PHYSICAL REVIEW A VOLUME 59, NUMBER 5 MAY 1999

Molecular dynamics and a simplified master equation for spectral line shapes

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(Received 21 September 1998)

Borrowing heavily from the literature, we develop a transport relaxation equation for the off-diagonal elements of the density matrix. It is applicable to a large range of topics in laser theory, nonlinear optics and spectral line shapes, etc. Applying this single equation to the case of infrared electric dipole transitions permits us to recover, quickly and simply, all of the well-known spectral line shapes found in the literature. It also offers further insight into the process of line mixing, particularly in the weak mixing limit. An outline of a new treatment of Dicke narrowing and other speed-dependent contributions to spectral profiles is also given in terms of the transport relaxation equation. The treatment also provides a numerical method for including the effects of statistical correlation between the evolution of the internal and translational degrees of freedom. [S1050-2947(99)11205-8]

PACS number(s): 32.70.Jz

INTRODUCTION

The static and dynamical properties of dilute gases enter into many areas of physics, including lasers, nonlinear optics, magnetic resonance, transport phenomena, and of course spectral line shapes (see, for example, Refs. [1–3]). However, each area has largely developed its own terminology and approach, a fact that conceals their commonality, hinders communication, and impedes the development of a broad overview. Here we attempt to rectify the problem. We do this primarily by an inspection of a number of pioneering papers [4–11], all of which are traceable in some way back to Boltzmann or Schrödinger.

Even such a simple system as a dilute gas is sufficiently complex that it is futile to try and develop a truly complete theory based on statistical mechanics, even for a single type of experiment. As a consequence the question becomes one of making approximations that are appropriate for a particular situation or class of experiments. One general approximation made here, and which appears to be widely accepted, is the semiclassical treatment of the dynamics, wherein the translational motion is treated classically, and the internal degrees of freedom quantum mechanically [12].

A common starting point for almost all many body problems is the Liouville equation for the density matrix ρ, for the entire system

$$\partial\rho/\partial t=-(i/\hbar)[H,\rho]. \tag{1}$$

Through a series of approximations [9], one contracts the description to one of free streaming of the molecules of interest (the active system) plus relaxation terms associated with their interaction with the so-called ‘‘bath.’’ In the theory of spectral line shapes it is all too common to entangle this contraction or ‘‘bath theory’’ with the derivation of a spectral profile. It is this entanglement that hides the connection to other areas of molecular dynamics. We shall keep them separated. The contracted form of Eq. (1) is a transport relaxation equation that may be applied to many problems in molecular physics, including laser theory and nonlinear optics. Here we present a simplified transport relaxation equation for the density matrix that captures most of the physics of spectral line shapes.

In the following section we introduce many of the basic ideas, using an approach common in the theory of lasers, wherein there is only a single transition of central importance. This is then generalized to include multiple transitions and an explicit account of translational motion. The final transport relaxation equation is then used to rederive many well-known cases of spectral profiles. In the case of line mixing, this approach enhances our understanding, particularly in the case of weak mixing. This is followed by an outline of a treatment of Dicke narrowing and a discussion of how speed-dependent effects in general may be treated. The paper concludes with some comments (in particular about the limitations of the approach used here), and a summary.

ELEMENTARY RELAXATION

In laser theory, the model used for the contracted form of Eq. (1) is often written as,

$$\partial\rho/\partial t=-(i/\hbar)[H,\rho]-\Gamma\rho, \tag{2}$$

where H consists of H_0, the Hamiltonian for the internal degrees of freedom of an isolated atom or molecule, plus, H_1, the interaction with any applied (optical) field. The relaxation operator Γ has a form that forces the populations (diagonal elements of the density matrix) towards their steady-state values and the coherences (off-diagonal elements) towards zero. As an introduction to the more general problem, we follow a well-trodden path and treat the case of electric dipole interaction. In linear spectroscopy or laser theory the interaction,[1] $-\mu\mathcal{E}$ would then involve a field $\mathcal{E}$ oscillating only at a single frequency ω. For nonlinear

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[1] In the interest of simplicity, we have ignored the vector nature of the interaction.

effects, in general, multicomponent fields would be considered. The next step consists of solving for ρ as a power series in the field(s). We follow common practice and use the eigenstates of H_0 as a basis set, when computing the matrix components of Eq. (2). Hiding an $\hbar$ in $\mu\mathcal{E}$, it is easy to show that the nth-order jk component of ρ is given by

$$[(\partial/\partial t)+i(\omega_j-\omega_k)+\gamma_{jk}](\rho^n)_{jk}$$
$$=+i\mathcal{E}\sum_l [\mu_{jl}(\rho^{n-1})_{lk}-(\rho^{n-1})_{jl}\mu_{lk}], \tag{3}$$

where ω_j is the energy of the jth level of the free molecule. The quantity γ_{jk} is the relaxation rate of the off-diagonal element ρ_{jk}, and μ_{jl} is a matrix element of the electric dipole moment. For linear spectroscopy all we need is a solution to first order in the field, $\mathcal{E}$. Thus only the zeroth-order equilibrium populations (diagonal elements of ρ) will appear on the right-hand side of Eq. (3). The zeroth-order coherences (off-diagonal elements) are zero.

We now solve the equation for a two-level molecule. We confine our treatment to cw spectroscopy, i.e., to stationary fields. Let the field be given by, $\mathcal{E}=E\exp[-i(\omega t-kz)]+\text{c.c.}$ There are two levels, a the lower and b the upper. Write the thermal equilibrium populations $(\rho^0)_{aa}$ and $(\rho^0)_{bb}$ as n_a and n_b molecules per unit volume, respectively. Equation (3) for the component $(\rho^1)_{ba}$ then becomes

$$[(\partial/\partial t)+i(\omega_b-\omega_a)+\gamma_{ba}](\rho^1)_{ba}$$
$$=i\{E\exp[-i(\omega t-kz)]+\text{c.c.}\}[n_a-n_b]\mu_{ba}. \tag{4}$$

If we look for steady state solutions of the form

$$(\rho^1)_{ba}=\{\rho^-\exp[-i(\omega t-kz)]+\rho^+\exp[+i(\omega t-kz)]\}, \tag{5}$$

the resulting equations for the amplitudes ρ^- and ρ^+ are

$$\rho^-=E[n_a-n_b]\mu_{ba}/\{-\omega+\omega_{ba}-i\gamma_{ba}\}, \tag{6a}$$

$$\rho^+=E^*[n_a-n_b]\mu_{ba}/\{+\omega+\omega_{ba}-i\gamma_{ba}\}, \tag{6b}$$

where ω and $\omega_{ba}=(\omega_b-\omega_a)$ are positive numbers. We see that only the ρ^- term may resonate. Making the rotating wave approximation, i.e., neglecting the antiresonant term,[2] ρ^+ we have, for $(\rho^1)_{ba}$,

$$(\rho^1)_{ba}=\{[n_a-n_b]\mu_{ba}/[(\omega_{ba}-\omega)-i\gamma_{ba}]\}$$
$$\times E\exp[-i(\omega t-kz)]. \tag{7}$$

For $(\rho^1)_{ab}=(\rho^1)^*_{ba}$, it is the ρ^+ term that resonates. As we shall see in the next paragraph, $(\rho^1)_{ab}$, which varies as $\mathcal{E}^*$, will not be required in our treatment of linear spectroscopy.

