Model for vibrational relaxation: Pure-dephasing and depopulation

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Abstract. The three dominant mechanisms giving major contributions to vibrational relaxation in molecular systems are (a) pure dephasing, (b) depopulation (or energy relaxation), and (c) resonant transfer. Here (c) is not considered but the effects due to the *simultaneous* occurrence of (a) and (b) are treated within a stochastic model. In dealing with (a), the vibrational frequency is assumed to undergo random uncorrelated 'jump', due to fluctuations in the environment of the active molecule between a continuous set of values. The ensuing results are somewhat different from those of the commonly used Kubo model of vibrational dephasing, especially at long times and appear to be better suited in interpreting certain experimental data. The model is next extended to include the simultaneous occurrence of (b). The calculation leads to two important conclusions: (i) the lineshape is not just the convolution of those due to (a) and (b), and (ii) the lineshape is asymmetric, if the intermolecular interactions are not isotropic.

1. Introduction

Vibrational relaxation, as studied by infrared absorption, Raman spectroscopy (conventional and picosecond) (Bailey 1974; Laubereau and Kaiser 1978), neutron scattering (Janik and Kowalska 1965), or ultrasonic attenuation (Herzfeld and Litovitz 1959) is an important tool for probing interactions between molecules in gases, liquids and molecular solids (for recent reviews, see Bratos *et al* 1978 and Oxtoby 1979). In simple physical terms, the phenomenon can be understood easily for dilute gaseous molecules for which the most dominant collision events are of the binary type. The vibrational wavefunction of a molecule is determined by the occupation number of the various normal modes and an overall phase factor. Collisions with other molecules may induce the following three distinct effects. (1) Elastic collisions cause phase shifts resulting in fluctuations of the vibrational frequency (*pure dephasing*). (2) Inelastic collisions, on the other hand, may lead to direct transitions between the vibrational levels so as to induce population or energy relaxation (*depopulation*). In this process, the vibrational energy is transferred to translational, rotational or different vibrational degrees of freedom. (3) Finally, in an inelastic collision involving a vibrationally excited molecule with a ground state molecule of the same species, the vibrational excitation can be resonantly transferred to the latter causing no net change in the vibrational population (*resonant transfer*).

In a liquid or solid, the same relaxation mechanisms are still operative, although many body effects make their description much more complicated than that in the

gas phase.   However in many a situation *e.g.* involving solute molecules in a solvent medium, resonant transfer may be neglected and the gas type binary collision picture of pure dephasing and depopulation is expected to provide a reasonable model (Fischer and Laubereau 1975). Concurrently, it may be assumed that the phases of vibrations on neighbouring molecules are uncorrelated so that the vibrational correlation function assumes the form $\langle Q(t) Q(o) \rangle$ where $Q(t)$ and $Q(o)$ refer to the vibrational coordinates of the same molecule (Bartoli and Litovitz 1972; Campbell *et al* 1974; Harris *et al* 1977).   This is the situation to which we restrict our discussion in the present paper.

Recently, there have been several attempts to show that pure dephasing and resonant transfer are not independent (Lynden-Bell 1977; Wertheimer 1978; Oxtoby *et al* 1978).   In other words, the vibrational correlation function cannot be factored as $C(t) = C_d(t) \, C_r(t)$ where $C_d(t)$ and $C_r(t)$ refer to pure dephasing and resonance transfer respectively.   One of the aims of this paper is to demonstrate, within a simple stochastic model, that a factorization of $C(t)$ is *not* permitted even when just pure dephasing and depopulation are present and resonant transfer is absent, *i.e.* $C(t) \neq C_d(t) \, C_p(t)$, where $C_p(t)$ specifies the contribution to the correlation function due to population relaxation.   This result is contrary to what is usually assumed in the literature (Fischer and Laubereau 1975; Schoreder *et al* 1977a, b; Oxtoby and Rice 1976).

Before we address to the task mentioned in the preceding paragraph, we shall first consider pure dephasing alone.   This is done with two reasons in mind (i) in recent experiments using picosecond laser excitation, it has been possible to separately measure contributions to the vibrational correlation function of pure dephasing (Laubereau and Kaiser 1978), (ii) we ought to be able to construct a model of pure dephasing which facilitates the subsequent generalization to include the simultaneous presence of depopulation.

