term on the RHS omitted]

$$d\mathbf{n}/dt = -\pi \cdot \mathbf{n}. \qquad (C8)$$

Equations (C7) and (C8) are the starting point of Gordon's analysis of MMDR experiments.

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[28]If V is real, then $V = K V K^{-1}$, where K is the complex conjugation operator. Also, V is Hermitian: $V = V^\dagger$. By definition, $V^\dagger = T K V K^{-1} T^{-1}$, where T is the transpose operator. Thus $V = T V T^{-1}$ and so $\langle A | V | B \rangle = \langle B | V | A \rangle$. From the Lippmann—Schwinger equation for the t-matrix (see e.g., Ref. 41, § 2.5), $t = V + V(E - H_0 + i\epsilon)^{-1}t$, it follows that t is symmetric. From (A26), S is symmetric also.

[29]One notes that ρ_b in Eq. (2.5) is proportional to $\exp(-E_b/k_B T)$. If we write out from Eq. (2.5) the explicit expression for $\Lambda_{l'l',ll}$ and $\Lambda_{ll,l'l'}$ and note that $E_b = E_I - E_l$, $E_{b'} = E_I - E_{l'}$, and use the fact that S is symmetric, Eq. (2.8a) follows immediately.

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[32]H. C. Torrey, Phys. Rev. 76, 1059 (1949).

[33]U. Fano and G. Racah, *Irreducible Tensorial Sets* (Academic, New York, 1959), p. 100, Eq. (18.1), which we have used noting that j_f, j_i, and K are integers.

[34](a) A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton U. P., Princeton, 1960), p. 47; (b) cf. Eq. (5.4.1) and (3.7.5)—(3.7.6); (c) chap. 4.

[35]For the case of $j = 0 \leftrightarrow 1$ transition, no such approximation is needed since only the $(j, m) = (0, 0) \leftrightarrow (1, 0)$ sublevels are coupled by the electromagnetic field; hence it is a "true" 2-level system even in the absence of static fields. In this case, the sum in the second term on the RHS of (4.15) contains only the

$m = 0$ term, and (4.16) can be used (with $m = 0$); then, using (3.36)–(3.37), one finds $1/T_2 = \text{Re}\Lambda \mid_{10,10} 1/T_1$.

$$= \tfrac{1}{2}[\langle\langle 00,00 \mid \Lambda \mid 00,00\rangle\rangle - \langle\langle 10,10 \mid \Lambda \mid 00,00\rangle\rangle + \langle\langle 10,10 \mid \Lambda \mid 10,10\rangle\rangle$$
$$- \langle\langle 00,00 \mid \Lambda \mid 10,10\rangle\rangle].$$

[36] Assuming a single time constant ($T_1 = T_2 \equiv \tau$) for all relaxation processes (for corroborative data, see Ref. 11), Eq. (54) of Ref. 10(b) is applicable for calculating the absorption coefficient for each m transition. The total absorption in our numerical tests was found by summing the absorption for each allowed m transition, and the result was fitted to the on resonance expression [Eq. (54) of Ref. 10(b)] for a 2-level system. In the high power case [$\Omega = 4.4$ MHz, using the notation of Ref. 10(b)], we obtained τ's of 0.925 and 0.97 μsec for the $j = 2 \leftrightarrow 3$ and $j = 1 \leftrightarrow 2$ transitions, respectively, instead of the correct value of 1.0 μsec. In the case of lower power, when $\Omega = 3.4$ MHz, τ's of 0.95 and 0.97 μsec for the $j = 2 \leftrightarrow 3$ and $1 \leftrightarrow 2$ transitions, respectively, were obtained instead of the correct value of 1.0 μsec. We obtained similar results for the off-resonance case. This approximation is thus seen to be a reasonable one, at least for the case studied ($T_1 \simeq T_2$).

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[38] In the rare case that this fitted parabola for $j^f(\overline{q}_j)$ then gave rise instead to two real stationary phase points, the corresponding Airy formula for transition probability [Eq. (4.10) of Ref. 22(c)] was used.[22o]

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[42] In the microwave region, the time interval in which the collision occurs is typically short compared with $1/\omega$ and so then one could choose instead $|i\rangle$ and $|f\rangle$ to be eigenstate of $H^s + \mathcal{K}$. E_i and E_f in this case are the corresponding instantaneous energy eigenvalues.

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[44] These Liouville vectors are constructed similarly to those constructed by Eq. (4.4). $|(j_i l_i) J_i [(J_f l_f) J_f]^+; KQ\rangle\rangle$ is an eigenvector of the following Liouville operators: $[j^2,]$ $[l^2,]$ $[J^2,]$, $[\mathcal{K},]$, where $[,]$ denotes a commutator, with corresponding eigenvalues $[j_i(j_i+1) - j_f(j_f+1)]$, $[l_i(l_i+1) - l_f(l_f+1)]$, $[J_i(J_i+1) - J_f(J_f+1)]$, and $E_i - E_f$. It also transforms as a spherical tensor of order (K,Q) in ordinary Hilbert space of eigenvectors for the Hamiltonian $\mathcal{K}$ (defined in Eq. (A10)].

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