We have, at this point, solved Eq. (2) to first order in an applied field, using a simple form for the relaxation. Now we make the connection to the spectral profile. First we calculate the macroscopic polarization (dipole moment per unit volume) P, using $P=\text{Tr}[\rho^1\mu]$. The dipole and density matrices are $\left[\begin{smallmatrix}0 & \mu_{ab}\\ \mu_{ba} & 0\end{smallmatrix}\right]$ and $\left[\begin{smallmatrix}0 & \rho_{ba}\\ \rho_{ab} & 0\end{smallmatrix}\right]$, where, for conciseness, we have dropped the superscript, 1 on ρ. Thus P, a real quantity, is just $\rho_{ab}\mu_{ba}+\rho_{ba}\mu_{ab}$. In order to see the phase shift between the applied field and the polarization, it is simpler to express the material polarization in the form $P=\epsilon_0\chi\mathcal{E}$, where P, $\mathcal{E}$, and χ are all now complex. With this convention, P is to be written as $P=\rho_{ba}\mu_{ab}$, i.e., the term in ρ_{ab} is to be dropped because it varies as $\mathcal{E}^*$. Thus we find the complex susceptibility χ, for our two-level system, is given by,

$$\chi=[n_a-n_b]\mu_{ba}\mu_{ab}/\hbar\epsilon_0\{(\omega_{ba}-\omega)-i\gamma_{ba}\}$$
$$=N/\{(\omega_{ba}-\omega)-i\gamma_{ba}\}. \tag{8a}$$

where N is a positive number for systems in thermal equilibrium. For dilute systems, the real part of χ is related to the index of refraction by, $n-1=\chi_r/2$, while the corresponding absorption coefficient is given by, $\alpha=k\chi_i$, where k is the wave vector in vacuum. Thus it follows that (n^2-1) is given by the well-known dispersion curve,

$$n^2-1=(\omega_{ba}-\omega)N/\{(\omega_{ba}-\omega)^2+(\gamma_{ba})^2\}, \tag{8b}$$

while the absorption coefficient is given by the well-known Lorentzian profile

$$\alpha=k\gamma_{ba}N/\{(\omega_{ba}-\omega)^2+(\gamma_{ba})^2\}. \tag{8c}$$

Thus the simple form chosen for our relaxation equation has led to a dispersion curve for the index of refraction and a Lorentzian profile for the absorption. The half width at half maximum of the absorption profile, measured in radians per second, is the relaxation rate γ_{ba}. If γ_{ba} is complex, there will also be a frequency shift in radians per second equal to the imaginary part of γ_{ba}. Later we will see that these relationships between the real and imaginary parts of the relaxation rate γ_{ba}, and the width or shift, are not always exact, even in the so-called collision-dominated regime.

A GENERAL RELAXATION TRANSPORT EQUATION

It is clear from the preceding sections that a Lorentzian line shape follows directly from the form assumed for Eq. (2). For a more general case we need to consider the physics that is omitted in the example above. As was recognized by Rautian and Sobelman [13] and others (see Ref. [9] and references therein), one must think in terms of molecular distribution functions (of which ρ, as used above, is an example in terms of the internal states) and some generalization of the Boltzmann equation (which is an equation involving the translational states). In other words, what we are seeking is a semiclassical generalization of ρ such that it is also a function of **r**, **v**, and, t, where **r** is a position vector, **v** the velocity, and t is the time. Before proceeding with details of a

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[2] Making the rotating-wave approximation removes nonresonant and microwave absorption from consideration.

refined relaxation equation, we make some general comments to set the scene for those readers not familiar with the hierarchy of transport relaxation equations that exists in statistical mechanics.

For *structured* particles, such as molecules with internal degrees of freedom, we can still write, in a semiclassical treatment, $\rho=\rho(\mathbf{r},\mathbf{v},t)$, but we must now consider the matrix character of ρ, i.e., how it depends upon the discrete internal states. In transport phenomena the transport/relaxation equation for the populations or *diagonal elements* of ρ is known as the Wang-Chang–Uhlenbeck (W-CU) equation if the internal states are nondegenerate [14], and as the Waldmann-Snider (WS) equation [6,7] if spatial degeneracy is included. Tip [9] derived an equation, analogous to the WS equation, for the *off-diagonal elements*. In the literature, this is referred to as a generalized WS equation. It is clear from the introductory treatment above that all we need consider for linear spectroscopy is the off-diagonal elements. Furthermore, since we will continue to ignore the vector nature of the problem, we can ignore the spatial degeneracy of the states. Thus our treatment can be at the W-CU level and the final transport/relaxation equation to be presented could be described as a generalized W-CU equation.

Central to all Boltzmann-like equations is the treatment of the relaxation term $\Gamma\rho$. Smith *et al.* [10] developed an equation equivalent to the generalized WS equation from which the dipole absorption spectrum could be determined. The only significant difference between the treatment in Refs. [9] and [10] (from the point of view of this paper) is the handling of the relaxation terms. Smith *et al.* wrote the interaction between the active molecules and the bath explicitly as V_0+V_1 where V_0 is the isotropic part of the interaction that is independent of the internal coordinates. V_1 depends both upon the separation of the centers of mass and on the internal coordinates. This is a well-known decomposition for the interaction between molecules. This decomposition generates three types of relaxation terms [see Eq. (3.14), page 1573, in Ref. [10], but read F_{ab} as if it were ρ_{ab}]. Type I, of which γ in Eqs. (3) or (4) is an example, involve matrix elements of V_1 and describe the relaxation of only the internal ''motion.'' Type II involves matrix elements of V_0 and describes the relaxation of only the translational motion. Type III involve both V_0 and V_1 and encompasses the statistical correlation in the relaxation process between the two types of motion. In Ref. [10], these three terms are contained in the first, second, and third lines of the right-hand side of Eq. (3.14). (The basis of this classification will be modified near the end of this paper.) We follow Smith *et al.* [10] except we separate the question of a relaxation transport equation for the density matrix, from the problem of calculating a spectral profile. This is done by inspection, much in the spirit of the original derivation of the Boltzmann equation. We now justify, on physical as opposed to mathematical grounds, a relaxation transport equation for the off-diagonal elements of the density matrix that is more refined than in the introductory sample calculation above.

Let ρ_{ba} be a general off-diagonal element, with level b above level a. It is a function of position and velocity. Because we are adding the translational motion to the density matrix, we must add the free-streaming term $-\mathbf{v}\cdot\boldsymbol{\nabla}\rho_{ba}$ for the translational motion to the free-streaming term, $-(i/\hbar)[H,\rho]$ for the internal molecular motion. We saw already that a traveling-wave field produced an off-diagonal element that varied spatially as exp(*ikz*). It is the gradient term acting on such a spatial term that produces the familiar kv_z term found in any elementary treatment of Doppler broadening or in a derivation of the Voigt profile.

