Dicke narrowing as an example of line mixing

S. Dolbeau, R. Berman, J. R. Drummond, and A. D. May*

Department of Physics, University of Toronto, Toronto, Canada M5S 1A7

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In the preceeding paper it was shown that the general problem of spectral line shapes in multiline, IR spectra may be determined by solving a transport relaxation equation for the off-diagonal elements of the density matrix. This is a semiclassical equation at the Wang-Chang–Uhlenbeck level, i.e., it treats the quantized internal states as nondegenerate. Here we apply the master equation to the case of Dicke narrowing, and by discretizing the velocity distribution show that Dicke narrowing of a single line may be treated in exactly the same manner as line mixing. Both effects lead to a narrowing of a spectral distribution. We indicate how the numerical technique can be extended and used to calculate profiles in the general case of spectra with speed-dependent broadening, shifting, and line mixing. [S1050-2947(99)11305-2]

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INTRODUCTION

In the last few years, high-resolution infrared and Raman studies in low-density gases [1–4] have revealed a remarkable fact. In spite of some 50 years and many papers on the subject (see, e.g., Refs. [5,6]), there is still no satisfactory theory of spectral profiles that includes one important physical property, namely, the speed dependence of the collisional relaxation processes [1]. This lack of a calculable profile which includes the speed dependence is a serious impediment to atmospheric physics where there is a need to model IR-absorption profiles accurately for an entire band over a range of temperature and pressure, in mixtures with foreign gases. In the preceding paper [7], hereafter referred to as I, one of us proposed a master equation suitable for a determination of spectral line shapes under just those conditions. Here we apply the equation to the problem of an isolated line to demonstrate the equivalence of Dicke narrowing [8] to line mixing [9]. In the process, we show, with a certain proviso, how the problem of speed-dependent effects may be handled numerically, even in the case of a multiline spectra with both Dicke narrowing and line mixing. Existing methods, theories, or model profiles are far from being able to handle such a general case.

For completeness we begin with a brief summary of the transport relaxation equation for the off-diagonal elements of the density matrix and its relation to IR absorption. This is followed by an even briefer discussion of line mixing. Finally we come to the main subject of the paper, the treatment of an isolated line undergoing Dicke narrowing. First we show the equivalence between Dicke narrowing and line mixing. Then, to illustrate our approach, we treat two cases: (i) Dicke narrowing with speed-independent collision broadening, and (ii) Dicke narrowing in the presence of speed-dependent broadening and shifting. Proof of the equivalence is accomplished by discretizing the velocity distribution and applying the same matrix techniques [10,11] as used in the theory of line mixing. We conclude with some remarks about the application of the matrix inversion method to the broader problem of speed-dependent effects in multiline spectra.

A TRANSPORT RELAXATION EQUATION

In a semiclassical treatment of spectral profiles, what is required is an equation in the off-diagonal elements of the density matrix ρ_{ba}, that treats the internal states, b,a, etc. as discrete and is classical in position $\mathbf{r}$ and velocity $\mathbf{v}$. For electric dipole interaction and a uniform field $\mathcal{E}$, oscillating at a frequency ω, ρ_{ba} is the solution of the equation (see I)

$$[(\partial/\partial t)+i(\omega_b-\omega_a)+\mathbf{v}\cdot\boldsymbol{\nabla}]\rho_{ba}=-\gamma_{ba}\rho_{ba}+\sum_{dc} W(ba\leftarrow dc)\rho_{dc}-\nu\rho_{ba}$$

$$+\int A(\mathbf{v}\leftarrow\mathbf{v}')\rho'_{ba}d^3v'+i(\mu_{ba}/\hbar)\{E\exp[-i(\omega t-kz)]+\text{c.c.}\}n_af_0(v), \quad (1)$$

where $\rho'=\rho(r,v',t)$, E is the amplitude of the field and $f_0(v)$ is the Maxwellian or equilibrium velocity distribution

function, normalized to unity. Here we have assumed that only the lower level (a) is populated, with n_a molecules per unit volume. The off-diagonal elements of the density matrix are often referred to as the optical coherence. The ba component of the optical coherence has dimensions of per unit volume, per unit of velocity space. Here γ_{ba} is the collisional

*Author to whom correspondence should be addressed. Electronic address: dmay@physics.utoronto.ca

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relaxation or rate of removal of the ρ_{ba} component of the optical coherence with velocity $\mathbf{v}$ to all other components of the same $\mathbf{v}$. In general, γ_{ba} is complex and speed dependent, and is the source of broadening and shifting of an isolated line. $W(ba\leftarrow dc)$ is the return rate to the component ρ_{ba} from the component ρ_{dc} and is the source of line mixing. The sum over dc does not extend to ba. The relaxation rates ν, and the so-called collision kernel $A(\mathbf{v}\leftarrow\mathbf{v}')$, are the analogous terms for changes of speed classes for the single component ρ_{ba} of the optical coherence. It is common practice to assume that the transport of the optical coherence is the same as the transport of the molecule and to treat the collision frequency ν and the collision kernel $A(\mathbf{v}\leftarrow\mathbf{v}')$ exactly as in the Boltzmann equation [12]. The rest of the symbols have

their usual meaning. In Eq. (1), the relaxation rates between both velocity groups and components of the coherence, which we could designate by $M(ba,\mathbf{v}\leftarrow dc,\mathbf{v}')$, are assumed to be zero. The equilibrium population distribution function $n_a f_0(v)$ appears in Eq. (1) because the density matrix has been written only to first order in the optical field $\mathcal{E}$, as is appropriate for most IR spectroscopy.

Within the rotating wave approximation (RWA) the c.c. term in the field will not survive in the solution to Eq. (1) if level b is above level a. Furthermore, in the steady state all components of the optical coherence will vary at the frequency of the field. It is thus convenient to write ρ_{ba} as $\rho_{ba}E\exp[-i(\omega t-kz)]$ and to set $\hbar$ equal to 1. In this case Eq. (1) reduces to

$$[\omega_{ba}-\omega+kv_z]\rho_{ba}=i\gamma_{ba}\rho_{ba}-i\sum_{dc}W(ba\leftarrow dc)\rho_{dc}+i\nu\rho_{ba}-i\int A(\mathbf{v}\leftarrow\mathbf{v}')\rho_{ba}(v')d\mathbf{v}'+n_af_0(v)\mu_{ba}, \quad (2)$$

where ω_{ba} equals $(\omega_b-\omega_a)$. (We label the states so that quantities like ω_{ba} are always a positive number.) There is a separate equation for each component of the optical coherence, ρ_{ba}, etc. Thus Eq. (2) represents a set of coupled linear *integral* equations.[1]

There is a direct connection between the components of the optical coherence and the spectral profile. The macroscopic polarization (dipole moment per unit volume) P is given by, $P=\mathrm{Tr}[\rho\mu]$. If we agree to write P in complex form then within the RWA, it is easy to show that P is given by $P=\Sigma_{ba}\rho_{ba}\mu_{ab}=\Sigma_{ba}\rho_{ba}\mu_{ab}E\exp-i(\omega t-kz)$. Thus, within some constant that does not concern us here, the complex susceptibility for the velocity class $\mathbf{v}$ is given by $\chi_v=\Sigma_{ba}\rho_{ba}\mu_{ab}d\mathbf{v}$. Of course, for an isotropic system such as a dilute gas, χ_v will only depend upon the speed of the active molecule. The total susceptibility χ is found by summing (integrating) over the velocity classes. 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, within a constant, just the imaginary part χ_i. If the speed

dependence of the relaxation rates are given, then the problem of determining the spectral profile is well posed. However, to pose a problem well is only an essential first step. It remains one of idle curiosity if no solutions can be found. As stated above, there are no known, *physically realistic* solutions for spectral profiles, either analytical or numerical, which include the effects of speed dependence. For emphasis, we repeat that one of the objectives of this paper is to show that numerical solutions may be found using a rather simple matrix procedure. The other objective is to show the intimate connection between Dicke narrowing and line mixing.

LINE MIXING

It is instructive at this stage to see how the problem of line mixing is handled in the present formalism. Line mixing involves a band of lines and, as given in the literature, neglects *all* aspects of the translational motion, including the speed dependence of the relaxation rates. In this case, after integrating over the velocity, Eq. (2) reduces to

$$[\omega_{ba}-\omega]\rho_{ba}=i\gamma_{ba}\rho_{ba}-i\sum_{dc}W(ba\leftarrow dc)\rho_{dc}+n_a\mu_{ba}, \quad (3)$$

where by ρ_{dc} now means the total component of the optical coherence, not the component distributed between $\mathbf{v}$ and $\mathbf{v}+d\mathbf{v}$. Equation (3) represents a set of coupled linear, but no longer integral, equations and they may be solved using standard matrix techniques. In matrix notation, the γ's and W's are combined to become a relaxation matrix (still written as W) and the components ρ_{ba}, ρ_{dc}, etc. are treated as a column vector ρ. The band profile is proportional to the imaginary part of $\Sigma_{ba}\rho_{ba}\mu_{ab}$, and can also be expressed in matrix form. As pointed out by Baranger [9] and refined by Gordon and McGinnis [10], a solution for the band profile is easily obtained if one employs a matrix diagonalization and inversion technique (see below). This method of solving for a band