In addition to the free-streaming translational term, we must add the temporal evolution due to collisions with bath molecules. Two translational relaxation (transport) terms are to be added. The first is $-\nu\rho(\mathbf{r},\mathbf{v},t)_{ba}$ where, in common parlance, ν is the kinetic collision frequency or the rate at which molecules leave a velocity class $\rho(\mathbf{r},\mathbf{v},t)_{ba}$. The second is the rate of return to the velocity class from all the other velocity classes. We write this as $+\int A(\mathbf{v}\leftarrow\mathbf{v}')\rho'_{ba}d\mathbf{v}'$ where $\rho'_{ba}=\rho(\mathbf{r},\mathbf{v}',t)_{ba}$. In equilibrium, the distribution function is constant. This does not imply that the velocities of the molecules are constant, only that the rate at which molecules leave a velocity class is dynamically balanced by a counterflow from other velocity classes. Thus $\mathbf{v}$ and $\mathbf{v}'$ are post-collision and precollision velocities. If the only escape from a velocity class for ρ_{ba} is to another velocity class of ρ_{ba}, then the relationship between A and ν is

$$\nu=\int A(\mathbf{v}\rightarrow\mathbf{v}')d\mathbf{v}'. \tag{9}$$

Neither the forward nor backward translational relaxation terms should come as a surprise to a reader familiar with the Boltzmann equation [15]. Note, however, in the dynamical equation for ρ_{ba}, that the translational terms involve different velocity classes but only a single component of the optical (state) coherence, ρ_{ba}, i.e., the translational relaxation terms are both of type II and arise from the isotropic part of the interaction V_0.

Now we consider the local decay terms, i.e., those belonging to the first class or type I. There is the usual term describing the decay $-\gamma_{ba}\rho(\mathbf{r},\mathbf{v},t)_{ba}$ introduced in our simple relaxation equation, Eq. (3). In addition, there is the return contribution from other components of the optical coherence. Being discrete, this term is written as $+\Sigma_{dc}W(ba\leftarrow dc)\rho(\mathbf{r},\mathbf{v},t)_{dc}$ where the sum over dc excludes $dc=ba$.[3] It is the return of coherence that is the source of line mixing. Smith *et al.* [10] did not separate the two relaxation terms, nor did they comment on their physical significance. The *W*'s are the off-diagonal elements of the so-called relaxation matrix, while the γ's are the diagonal elements. (Our definition differs by a sign from the definition generally found in the literature.) Note that type-I terms involve only a single velocity, but all components of the optical coherence and arise from the V_1 term in the interaction.

Before discussing the third type of contribution to the transport relaxation equation for an off-diagonal term in the combined density-matrix distribution function, it is worthwhile to discuss the various relaxation rates introduced so far. It is bath theory that tells us exactly what microscopic average over the distribution of perturber states is to be calculated. In the usual *linearized* transport relaxation equation,

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[3] Paired subscripts, like *ba*, are to be treated as a single index.

one uses the equilibrium distribution of the perturbers. Consequently, all relaxation rates are properties of the equilibrium state of the system and are independent of the perturbation. Clearly only a weak perturbation (absorption) is imagined.

There are many hundreds of papers dealing with various methods and approximations for calculating the rates or with calculations for specific intermolecular potentials. In this paper we are not concerned with such details. What does concern us is that most of the calculations of broadening and shifting of spectral lines deal with a calculation of the γ's in the center-of-mass frame of a colliding pair, including a Maxwellian average over both of the active and perturbing molecules. It is then assumed that the real and imaginary parts of γ give the width and shift of an isolated line. However, as we saw above, such a relationship only follows from a simple relaxation equation, such as Eq. (3). Furthermore, a relaxation rate is an average over the motion of the perturbers, but not over the motion of the active molecule. Thus the relaxation rates, which depend upon the relative velocity of the active molecule and the perturber, still depend upon the speed of the active molecule, even after averaging over the perturber motion. This point was clearly made by Nienhuis [15]. If the speed dependence is significant for both the relaxation and the transport terms, then the relaxation of the optical coherence and the translational motion are correlated. Here it is proposed to describe the internal and translation motions as ''coupled'' or ''speed correlated'' when both motions depend upon the speed of the active molecule. We will use the expression ''statistically correlated'' for the true statistical or type-III term(s). If the motions are correlated either way, the usual simple relationship between the rates and widths or shifts is broken; the correct relation between relaxation rates and widths and shifts, etc., of a spectral profile can only be established by solving a transport relaxation equation.

We now consider terms that involve statistical correlation. We give two speculative arguments which suggest that they may be neglected. First recall, in the semiclassical approach, that the relaxation rates for the internal degrees of freedom are calculated by averaging the effect of V_1 over classical collision paths, the latter being determined by the isotropic part of the potential V_0. Now consider two collision trajectories which are mirror images, the normal to the mirror surface being the apse line (see, for example, Ref. [16]). The change in velocity will be the same in size but of opposite sign. On the other hand, symmetry suggests that the effect of V_1 on the internal coordinates will be the same. Thus for each contribution to the change in the internal coordinates there are two equal but opposite changes in the translational motion. Averaged over all collisions, this argues for zero statistical correlation. The second argument depends upon the observation that calculations of γ's using curved but approximate classical paths do very well in determining widths and shifts if we ignore speed dependent effects, which are usually small. Such a calculation neglects the statistical correlation which arises from the fact that changes in the internal states and the translational states occur in the same collision. Both lines of reasoning argue, in spite of the fact that the two types of changes occur in a single collision, that the result is *statistically* unimportant. In the main part of this paper type-III terms are ignored. The same assumption is implicitly made in most of the model profiles currently in use. Near the end, we shall show that this assumption is more one of convenience as the central features of the transport relaxation equation remain even if such terms turn out to be significant.

This completes the presentation of the model transport relaxation terms that are to be added to Eq. (2) for the off-diagonal elements of the density matrix. In the case of linear spectroscopy and dipole absorption, the final master equation for this distribution function is

$$[(\partial/\partial t)+i(\omega_b-\omega_a)+\mathbf{v}\cdot\boldsymbol{\nabla}]\rho_{ba}=-\gamma_{ba}\rho_{ba}+\sum_{dc} W(ba\leftarrow dc)\rho_{dc}-\nu\rho_{ba}$$
$$+\int A(\mathbf{v}\leftarrow\mathbf{v}')\rho'_{ba}d^3v'+i\{E\exp[-i(\omega t-kz)]+cc\}[\rho_{aa}-\rho_{bb}]\mu_{ba}, \tag{10}$$

where all of the relaxation rates may be speed dependent. We repeat that ρ' stands for $\rho(\mathbf{r},\mathbf{v}',t)$. Here the equilibrium populations ρ_{aa} and ρ_{bb} are to be written as $n_a f_0(v)$ and $n_b f_0(v)$, where $f_0(v)$ is the Maxwellian distribution function, normalized to unity. Only one of the terms in the field will survive in the rotating wave approximation. Explicit mention of the field terms is the only entanglement of bath theory and spectral line shapes that we have permitted. The two may be disentangled simply by recognizing the field terms as a specific example of the *ba* matrix element of the free-streaming term $[H_1,\rho^0]$. Equation (10) was made concrete because we have our eye on infrared absorption. In the following sections we use our master equation, Eq. (10), to rederive most of the well-known model line shapes found in the literature.

TRANSPORT RELAXATION FOR AN ISOLATED LINE

Generalities

For an isolated line, the sum over *dc* is to be omitted. The conditions under which this is a reasonable approximation will be discussed in a section below on line mixing. Equation (10), as it stands, contains no statistical correlation. If γ_{ba} is speed independent, then the translational and internal degrees of freedom evolve independently. In this case ρ_{ba} can be written in the time domain as $\rho_{ba}=\exp(-\gamma_{ba}t)\tilde{\rho}(r,v,t)$. The proof of this is straightforward, and hinges on being able to pull the $\mathbf{v}'$-independent factor, $\exp(-\gamma_{ba}t)$, out from under the integral sign in the term $\int A(\mathbf{v}\leftarrow\mathbf{v}')\rho'_{ba}d^3v'$, and dividing through the entire equation by the exponential factor. As is well known, a product in time leads to a convolution in frequency space.