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[1]Note that ba is to be read as a single index. We have deliberately written the relaxation rate W as $W(ba\leftarrow dc)$ and not $W(dc\rightarrow ba)$. Later we will write the coupled set of linear equations in matrix form. There the components of the optical coherence, ρ_{ba}, ρ_{dc}, etc., will form a column vector and $W(ba\leftarrow dc)$ becomes a relaxation matrix $W_{ba,dc}$. Thus the order of the indices carries information about the direction of the relaxation. It is a common practice in line mixing to contract the doubled indices, like ba to a single index, 1, and to misleadingly describe ρ_1 as a ''line.'' In fact, line mixing is much more the effect, on one resonance, by the off-resonance of other lines and arises because collisions cause transitions between the components of the optical coherence, much as they cause the transfer between the diagonal parts of the density matrix, i.e., between the populations of the states. Nevertheless, we will adhere to common practice and will continue to describe the effect as line mixing.

profile is well known to the line mixing community. To complete the list of well-known results that are relevant to this paper, we remind the reader that all relaxation rates are proportional to the density of perturbers, and that one of the signatures of line mixing is the blending together of individual lines and the collapse of the entire band to a single narrow profile at high densities. Now let us see how this formalism for line mixing may be applied to Dicke narrowing.

DICKE NARROWING

The spectral profile of an isolated line, at densities so low that all collisional relaxation may be neglected, has the well-known Doppler profile.[2] This arises because each velocity class maintains its integrity (no transitions to other velocity classes) and has its own Doppler shifted frequency. Of course, the Doppler shift arises from the free streaming kv_z term in Eq. (2). As the density increases, the translational

relaxation rates ν and $A(\mathbf{v}\leftarrow\mathbf{v}')$ become important. Physically, at high densities, the molecules perform a random walk or diffusive motion. Thus one expects, perhaps naively, a linewidth (decay rate) which varies as k^2D, where D is the mass diffusion constant.[3] Since D varies inversely with density ρ, the contribution of the translational motion to the width decreases with increasing density. As first noted by Dicke [8], if the broadening is sufficiently small an isolated line may actually narrow. This effect is well documented in the literature (see, for example, Ref. [13]). Two models of the translational motion are commonly used to describe the narrowing, all the way from the Doppler limit to the diffusion narrowed regime. These are the soft collision [14] and hard collision (HC) [15] models. We now turn to the question of how Dicke narrowing can be treated using the transport relaxation equation.

For an isolated line the line mixing terms [W's in Eq. (2)] may be neglected. Thus Eq. (2) reduces to,

$$[\omega_{ba}-\omega+kv_z]\rho_{ba}=i\gamma_{ba}\rho_{ba}+i\nu\rho_{ba}-i\int A(\mathbf{v}\leftarrow\mathbf{v}')\rho_{ba}(v')d\mathbf{v}'+n_af_0(v)\mu_{ba}, \tag{4}$$

where γ_{ba} and ν may both be functions of the speed of the active molecule. Since ρ_{ba} represents a distribution over velocity, then $\rho_{ba}d\mathbf{v}$ is the amount of optical coherence per unit volume that lies between $\mathbf{v}$ and $\mathbf{v}+d\mathbf{v}$. If we multiply Eq. (4) by $d\mathbf{v}$, the three dimensional element of velocity space, it may then be written as

$$(\omega_{ba}-\omega+kv_z)\rho_{ba}=i\gamma_{ba}\rho_{ba}+i\nu\rho_{ba}-i\sum W(\mathbf{v}\leftarrow\mathbf{v}')\rho_{ba}(v')+n_af_0(v)\mu_{ba}, \tag{5}$$

where now $\rho_{ba}(v)$ is to be interpreted as the number of molecules per unit volume with an optical coherence ρ_{ba} that lie in a velocity cell centered around $\mathbf{v}$. More important is the fact that we have written the usual integral over $\mathbf{v}'$ as a sum over velocity classes $\mathbf{v}'$ and replaced $A(\mathbf{v}\leftarrow\mathbf{v}')d\mathbf{v}$ by $W(\mathbf{v}\leftarrow\mathbf{v}')$, the rate at which the coherence is transferred from a "$\mathbf{v}'$ cell" to a "$\mathbf{v}$ cell." Physically, the collision kernel $A(\mathbf{v}\leftarrow\mathbf{v}')$ describes both the rate at which molecules with a velocity $\mathbf{v}'$ are transferred and how they are distributed over v. Thus the larger the box, the more that are transferred per second. Thus $W(\mathbf{v}\leftarrow\mathbf{v}')$ really is a rate of transfer between discrete cells just as $W(ba\leftarrow dc)$ is the rate of transfer between discrete components of the optical coherence in the case of line mixing. That the analogy is complete may be seen by comparing Eq. (3) (which is for a single component of the optical coherence) to Eq. (5) (which is for a single speed class). Note in particular that the discrete resonant frequencies ω_{ba} in Eq. (3) for line mixing are replaced in Eq. (5) by the Doppler shifts kv_z. In matrix form, $-\omega$ in Eq. (3) becomes a diagonal matrix $-\omega I$ (see I). In the matrix form of Eq. (5) the equivalent diagonal matrix is $(\omega_{ba}-\omega)I$, since ω_{ba} is a constant for the isolated line. *Thus we have estab-*

lished that line mixing and Dicke narrowing are not merely related but are in fact mathematically equivalent. Furthermore they are almost physically identical since most of the quantities appearing in the equations have the same or similar physical meaning.

Writing the equation for one line in terms of discrete velocity groups allows us to use the same numerical diagonalization technique as that commonly used to solve the line mixing problem. Just as line mixing leads at high densities to a collapsed band, here we expect the exchange between the velocity groups to lead to a collapse of the Doppler profile, a profile which can always be considered as a band with a continuous distribution of "discrete" lines.

If we wish to illustrate this treatment of Dicke narrowing, we require a concrete expression for the collision kernel, $A(\mathbf{v}\leftarrow\mathbf{v}')$. We chose the hard collision model since it is the only known case where an analytical expression for a spectral profile has been found when the relaxation rate of the optical coherence γ_{ba} is either speed dependent or speed

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[2] Essentially, throughout this paper we will ignore the contribution of the natural line width to the spectral profiles.

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[3] One expects D to be the mass diffusion constant if $A(\mathbf{v}\leftarrow\mathbf{v}')_{ba}$ for the off-diagonal element is real, and the same as $A(\mathbf{v}\leftarrow\mathbf{v}')_{aa}$ for the population (diagonal element of the density matrix). In principle $A(\mathbf{v}\leftarrow\mathbf{v}')_{ba}$ could be complex, indicating a correlation between the evolution of the phase and the transport of ρ_{ba} [16]. Here we take $A(\mathbf{v}\leftarrow\mathbf{v}')_{ba}$ as real.

independent [17]. The hard collision model takes a collision kernel that distributes all $\mathbf{v}'$ classes over the same Maxwellian in v. This does not correspond to any known physical situation. Nevertheless, the hard collision model has the correct low- and high-density limits, satisfies detailed balance, is well behaved mathematically, and (what is important) leads to a benchmark profile, calculable by standard methods, against which we can compare solutions obtained by velocity discretization and matrix inversion. We consider two cases: (i) pure Dicke narrowing (negligible broadening) from the Doppler to the Dicke limit, and (ii) Dicke narrowing, near the minimum in the width, with a speed dependent broadening and shifting.

Pure Dicke narrowing (almost)

We wish to illustrate Dicke narrowing in the absence of collision broadening, from the low-density Doppler profile to the Dicke-narrowed profile at high densities. However, for the Doppler limit, it is not possible simply to set γ_{ba} and ν to zero in Eq. (5) (see I). In the absence of spontaneous radiation, setting the relaxation rate for the optical coherence to zero results in zero absorption. A correct treatment of Doppler broadening results from setting the kinetic collision frequency ν equal to zero, calculating the profile, and taking the limit as γ_{ba} approaches zero. For convenience, we shall take γ_{ba} as finite but small and speed independent. We could regard a small constant γ_{ba} as the natural width of the line.

For the hard collision model, ν is speed independent and the collision kernel is given by $A(\mathbf{v}\leftarrow\mathbf{v}')=\nu f_0(v)$, where

$f_0(v)$ is the normalized Maxwellian $(1/\sqrt{\pi}v_0)^3\exp-(v/v_0)^2$, and v_0 is the mean speed $(2kT/m)^{1/2}$. With $A(\mathbf{v}\leftarrow\mathbf{v}')$ given by the HC model and γ_{ba} independent of $\mathbf{v}$, Eq. (5) can be integrated over the x and y components of the velocity. This leads to an equation for a one dimensional distribution function, $\rho(v_z)=\int\rho dv_x dv_y$. Here we have dropped the superfluous index ba on ρ_{ba} since we are dealing with an isolated line. The normalized Maxwellian $f_0(v)$ appearing in $A(\mathbf{v}\leftarrow\mathbf{v}')$, and the term involving n_a also become one dimensional. When discretized, the elements of the relaxation matrix, off-diagonal in v_z, can be written as