Specific single line models

The first case we were tempted to consider was the Doppler profile. Here the collisional relaxation of the translational motion is set to zero but the free-streaming term $\mathbf{v}\cdot\boldsymbol{\nabla}$ is retained. To derive the Doppler profile one might also naively set the relaxation of the internal motion to zero. However, this would be unphysical since in the absence of damping there is no phase shift between the driving field and the polarization, and thus there is no absorption. Thus Doppler broadening should physically be considered as the limiting case of a Voigt profile. We treat the Voigt profile in detail, as it turns out to be rather generic, permitting a rapid and simple treatment of all other isolated line profiles that are consistent with the relaxation and transport of the off-diagonal elements of the density matrix. A shorter, but somewhat similar cataloging of profiles was given by Berman [17].

For the Voigt profile, the problem reduces to solving the equation,

$$[(\partial/\partial t)+i(\omega_b-\omega_a)+\mathbf{v}\cdot\boldsymbol{\nabla}]\rho_{ba} = -\gamma_{ba}\rho_{ba}+i\{E\exp[-i(\omega t-kz)]+\text{c.c.}\}n_af_0(v)\mu_{ba}, \tag{11}$$

where we have set the population of the upper level to zero. We solve the transport relaxation equation in the same manner as led to Eq. (7). Within the rotating wave approximation the c.c. term involving E^* may be dropped. Consequently we can approach the solution more directly by writing ρ_{ba} as $\wp_{ba}E\exp[-i(\omega t-kz)]$ instead of $\rho^-\exp[-i(\omega t-kz)]$. This leads directly to the equation

$$[\omega_{ba}-\omega+kv_z]\wp_{ba}=i\gamma_{ba}\wp_{ba}+n_af_0(v)\mu_{ba}, \tag{12}$$

which has the obvious solution

$$\wp_{ba}=n_af_0(v)\mu_{ba}/[\omega_{ba}-\omega+kv_z-i\gamma_{ba}]. \tag{13}$$

Since all molecules are observed, and the distribution function $\wp_{ba}$ is the amplitude of the optical coherence for a single speed class, the susceptibility is obtained by multiplying by $\mu_{ab}/\hbar\epsilon_0$ and integrating over the velocity. If the relaxation is speed independent, then the equation may be integrated over the x and y components of the velocity. The result is

$$\chi=n_a(\mu_{ba}\mu_{ab}/\hbar\epsilon_0)\int f_1(v_z)dv_z\bigg/[\omega_{ba}-\omega+kv_z-i\gamma_{ba}], \tag{14}$$

where $f_1(v_z)$ is the normalized one-dimensional speed distribution function $(\pi v_0^2)^{-1/2}\exp(-v_z/v_0)^2$, and v_0^2 equals $2k_bT/m$. Taking the imaginary part and multiplying by the wave vector leads to the following expression for the absorption coefficient for the speed independent Voigt profile:

$$n_a(\mu_{ba}\mu_{ab}/\hbar\epsilon_0)\int\gamma_{ba}f_1(v_z)d(kv_z)\bigg/[(\omega_{ba}-\omega+kv_z)^2+(\gamma_{ba})^2]. \tag{15}$$

While mathematically and physically correct, this is not the usual convolution expression found in the literature. However, note that the integral over the z component of the velocity can also be read as a convolution over the ''Doppler frequency'' $\omega'=kv_z$. Keeping the velocity distribution function explicit in Eq. (15) facilitates a comparison with other model profiles for isolated lines.

Having worked through one isolated line case in detail, we now ''clean up'' the presentation by writing the profiles as $I(\omega)$, and expressing them as the imaginary part of a complex function hiding many constants in a prefactor N. From the development above it is clear that the complex function is essentially $\wp_{ba}(v)$, except for the integration over the velocity groups.

We now systematically derive several isolated line profiles. First we repeat the *speed-dependent Voigt profile*, except we write it in complex form. From Eq. (13), we have,

$$I(\omega)=N\,\text{Im}\left\{\int f_0(v)d\mathbf{v}\bigg/[(\omega_{ba}-\omega+kv_z)-i\gamma_{ba}(v)]\right\}. \tag{16}$$

Generally, Eq. (16) cannot be integrated analytically. Second, for the *speed-independent Voigt profile*, Eq. (16) reduces to,

$$I(\omega)=N\,\text{Im}\left\{\int f_1(v_z)dv_z\bigg/[(\omega_{ba}-\omega+kv_z)-i\gamma_{ba}]\right\}. \tag{17}$$

Equation (17) contains a standard integral. In a third case, the Lorentz model, one neglects all aspects of the translational motion, including the free-streaming term. The results are derivable directly from Eq. (16). First we have the *speed-dependent Lorentz model*,

$$I(\omega)=N\,\mathrm{Im}\left\{\int f_0(v)d\mathbf{v}\Big/[(\omega_{ba}-\omega)-i\gamma_{ba}(v)]\right\}. \tag{18}$$

Again one anticipates that analytical expressions for the integral will be found only if γ_{ba} is some unique function of the speed. From Eq. (18), we then recover the elementary or *speed-independent Lorentz model* considered in the beginning,

$$I(\omega)=N\,\mathrm{Im}\{1/[(\omega_{ba}-\omega)-i\gamma_{ba}]\}, \tag{19}$$

by taking γ_{ba} constant in Eq. (18) and integrating over the normalized velocity distribution.

We now treat the case of *pure Doppler broadening*. As pointed out above, we must consider a Voigt profile and take the limit $\gamma_{ba}\rightarrow 0$. Since the relaxation is eventually to be removed from the problem, we might just as well start with the simplest case, the speed-independent Voigt model. Here, it is convenient to use the Voigt absorption profile, Eq. (15), rather than the complex susceptibility, Eq. (17). Recall that the Dirac δ function [18] can be written as $\delta(x-x_0)=(1/\pi)\lim_{\epsilon\rightarrow 0}\{\epsilon/[(x-x_0)^2+\epsilon^2]\}$. Identifying γ_{ba} in Eq. (15) with ϵ, kv_z with x, and $(\omega_{ba}-\omega)$ with x_0 leads immediately to the well-known Doppler profile,

$$I(\omega)=N\exp\{-[(\omega_{ba}-\omega)/kv_0]^2\}. \tag{20}$$

The five models above neglect the direct effect of collisions on the translational motion. We now turn to cases of an isolated line where these effects are no longer neglected. We treat the speed-dependent hard collision model. The hard collision model is a mathematical model that distributes molecules over the Maxwellian distribution function, independent of precollision velocities. Smith *et al.* [10] considered the same problem, and used their formulation of the dipole correlation function to give a sound basis to an earlier classical model developed intuitively by Rautian and Sobelman [13] to describe Dicke narrowing [19]. Here we use our master relaxation transport equation as the starting point. Following the same procedures as above leads directly to the general transport relaxation equation for an isolated line,

$$[\omega_{ba}-\omega+kv_z]\rho_{ba}=i\gamma_{ba}\rho_{ba}+i\nu\rho_{ba}-i\int A(\mathbf{v}\leftarrow\mathbf{v}')\rho_{ba}(v')d\mathbf{v}'+n_af_0(v)\mu_{ba}, \tag{21}$$

where γ_{ba} and ν may both be functions of the speed of the active molecule. In the hard collision model the translational relaxation terms are given by $\nu\rho_{ba}$ and $\nu f_0(v)\int\rho_{ba}(v')d\mathbf{v}'$, where ν is independent of $\mathbf{v}$ (see, for example, Refs. [13] or [20]). Thus our equation for ρ_{ba} becomes

$$[\omega_{ba}-\omega+kv_z-i\gamma_{ba}-i\nu]\rho_{ba}=-i\nu f_0(v)\int\rho_{ba}(v')d\mathbf{v}'+n_af_0(v)\mu_{ba}. \tag{22}$$