$$W_{ij}=W(v_{zi}\leftarrow v_{zj})=(\nu K/\sqrt{\pi}v_0)\exp[-(v_{zi}/v_0)^2], \quad (6)$$

where K is a normalizing constant, determined by the size of the velocity cell. The subscripts i and j identify post-collisional and precollisional values. As stated above, and shown by Eq. (6), the kernel for the hard collision model is independent of the velocity of the active molecule ($\mathbf{v}'$) before a collision, i.e., independent of the subscript j. Thus the off-diagonal elements in the same row of the relaxation matrix are equal. The diagonal elements are written[4] as,

$$W_{ii}=-\gamma_{ba}-\nu\{1-(K/\sqrt{\pi}v_0)\exp[-(v_{zi}/v_0)^2]\}, \quad (7)$$

When Eqs. (6) and (7) are introduced into Eq. (5), the transport relaxation problem, in the case of a speed independent γ_{ba}, reduces to a set of coupled linear equations of the form,

$$(\omega_{ba}-\omega+kv_{zi})\rho_i=i\gamma_{ba}\rho_i+i\nu\{1-(K/\sqrt{\pi}v_0)\exp[-(v_{zi}/v_0)^2]\}\rho_i$$

$$-i\sum(\nu K/\sqrt{\pi}v_0)\exp[-(v_{zi}/v_0)^2]\rho_j(v_{zj})+n_a f_0(v_{zi})\mu_{ba}, \qquad (8)$$

where the sum Σ is, over j, not equal to i. If we define a column vector ρ, where the elements are the values of ρ for the different "v_z cells," then the set of equations can be can be written as

$$[\omega_0+iW-\omega I]\rho=N\mu, \qquad (9)$$

where ω_0 is a diagonal matrix of Doppler transition frequencies, $\omega_{ba}+kv_{zi}$, I is the unit matrix, N is a diagonal matrix of populations in the "v_z cells," and μ is a column vector of dipoles, all equal because the transition dipole is independent of the molecular velocity. Equation (9), for Dicke narrowing, is identical to Eq. (15) of I for line mixing, and may be solved in the same manner. For completeness, we repeat the treatment given there.

Briefly, to solve Eq. (9), we look for a transformation A such that $G=[\omega_0+iW]$ becomes diagonal, i.e., we solve the equation $\Lambda=A^{-1}GA$. This transformation also diagonalizes $[\omega_0+iW-\omega I]$. Then Eq. (9) can be written

$$A^{-1}[\omega_0+iW-\omega I]AA^{-1}\rho=[\Lambda-\omega I]A^{-1}=A^{-1}[N\mu], \qquad (10)$$

which has as a solution

$$\rho=A[\Lambda-\omega I]^{-1}A^{-1}[N\mu]. \qquad (11)$$

As the susceptibility is proportional to $\mu^{\dagger}\rho$, the spectral profile can be determined by multiplying Eq. (11) by the row vector $\mu^{\dagger}$ and taking the imaginary part. Thus, as stated, the spectral profile may be determined directly from the set of coupled linear equations, using matrix techniques. The problem is easily handled on a desk top computer. In the present case, the diagonal elements of the relaxation matrix W contain a constant part, $(\gamma_{ba}+\nu)I$ which could be separated out

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[4]The presence of the term in K is understandable. Even in the integral form the collision kernel contains a diagonal component, viz. $A(\mathbf{v}\leftarrow\mathbf{v}'=v)d\mathbf{v}'$. It is of course infinitesimally small. For a finite number of cells, we must take it into consideration and add it to the usual diagonal term. K is determined by the sum rule $\Sigma_i W_{ij}=-\gamma_{ba}$.
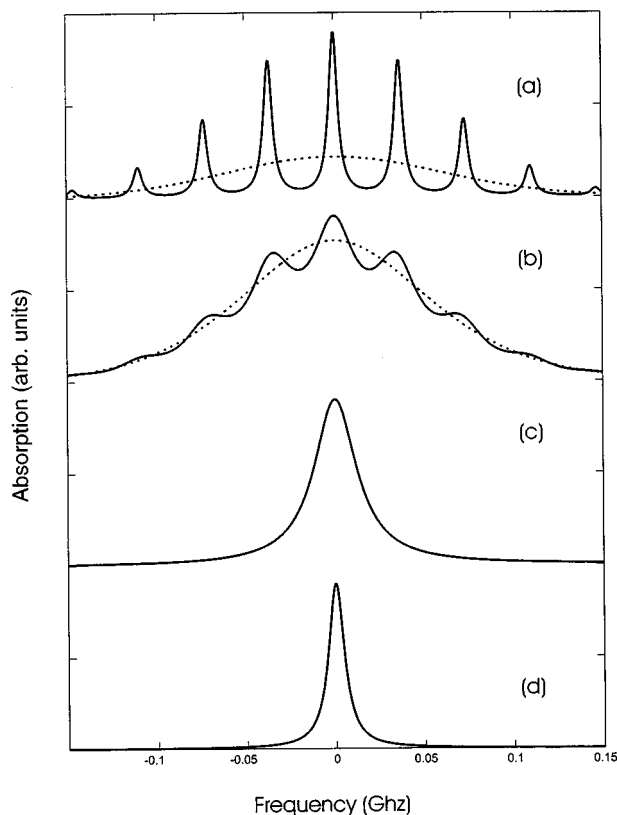
FIG. 1. Solid curve: Dicke narrowing of an isolated line, calculated by the matrix technique using 25 classes of v_z and a constant broadening of 3 MHz. The collision frequency ν was (a) 0, (b) 15 MHz, (c) 300 MHz, and (d) 1.5 GHz. Dashed curve: as above, except calculated numerically from the analytical expression [17].