Now divide by $[\omega_{ba}-\omega+kv_z-i\gamma_{ba}-i\nu]$, multiply by the volume element of the velocity, $d\mathbf{v}$, and integrate over the velocity. To keep the nomenclature compact, call $\int\rho_{ba}d\mathbf{v}$, $\rho_{ba}(k,\omega)$. Our equation then becomes,

$$\rho_{ba}(k,\omega)=-i\rho_{ba}(k,\omega)\nu\int f_0(v)d\mathbf{v}\Big/[\omega_{ba}-\omega+kv_z-i\gamma_{ba}-i\nu]+n_a\mu_{ba}\int f_0(v)d\mathbf{v}\Big/[\omega_{ba}-\omega+kv_z-i\gamma_{ba}-i\nu]. \tag{23}$$

Rearranging terms, and defining $1/[\omega_{ba}-\omega+kv_z-i\gamma_{ba}(v)-i\nu]$ as the complex Lorentzian $\mathcal{L}(v_z)$, we have

$$\rho_{ba}(k,\omega)=n_a\mu_{ba}\int f_0(v)\mathcal{L}(v_z)d\mathbf{v}\Big/\left\{1+i\nu\int f_0(v)\mathcal{L}(v_z)d\mathbf{v}\right\}, \tag{24}$$

which when multiplied by $\mu_{ab}/\hbar\epsilon_0$ is the complex susceptibility. The imaginary part is equal to the speed-dependent hard collision profile given by Rautian and Sobelman [13] and by Smith *et al.* [10].[4] The Dicke narrowing of the profile at high densities arises from the term in ν in the denominator. It is the mathematical (but unphysical) properties of the collision kernel, $A(\mathbf{v}\leftarrow\mathbf{v}')$, that permit an analytical solution of the transport relaxation equation to be found in this case. In none of the speed-dependent cases above is the line Lorentzian with a width given by the thermal average $\langle\gamma(v)\rangle=\int f_0(v)\gamma(v)d\mathbf{v}$.

There exists another, but rarely quoted, analytical solution for a spectral profile that includes speed-dependent relaxation and transport. This has been given by Dattagupta and Turski [21]. It deals with the so called Lorentz gas, a system of massive (stationary) perturbers of rigid spheres. Since each active molecule maintains its speed in such a model, it is an extreme case of inhomogeneous broadening and shifting. However, since there is no relaxation between speed classes, the model has the unphysical property that any speed

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[4] Although the expressions given here appear to differ from those found in the literature, the apparent difference arises because in one case the real part of a complex function is to be evaluated, while here it is the imaginary part. Furthermore, many authors reference their frequencies to the free molecule line center, defining $\Delta\omega=\omega-\omega_{ba}$. Here we write frequency factors in terms of $\omega_{ba}-\omega$.

distribution function is a stationary solution. It also exhibits problems with respect of convergence to a hydrodynamic (high-density) limit [22]. Perhaps these are the reasons this model has not been applied to the analysis of experimental data. We confine a discussion of the Lorentz gas to the Appendix.

On the other hand, there exists a model for an isolated line which has been used routinely to treat both transport and relaxation. This is the so-called soft collision model [23], and is applicable to the case of very light perturbers with speed-independent broadening. We do not discuss the soft collision model in this paper for two reasons. The first is that it happens to be far more convenient to do so in the time domain rather than the frequency domain used here. The second and more cogent reason is that it does not follow *directly* from our transport relaxation equation but rather from a Fokker-Planck approximation [24] to our basic equation. In this sense, a solution starting from a relaxation transport equation already exists in the literature [24,22]. (For a treatment in the frequency domain, see Refs. [13,22].)

TRANSPORT RELAXATION FOR A BAND

So far we have used our master equation to treat the case of an isolated line. As first shown by Baranger in three pioneering papers [4], closely spaced lines in a band may interfere or mix. Here we rederive his well-known result. (For recent review article on spectral line shapes, including an introduction to line mixing, see Ref. [25].) The standard treatment of line mixing suppresses all aspects of the translational motion. Starting with the master equation [Eq. (10)], and following the same steps as above, leads to the relaxation equation for ρ_{ba},

$$(\omega_{ba}-\omega)\rho_{ba}=i\gamma_{ba}\rho_{ba}-\sum_{dc} iW(ba\leftarrow dc)\rho_{dc}+n_a\mu_{ba}. \tag{25}$$

There is a similar equation for each transition, i.e., for each component ρ_{dc}, etc, of the optical coherence. Thus we have a set of coupled linear equations, which in matrix notation may be written as

$$[\boldsymbol{\omega}_0+i\mathbf{W}-\omega\mathbf{I}]\cdot\boldsymbol{\rho}=\mathbf{N}\cdot\boldsymbol{\mu}, \tag{26}$$

where $\boldsymbol{\omega}_0$ is a diagonal matrix of free molecule transition frequencies, $\mathbf{W}$ is the relaxation matrix, $\mathbf{I}$ is the unit matrix, $\boldsymbol{\rho}$ is a column vector of the components ρ_{ba}, $\mathbf{N}$ is a diagonal matrix in populations and $\boldsymbol{\mu}$ is a column vector of transition dipoles. As defined, the off-diagonal element $\mathbf{W}_{ba,dc}$ is positive and just $W(ba\leftarrow dc)$. As pointed out earlier, it describes the back flow of the component, ρ_{dc} to ρ_{ba}. The diagonal element $\mathbf{W}_{ba,ba}$ is negative and just the complex relaxation rate γ_{ba}. It represents the outflow of coherence from the *ba* component of the optical coherence to all other components. In the steady state, all parts of the optical coherence oscillate at the driving frequency ω, not their natural frequencies ω_{ba}, ω_{dc}, etc.

Now the solution of a set of coupled linear equations is usually expressed as a ratio of determinants, the determinant in the denominator being $[\boldsymbol{\omega}_0+i\mathbf{W}-\omega\mathbf{I}]$. This makes the calculation of the spectral profile tiresome, since the determinants have to be evaluated at each frequency for every density. However, as pointed out by Baranger [4] and refined by Gordon and McGinnis [26], there is a well-known technique of diagonalization that simplifies the problem. Look for a transformation A such that $\mathbf{G}=[\boldsymbol{\omega}_0+i\mathbf{W}]$ becomes diagonal, i.e., solve the equation, $\Lambda=A^{-1}\mathbf{G}A$. Then Eq. (26) can be written

$$\begin{aligned}A^{-1}[\boldsymbol{\omega}_0+i\mathbf{W}-\omega\mathbf{I}]AA^{-1}\cdot\boldsymbol{\rho}&=[\Lambda-\omega\mathbf{I}]A^{-1}\cdot\boldsymbol{\rho}\\&=A^{-1}[\mathbf{N}\cdot\boldsymbol{\mu}],\end{aligned} \tag{27}$$

which has as a solution

$$\boldsymbol{\rho}=A[\boldsymbol{\Lambda}-\omega\mathbf{I}]^{-1}A^{-1}[\mathbf{N}\cdot\boldsymbol{\mu}]. \tag{28}$$

As the inverse of a diagonal matrix is a diagonal matrix of the inverse elements, $[\Lambda-\omega I]^{-1}$ is just a diagonal matrix of Lorentzian factors like, $L_{ba}=1/[(\Lambda^r_{ba}-\omega)+i\Lambda^i_{ba}]$. Here we have anticipated that there is a one-to-one correspondence between the eigenvalues and the components *ba* of the optical coherence. In fact one expects Λ^r_{ba} to approach $\omega_{ba}-\gamma^r_{ba}$, and Λ^i_{ba} to approach $-\gamma^i_{ba}$ as the density is reduced toward zero. (We justify this below in the weak mixing limit.) To construct the susceptibility from Eq. (28), we need to multiply $\boldsymbol{\rho}$ by $\boldsymbol{\mu}^\dagger/\hbar\epsilon_0$. This yields

$$\chi=(\boldsymbol{\mu}^\dagger/\hbar\epsilon_0)A[\Lambda-\omega\mathbf{I}]^{-1}A^{-1}[\mathbf{N}\cdot\boldsymbol{\mu}]. \tag{29}$$

Up to this point we have used the language and nomenclature traditionally associated with the density matrix. One of the reasons for this was to keep a connection open to other areas of molecular dynamics. However, in line mixing, it is customary to use a contracted notation, labeling the relaxation rates such as $W(ba\leftarrow dc)$ not by a pair of doubly subscripted quantities, the components of the optical coherence, but rather by the associated line. Thus *dc* would be replaced by, say, *l*, signifying a line or transition. Changing nomenclature does not pose a problem, since quantities like ρ_{cd} have been treated as a single quantity. The drawback to line space nomenclature is that there is no way to label diagonal elements of the density matrix, and thus the same nomenclature cannot be kept if one wants to generalize the treatment to include population dynamics in other transport phenomena or laser theory, etc. We will confine our use of line space terminology mostly to this section.

Now $A^{-1}[\mathbf{N}\cdot\boldsymbol{\mu}]$ is a column vector. In ''line space'' notation the mth component of $A^{-1}[\mathbf{N}\cdot\boldsymbol{\mu}]$ is given by $A^{-1}_{mk}N_k\mu_k$, where repeated subscripts means a sum. Since $[\boldsymbol{\Lambda}-\omega\mathbf{I}]^{-1}$ is diagonal with the mth component given by $L_{ba}\equiv L_m$, the mth component of the column vector $[\boldsymbol{\Lambda}-\omega\mathbf{I}]^{-1}A^{-1}[\mathbf{N}\cdot\boldsymbol{\mu}]$ is given by, $A^{-1}_{mk}N_k\mu_kL_m=B_mL_m$. Furthermore, $(\mu^\dagger/\hbar\epsilon_0)A$ is a row vector with the mth component given by $C_m=(\mu^\dagger_j/\hbar\epsilon_0)A_{jm}$. Thus the susceptibility can be written as

$$\chi=\{\mu^\dagger_j/\hbar\epsilon_0)A_{jm}\}\{A^{-1}_{mk}N_k\mu_kL_m\}=C_mB_mL_m. \tag{30}$$

Since C_m and B_m are complex, the absorption coefficient $\mathrm{Im}\chi$ can be written as the sum of absorptive and dispersive parts. This is identical to a well-known form for line mixing in electric dipole absorption [24].[5]

It is also a simple matter to rederive the Rosenkranz approximation [27] for weak mixing. We return to the set of starting equations, writing them as

$$[(\omega_{ba}-\omega)-i\gamma_{ba}]\rho_{ba}+\sum_{dc} iW(ba\leftarrow dc)\rho_{dc}=n_a\mu_{ba}. \tag{31}$$

The solution to zeroth order in the mixing is found by setting all the W's equal to zero. This gives back the familiar complex Lorentzian for each component of the optical coherence. The solution, to first order in W, may then be found by inserting the zeroth-order solution for ρ_{dc} into the equation for ρ_{ba}, multiplying the result by $\mu_{ba}/\hbar\epsilon_0$ and summing over all ρ_{ba} to find the band susceptibility. This yields a sum of Lorentzians (the symmetric terms referred to above) and mixing terms (the asymmetric terms referred to above). In the case of a two-line spectrum, the *total complex mixing term* for the band absorption is given by the imaginary part of

$$\begin{aligned}\chi_m=&-i[W(ba\leftarrow dc)/\hbar\epsilon_0]\{n_c\mu_{ab}\mu_{dc}/[(\omega_{dc}-\omega)-i\gamma_{dc}][(\omega_{ba}-\omega)-i\gamma_{ba}]\}\\&-i[W(dc\leftarrow ba)/\hbar\epsilon_0]\{n_a\mu_{cd}\mu_{ba}/[(\omega_{ba}-\omega)-i\gamma_{ba}][(\omega_{dc}-\omega)-i\gamma_{dc}]\}.\end{aligned} \tag{32}$$

This is an expression for the case of weak mixing in a two-line band. Being complex, it expresses the changes not only in the absorption profile but also in the dispersion. It may easily be generalized to the complex susceptibility of a weakly interfering, multiline band.

The usual Rosenkranz form for weak mixing in the absorption profile may be recovered from Eq. (32). Near line ba the factor $(\omega_{dc}-\omega)$ may be replaced by $(\omega_{dc}-\omega_{ba})$. The damping part $i\gamma_{dc}$ may be neglected, and the real part of $1/[(\omega_{ba}-\omega)-i\gamma_{ba}]$ is just $(\omega_{ba}-\omega)/[(\omega_{ba}-\omega)^2+\gamma_{ba}^2]$. Thus near the transition $a\rightarrow b$ the mixing term for the absorption may be approximated as

$$\begin{aligned}&-[W(ba\leftarrow dc)/\hbar\epsilon_0]\{n_c\mu_{ab}\mu_{dc}/(\omega_{dc}-\omega_{ba})\}\{(\omega_{ba}-\omega)/[(\omega_{ba}-\omega)^2+\gamma_{ba}^2]\}\\&-[W(dc\leftarrow ba)/\hbar\epsilon_0]\{n_a\mu_{cd}\mu_{ba}/(\omega_{dc}-\omega_{ba})\}\{(\omega_{ba}-\omega)/[(\omega_{ba}-\omega)^2+\gamma_{ba}^2]\}.\end{aligned} \tag{33}$$

The usual mixing parameter Y is the sum of the coefficients of the common Lorentz dispersive factor $(\omega_{ba}-\omega)/[(\omega_{ba}-\omega)^2+\gamma_{ba}^2]$. Setting $\hbar\epsilon_0=1$, we find, in the case of weak mixing,

$$Y_{ba}=-\{W(ba\leftarrow dc)n_c\mu_{ab}\mu_{dc}+W(dc\leftarrow ba)n_a\mu_{cd}\mu_{ba}\}/(\omega_{dc}-\omega_{ba}). \tag{34}$$

Except for a sign, this is the familiar amplitude of the asymmetric component of the transition, $a\rightarrow b$. The sign reversal comes about because we have written the numerator for the dispersion curve as $(\omega_{ba}-\omega)$ rather than in the more common form $(\omega-\omega_{ba})$. If ω is near the transition $c\rightarrow d$, the *same expression* for the susceptibility [Eq. (32)] yields the mixing parameter Y_{dc}. Equation (34) can be used to show that the asymmetry is such that the intensity between the lines is increased, while the intensity beyond the lines decreases. Thus the two lines appear to coalesce. This is always considered as the main signature of line mixing. Equation (34) also shows that mixing is negligible if the lines are well separated. Finally, this example has illustrated that the band may be expressed as a sum of symmetric and antisymmetric components, and that the eigenvalues have the weak mixing properties anticipated above.