and treated in the same manner as ωI. We do not labor the reader with this and other minor points, but rather proceed directly to the results.

Figure 1 shows the computed line profile (solid lines) for γ_{ba} equal to 3 MHz and ν equal to 0, 15, 300, and 1500 MHz. The mean speed v_0 and the Doppler parameter kv_0 were chosen to represent a rovibrational line of CO at room temperature. We have deliberately chosen the spacing between the v_z cells to be large, so that discrete but fictitious ''lines'' appear when the kinetic collision frequency is low. A total of 25 speed groups were used, although Fig. 1 is plotted over a frequency range that displays the presence of only nine of them. At ν equal to zero, the widths of the spectral components [half width at half maximum (HWHM)] is just the constant relaxation rate, $\gamma_{ba} = 3$ MHz. We see, as the collision frequency is increased, that the fictitious lines in our band, broaden, overlap, and collapse to a narrow single line; these details of Dicke narrowing, which are identical to those observed in line mixing, would not have been apparent if we had binned the v_z speed classes on a scale fine compared to the collisional width γ_{ba}. This example is very reminiscent of Dicke's original paper. There he considered a one-dimensional problem, and described the system in terms of just two v_z classes.

Also shown in Fig. 1 are the curves for the HC model (dotted line), calculated numerically, but using the standard analytic solution [17]. What is surprising is how quickly the coarse-grained matrix solutions approach the full solution as
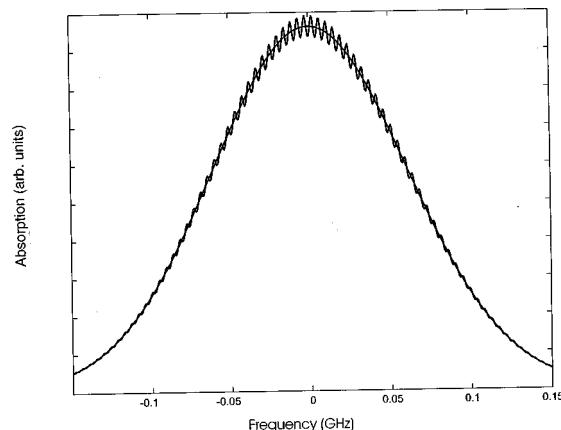

FIG. 2. Oscillating curve: Dicke narrowing of an isolated line calculated by the matrix technique using 200 classes of v_z with a broadening of 3 MHz and kinetic collision frequency of zero. Smooth curve: calculated numerically from the analytical expression [17].

the density (collision frequency) is increased. This has a practical consequence. The more severe the Dicke narrowing, the coarser the speed graining can be. This reduces the size of the matrix that must be diagonalized. The down side of this is the fact that the lower the density, i.e., the closer one is to the Doppler limit, the finer the speed graining must be to capture the spectral line shape accurately.

The practical choice of bin size is also determined by the value of γ_{ba}. Figure 2 shows the matrix solution for $\gamma_{ba} = 3$ MHz (the same as for Fig. 1) and $\nu = 0$. Even with 200 bins, spanning the same range of v_z as above, the result (oscillating line) is not an accurate representation of the standard solution (smooth curve). The latter is actually a Voigt profile, and is nearly a pure Gaussian under the chosen conditions. By comparing the change in the calculated profile, for ν changing from 0 [Fig. 1(a)] to 15 MHz [Fig. 1(b)], it is clear that 200 channels and $\nu = 15$ MHz would simulate reasonably well the full solution in Fig. 2.

As a final demonstration of the matrix solution in this nearly pure Dicke narrowing case, in Fig. 3 we show a plot of the width (HWHM) as a function of the kinetic rate ν, for
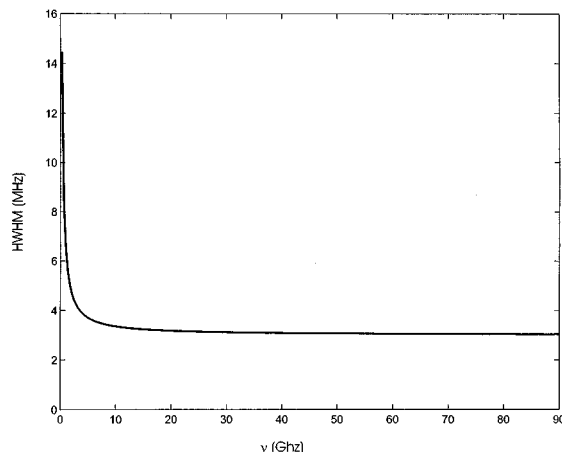

FIG. 3. HWHM of a line calculated using the matrix technique with a constant broadening of 3 MHz and varying kinetic collision frequency.

the 25 bin case and ν varying from 0.3 to 90 GHz. The HWHM were measured directly from the profiles. We see the inverse dependence on the density ($\nu \sim$ density), characteristic of Dicke narrowing, and the asymptotic approach to the fixed relaxation rate γ_{ba}.

In the examples above, the relaxation rate of the optical coherence was kept constant and small. This was convenient for illustrating the well-known properties of Dicke narrowing, but not realistic. Physically, both γ and ν scale with density and maintain a fixed ratio, one with respect to the other. The same procedure for establishing the matrix equation as outlined above may be used to generate spectra, provided both γ and ν remain speed independent. We have computed spectral profiles for several ratios of γ/ν over a range of the kinetic collision frequency or what is equivalent a range of density. In all cases there was agreement between the matrix and standard profile, provided the binning of the v_z classes was fine enough. In the case of γ small compared to ν a plot of the HWHM of the profiles as a function of kinetic collision frequency (density) showed the characteristic Dicke minimum [13]. In summary, by considering a concrete example, we have shown that the matrix inversion technique, as used in the theory of line mixing, is a viable numerical method of solving the transport relaxation equation for an isolated line with speed-independent broadening.

Dicke narrowing with speed-dependent broadening and shifting

In the case of speed-independent broadening it was possible to integrate over the x and y components of the velocity before discretizing the distribution. When γ is speed dependent, then a slightly different treatment is required. In an isotropic system, such as a gas in equilibrium, the various relaxation rates can depend at most upon the magnitude of the velocity. Due to the appearance of the kv_z term in the master equation, it therefore becomes convenient to chose spherical coordinates (v, θ, ϕ) for the velocity with z as the polar axis. Then we can integrate over ϕ before dividing the velocity distribution over v and θ. In practice, we find that discretizing in θ rather than in v_z (another option) reduces the irregularities in the computed profile arising from the coarseness of the binning. Such irregularities are plainly visible in Figs. 1(a) and 1(b). Previously, the distribution function was only divided over v_z. Now it is divided over θ and v. Consequently, ρ is a longer column vector (more elements). The number of elements in the relaxation matrix increases quadratically with the length of ρ. Nevertheless, the resulting equation takes on the same form as Eq. (9), and may be solved in the identical manner.

For illustrative purposes, we have again used the HC model to describe the translational dynamics of the distribution function. For speed-dependent broadening and shifting, we now need an explicit model for γ_{ba}. For convenience, we have used the simple, inverse power, straight line collision model described in Ref. [18]. In this case, the speed dependence of the broadening and shifting rates are given by

$$\gamma_{ba} = \gamma(v) + i\delta(v)$$

$$= (1+\lambda)\beta M[\beta, \tfrac{3}{2}, -\lambda(v/v_0)^2]\langle \gamma(v) + i\delta(v)\rangle,$$
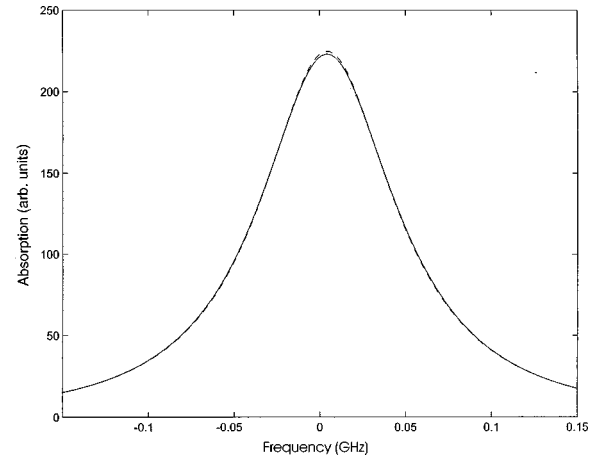