This completes the list of profiles, as found in the literature, that follow directly from our proposed scalar version of the generalized Waldmann-Snider equation. None of them include the effects of statistical correlation. There exist at least three partly phenomenological theories that address the question of correlation [13,28,29]. At the end of this paper we will indicate, with certain provisos, how numerical solutions may be found not only for an isolated line, but also for any speed-dependent multiline spectrum. With a simple extension of the transport relaxation equation, even the effects of statistical correlation may be included. It remains to be seen if such an extension will lead to results in accord or not with those earlier treatments of statistical correlation effects in spectral profiles [13,28,29]. In the following paragraphs we outline an approach to Dicke narrowing. It forms a logical bridge between the transport relaxation equation used above and a more general equation that allows for statistical correlation. Details of the approach to Dicke narrowing are given in the following paper.

In the hard collision model we illustrated the use of the transport relaxation equation to treat the combined effects of

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[5] In the literature, but not in Baranger's original paper, there appears to be a relative sign error in the complex Lorentzian L_m. This is of no consequence, if only the imaginary part is to be used. However, if the expressions in the literature are to be interpreted as a susceptibility, then causality is not satisfied and the computed dispersion $(n-1)$ will have the wrong sign, i.e., the dispersion will decrease with increasing frequency if one approaches an absorption line from below resonance. This is clear from Eq. (8b). The denominator in Eq. (8b) must appear as $[(\omega_{ba}-\omega)-i\gamma_{ba}]$, not as $[(\omega_{ba}-\omega)+i\gamma_{ba}]$.

relaxation and transport for an isolated line. As is well known, at high densities, molecules perform a random walk or diffusional motion through the applied optical field. Under these conditions the usual Doppler width is replaced by a diffusional width that varies as k^2D, where D is the mass diffusion constant. Since D varies inversely with the density, a line narrows with increasing density. This is known as Dicke narrowing [19] and, as mentioned earlier, arises from the factor ν in the denominator of Eq. (24). Here we sketch out a treatment of Dicke narrowing which shows how it is intimately related to the process of line mixing.

The relaxation transport equation for an isolated line may be written in the form,

$$(\omega_{ba}-\omega+kv_z)\rho_{ba}=i\gamma_{ba}\rho_{ba}+i\nu\rho_{ba}-i\Sigma W(\mathbf{v}\leftarrow\mathbf{v}')\times\rho_{ba}(\mathbf{v}')+n_a f_0(v)\mu_{ba} \qquad (35)$$

where we have written the usual integral as a sum over velocity classes $\mathbf{v}'$, and replaced the collision kernel, A by W in order to draw attention to the analogy between Dicke narrowing and line mixing. Since $\rho_{ba}(v)$ is for a speed class, there is one equation like Eq. (35) for each of them, just as there was one equation like Eq. (25) for each ρ_{ba} component of the optical coherence. Thus writing the equation for one line in terms of discrete velocity groups yields a set of equations which are formally identical to the equations for one velocity group and discrete lines. Therefore we can use the same diagonalization technique as that used to solve the line mixing problem, to treat the translational motion for an isolated line. Just as line mixing leads at high densities to a collapsed band, here exchange between the velocity groups leads to a collapse of the ordinary Doppler profile. It has long been recognized that line mixing and Dicke narrowing were related. Here we have established that they are formally identical. Using a hard collision model for W, we establish in the following paper that one can completely recover by diagonalization, the spectral profile generated using the conventional treatment given earlier in this paper.

In the analysis above, there was one all important proviso: we must be able to calculate or model the speed dependence of γ_{ba}, ν, and $W(\mathbf{v}\leftarrow\mathbf{v}')$. We have made this assumption throughout the paper, and have focused our attention on establishing a transport relaxation equation for specific cases and to solve it to determine a spectral profile. It is clear that posing a problem and solving it are two different things. If speed dependence is to be included it is safe to say that there are no known analytical solutions that are *physically* realistic. Thus numerical techniques must be employed. Here our treatment of Dicke narrowing provides a significant advantage. By binning or boxing the speed classes into cells, even the most general multiline speed-dependent case may be expressed as a set of coupled linear equations. With the apparently unending growth in computer memory and power, the numerical solution by matrix techniques becomes easier, almost on a daily basis.

Discretizing the velocity carries another benefit. It encourages us to couch our nomenclature and mode of attack on the problem of line shapes in terms of classes of molecules, and to worry about how one classifies the different boxes and consequently to classify transitions between them. A box is labeled with a set of indices (subscripts). Here we have an index *ba*, *dc*, etc. for the component of the off-diagonal element of the density matrix. Each of these boxes or cells is subdivided by a second index v, indicating the speed class. For the problems considered in this paper, these must be further subdivided according to the z component of the velocity and carry an index v_z. For convenience we lump the last two together into a velocity class. The mathematical problem is established once the rates between the different boxes are calculated or modeled. (A channel is said to be open if the rate is significantly different from zero.) We can now re-examine the classification of the off-diagonal relaxation rates [the W's and A in Eq. (10)] introduced at the beginning. In the master transport relaxation equation, relaxation rates, diagonal in v, but off-diagonal in component of the optical coherence, are type I. The reverse terms are type II. Terms off-diagonal both in the component of the optical coherence and in velocity belong to type III. Our assumption that type-III terms were zero simplified the equation but did not alter its basic characteristics. Thus even the most general problem may be solved given the various relaxation rates between the boxes. Furthermore, the relaxation rates may be classified in this manner, independent of the form of the interaction between the active molecules and the bath of perturbers. Thus the assumption about the division of the interaction into a V_0 and a V_1 term, as used by Smith *et al.* [10] and adopted here, may be discarded.

GENERAL COMMENTS

There is one very general aspect that has not been dealt with, up to this point, and that is a treatment of spectral profiles in terms of time correlation functions. The use of correlation functions depends upon the fluctuation dissipation theorem, which states that the response of a system to a fluctuation is the same as its linear response to an applied perturbation. This leads to the spectrum as being the Laplace transform of a time correlation function. Here we have actually calculated the response to an applied field. The advantage is that such a treatment can be carried beyond first order, whereas the fluctuation dissipation theorem only applies to the linear response of a system. Nevertheless, one can identify in our master equation, the main ingredients that appear in a treatment using correlation functions. In Eq. (10), the linear perturbation term in the field would be dropped. Taking a Laplace transform introduces an ω and a value at $t=0$. These appear in Eq. (12), the constant for $t=0$ appearing in our equation as the term in n_a. An extensive review of time correlation functions, relevant to this paper, was given by Berne and Harp [30]. To reiterate, the drawback to the use of the fluctuation dissipation theorem is that it is applicable only to the linear response of a system to the perturbation H_1.