FIG. 4. A comparison of spectral profiles for a Dicke-narrowed line including speed-dependent broadening and shifting. Solid curve, calculated by discretizing the velocity. Dashed line; calculated by direct numerical calculation from the analytical form [17].

where λ is the perturber to absorber mass ratio, $\beta = -(q-3)/(2q-2)$, and M is a confluent hypergeometric function. The brackets indicate an average over the Maxwellian speed distribution, and r^{-q} describes the radial dependence of the intermolecular interaction responsible for the broadening and shifting. For such a simple collision model, no physical meaning should be attached to the value of q. It is a parameter that allows one to alter the speed dependence of the broadening and shifting. Duggan et al. [1] used a speed-dependent broadening determined by the same collision model, and an empirical spectral profile to fit their CO data broadened by Ar and He. For q, they found that a value near 6 fitted their data. For no other reason we have chosen this value of q to illustrate the use of the matrix technique for the combined effects of Dicke narrowing and speed-dependent broadening and shifting. For $\lambda = 1$ and $q = 6$, the calculated width $\gamma(v)$ varies approximately quadratically with v over the range of v from 0 to $2v_0$, being some 50% larger at $2v_0$ as compared to the value at v equal to zero. We have chosen the kinetic collision frequency, ν such that $\langle \gamma(v)\rangle/\nu$ is equal to $\frac{1}{5}$. This produces a well-defined Dicke minimum. A spectral profile was computed for ν near the Dicke minimum where the two contributions to the width of an isolated line are about equal. Figure 4 shows a plot of the profile computed by the matrix technique. Only five bins in v and θ, for a total of 25, were used. That a smooth curve results illustrates again that only coarse graining of the velocity is required in the line narrowing region. In line mixing it is recognized that the details of the relaxation matrix are not important in determining the band profile in the case of *severe mixing*. The present work suggests that details of the free molecule line position, etc., are also not critical in this region. Also shown in Fig. 4 is the profile (dashed curve), computed numerically from the known analytical solution of the same model [17]. The high level of agreement between the two spectra, in spite of the coarse graining of the velocity, illustrates the two main points of this paper; (i) that the matrix technique may be used to solve the transport relaxation equation for isolated lines; and (ii) that there is an intimate relationship between line mixing and Dicke narrowing. Our treatment of narrowing and broadening is to be

contrasted with treatments based on the generalized Waldmann Snider equation [19,20].

SUMMARY AND CONCLUDING REMARKS

By discretizing the translational motion we have been able to establish the close relationship that exists between Dicke narrowing and line mixing. Furthermore, borrowing matrix techniques from the mixing has allowed us to treat numerically the general problem of combined Dicke narrowing and speed-dependent broadening and shifting. There was one all-important proviso, and that that is we must be able to calculate or model the speed dependence of the various relaxation rates. Our treatment of Dicke narrowing provides a valuable lesson. 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. We need simply restore the index ba, suppressed in the treatment of an isolated line. In the multiline case, the relaxation rates and the specification of the boxes for the distribution function will carry three indices: one for the component of the optical coherence, one for the speed class, and one for the angular or v_z class. Preliminary calculations along these line were reported in Ref. [21].

The master equation proposed in I excluded transitions between boxes that differed both in the component of the optical coherence and in the velocity. However, it is clear from the discussion that no difficulty will arise if the relaxation matrix has a general form $W(l,v,\theta \leftarrow l',v',\theta')$ where, in standard line mixing terminology, l stands for line or transition. (Such terms are the source of statistical correlation between the evolution of the internal and translational degrees of freedom.) With the apparently unending growth in computer memory and power, the numerical solution by matrix techniques becomes easier, almost on a daily basis. The present calculations were carried out on a desktop computer. The biggest problem solved involved diagonalizing a 350×350 matrix, and required about 10 min. Most of the profiles only required on the order of 1 min of computer time. Computing power is then not a serious bottleneck to the general application of the ideas expressed in this paper. What presently represents an impediment is the lack of any physically realistic models of the speed dependence of the various relaxation rates. Microscopic, semiclassical calculations could be used to create such models. At that stage one could begin to look for signatures in the spectral profiles of specific aspects of the speed dependence of the various relaxation rates or of the presence of statistical correlation. Hopefully, the signatures will be unique.

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