As one of the objectives of this paper has been to provide a basic equation for the relaxation and transport of the density matrix that could be applied generally to line shapes, laser physics, nonlinear optics, etc., it is important to spell out what is included and what is excluded by the master equation. As the master equation neglects the degeneracy of the internal states it is not capable of describing polarization effects. For example, it is inadequate for a discussion of some of the finer details of the transport of the optical coherence [31] or of polarization spectroscopy. For this and similar problems one must return to the generalized Waldmann-Snider equation [9]. However, the isotropy of space and vector coupling techniques can always be used to express the problem in terms of reduced matrix elements and tensor components of the density matrix [30]. In this form the structure of the equation is not radically different from the structure or form of the equation used here. [Compare for example Eq. 2.3 in Ref. [32] with our Eq. (10).] As pointed out by Tip [9], the same claim can be made about the master equation for the diagonal components of the density matrix at the Waldmann-Snider level (degenerate states) as compared to that at the Wang-Chang–Uhlenbeck level (nondegenerate levels). The use of a scalar transport relaxation equation does not imply that all ''vector'' or symmetry properties of the molecules are lost. These properties are often simply reflected in the *values* of the components of the relaxation matrix (see, for example, Ref. [33]). On the other hand, there is a large body of physics connected to transport which may not be treated by our equation. Here we have assumed a uniform dilute gas. Obviously, additional terms must be added to account for gradients in temperature or concentration [1,34]. Such terms are routinely included even in the lowest member of the hierarchy of transport relaxation equations, viz. the Boltzmann equation [15].

While the basic idea for the approach used in this paper was triggered by Ref. [10], in fact many of the ideas can be traced to a very large number of papers. To give accurate and due credit to all of these would require an extensive review. Such was not the object of this paper. The papers cited were chosen not only for their contribution but also with the idea that they provide the interested reader with a suitable introduction to the literature. However, it would be an oversight not to mention several other papers also dealing with spectral line shapes [35–38] which use approximations to solve a transport relaxation equation. The method suggested above for a solution of the general problem is exact in the same sense that any numerical treatment is exact.

SUMMARY AND CONCLUSIONS

The main purpose of this paper has been to show how a transport relaxation equation for a semiclassical density-matrix distribution can be used to derive spectral profiles in dilute molecular gases. The basic dynamic equation for the rate of the distribution function adds to the free-streaming terms $[(H_0+H_1),\rho]$ and $-\overline{v}\cdot\nabla\rho$, two classes of collision relaxation processes, one for the internal states and one for the translational states. Each class has two contributions, a decay term and a return from other classes. The internal and translational motions may be coupled by the mutual speed dependence of the two types of relaxation rates. Statistical correlation between the two motions has been neglected but could be incorporated. It was in the treatment of Smith *et al.* [10] that the statistical term and the other relaxation processes were clearly identified.

There are a number of advantages to the formalism presented here. First it separates the microscopic aspects of the problem, the calculation of various relaxation coefficients from the problem of solving a transport relaxation equation for the response of the system to some applied field. Being couched in terms of a Boltzmann-like equation for the density matrix, it clearly identifies the links between laser physics, nonlinear optics, and the usual transport problems of statistical mechanics. Purely from the point of view of spectral line shapes it allows one to treat speed-dependent effects not only for isolated lines but also in the case of line mixing. Use of the transport relaxation equation for the off-diagonal elements of the density matrix has been illustrated by rederiving many well-known results simply and quickly. It also provided additional insight into the process of line mixing. A technique has been suggested for treating the Dicke narrowing of an isolated line. From this it followed that the most general multiline spectrum, with speed-dependent relaxation and transport, could be solved, given a model for the speed dependence of the various relaxation rates and a large computer.

ACKNOWLEDGMENTS

The author wishes to acknowledge a number of very fruitful discussions with F. McCourt, S. Hess, and W.-K. Liu. Financial support of the Natural Sciences and Engineering Research Council of Canada is also gratefully acknowledged.

APPENDIX: LORENTZ MODEL

If the perturbers are massive we can consider them to be at rest and the active molecule to move among them with a constant speed. The Lorentz model is thus an inhomogeneous model for the translational motion. The distribution function for a (sub)ensemble of active molecules with a speed v, then depends upon r, t, and θ, and ϕ. The latter two variables describe the direction of motion. The master equation for an isolated line is Eq. (2) of the text. For rigid spheres perturbed by fixed rigid spheres the transport relaxation terms involving ν and $A(\mathbf{v}\leftarrow\rightarrow\mathbf{v}')$ are to be replaced by $\pi v n a^2(1-P)\varrho_{ba}$ where n is the number density of perturbers, a is the hard sphere collision radius, and P is merely an integral operator that integrates over the direction of motion [22,39]. Explicitly, operating by P, as used here, is defined by the equation $P\rho_{ba}=\int\rho_{ba}(v,\theta,\phi)\sin\phi\,d\theta\,d\phi$. It differs by a factor of 4π from the usual definition found in the literature. Consequently, the transport relaxation equation for an isolated line takes the form,

$$[\omega_{ba}-\omega+kv_z]\varrho_{ba}=i\gamma_{ba}\varrho_{ba}+i\nu_v(1-P)\varrho_{ba}+n_a f_0(v)\mu_{ba}, \tag{A1}$$

where the relaxation rate (kinetic collision frequency for the subensemble of molecules with a speed v) ν_v is given by $\nu_v=\pi v n a^2$. Here n is the number density of perturbers and a the collision radius. Equation (A1) may be rearranged to read

$$\varrho_{ba}=n_a f_0(v)\mu_{ba}\mathcal{L}-i\nu_v(P\varrho_{ba})\mathcal{L}, \tag{A2}$$

where $\mathcal{L}$ is a complex Lorentzian given by $\mathcal{L}=[\omega_{ba}-\omega+kv_z-i(\gamma_{ba}+\nu_v)]^{-1}$. As part of calculating the total susceptibility, we integrate over the direction of motion. Later we will integrate over the speed. The integration over angle is done by operating on Eq. (A2) with P. Remembering that a single averaging removes the angular dependence ($PP=P$) and that ν_v is independent of θ and ϕ we find, after some rearrangement,

$$P{\not\rho}_{ba}=n_a f_0(v)\mu_{ba}P\mathcal{L}/[1+i\nu_v P\mathcal{L}]. \tag{A3}$$

The complex susceptibility is then given by

$$\chi=N\int v^2\exp[-(v/v_0)^2]dv\{P\mathcal{L}/[1+i\nu_v P\mathcal{L}]\}. \tag{A4}$$

This agrees with Lindenfeld's Eq. 4.10 if allowance is made for the fact that he has taken γ_{ba} equal to zero [22]. Note that the integral over the speed is over the entire function in curly brackets, and does not appear separately in the numerator and the denominator as in the HC model [see Eq. (24) in the main text]. The rigid sphere, Lorentz gas is thus the ultimate speed dependent inhomogeneous line shape. If k is taken along the polar axis then v_z equals $v\cos\theta$ and the calculation of the spectral profile is reduced essentially to the evaluation of $P\mathcal{L}$. After integration over ϕ the remaining integral,[6] B becomes $B=2\pi\int\sin\theta d\theta/[\omega_{ba}-\omega+kv\cos\theta-i(\gamma_{ba}+\nu_v)]$. Dropping the factor 2π and taking $\cos\theta=z$ as the variable of integration allows us to write B in the form $B(k,\omega,v)=\int dz/[i(\gamma_{ba}+\nu_v)+(\Delta\omega-kvz)]$ where the limits are -1 to 1. This may easily be evaluated and may be expressed as the ln of a complex function [Eq. (22)] or the arctan of a complex number [21,39] or it may be decomposed into a ln and arctan of real functions using any standard table of integrals.

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[6] B, as written here, differs from that of Ref. [22] by i and an unimportant numerical factor.

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