Now, the most widely used stochastic model of pure dephasing is a Kubo oscillator for which the frequency is assumed to be a continuous, stationary, Gaussian-Markov process (Kubo 1969; Rothschild 1976).   If the frequency modulation is viewed to occur due to a collision process, the corresponding collision operator, which describes the transition of the frequency (from ω to ω', say) obeys a Fokker-Planck equation (Kubo 1969).   In other words, each collision is assumed to alter the frequency by a very little amount.   Accordingly, the Kubo model (abbreviated hereafter as KM) has also been termed as a weak collision model in the theory of collision broadening of spectral lines in gases (Rautian and Sobel'man 1967).   In the latter area of research, it has been a common practice to treat the other extreme of the weak collision limit, the so-called strong collision model (SCM) in which each collision is assumed to completely randomise the frequency to its equilibrium value.   In addition to the study of collision broadening in atomic spectroscopy (Rautian and Sobel'man 1967; Dattagupta 1977), the SCM and its equivalents have been extensively applied in recent years to various lineshape problems involving time-dependent hyperfine spectra (for a recent review, see Dattagupta 1981).   Furthermore, the widely used *J*-diffusion model of rotational relaxation (Gordon 1966) in infrared and Raman spectroscopy, is also based on an assumption of strong collision nature (Dattagupta and Sood 1979).   Despite this wide range of applications in numerous lineshape problems, the use of SCM in the study of vibrational relaxation has not been considered so far, to the best of our knowledge.   We shall show (§ 2) that in some cases

the SCM gives a betteri nterpretation of the data on pure dephasing than the KM. The SCM has the further advantage that it can be generalized in a straightforward manner to account for the combined effects of pure dephasing and depopulation, the stated objective of the present work.

The paper is organized as follows. In § 2 we present the SCM and its comparison with the KM in the application to pure dephasing. It is found that $C_d^{SCM}(t)$ differs from $C_d^{KM}(t)$ appreciably at long times, the latter falling off faster. This difference appears to be important for a better agreement with the data on vibrational dephasing in certain systems studied earlier (Schroeder 1977a). In § 3, we deal with the situation in which the effects of pure dephasing and depopulation are present simultaneously. As the treatment relies heavily on our earlier work on collision broadening (Datta-gupta 1977), with appropriate changes in the interpretation of various terms, only the main results will be presented in § 2 and § 3. Finally, § 4 contains a brief summary of the paper and possible extensions to include resonant transfer as well.

2. Pure dephasing: Strong collision model

As stated in § 1 we assume that the phases of vibration of different molecules are uncorrelated. Hence the vibrational lineshape is given by the real part of (the analytic continuation to $s = j\omega$) the Laplace transform of a 'single-particle' correlation function (Oxtoby 1979).

$$I(\omega) = \text{Re} \int_0^\infty dt \exp(-st) \text{Tr}(\rho \, Q^+(0) \, Q(t)), \tag{1}$$

where ρ is the density matrix of the entire system, $Q(0)$ is the vibrational transition operator, and $Q(t)$ describes its time-development in the Heisenberg picture. We adopt here a stochastic model for evaluating the statistical average in (1). In this, the effect of the interactions between the molecule of interest and the other degrees of freedom is assumed to render the vibrational part of the Hamiltonian $\mathcal{H}_v$ randomly time-dependent. Accordingly, we may write

$$I(\omega) = \text{Re} \int_0^\infty dt \exp(-st) \text{Tr}_v \{\rho_v \, Q^+(0) \, [\langle \exp_T(i \int_0^t \mathcal{H}_v^\times(t') \, dt') \rangle$$

$$\times \, Q(0)]\}, \tag{2}$$

where $\text{Tr}_v \{....\}$ is carried out over the vibrational degrees of freedom with the aid of the density matrix ρ_v, $\exp_T(....)$ denotes a suitable time-ordering of the operators, and $\langle ....\rangle$ indicates an average over the stochastic properties of $\mathcal{H}_v(t)$. The super-script $\times$ on $\mathcal{H}_v$ defines the Liouville operator associated with $\mathcal{H}_v$ (Blume 1968).

We shall, for the sake of convenience, be concerned here with the ground and first excited vibrational levels, that is, the effect of hot bands will be neglected. It is most convenient to deal with the problem in a pseudo-spin language. The two lower

most vibrational levels can be represented by the eigenstates of the z-component S_z of a pseudo-spin operator S ($S = \frac{1}{2}$). The vibrational part of the Hamiltonian may be modelled as

$$\mathcal{H}_v(t) = [\omega_0 + \Delta\omega(t)] S_z, \tag{3}$$

where ω_0 specifies the static part of the vibrational frequency and $\Delta\omega(t)$ the fluctuations with zero mean. In this representation,

$$\rho_v = \exp(-\beta\omega_0 S_z) \left(2 \cosh\frac{\beta\omega_0}{2}\right)^{-1}, \tag{4}$$

while the transition operator Q^+ (or Q^-) may be replaced by S^+ (or S^-). The line-shape for *Stokes* Raman scattering or infrared absorption may be written from (2) and (4) as

$$I_d(\omega) = \exp(\tfrac{1}{2}\beta\omega_0) \left(2\cosh\frac{\beta\omega_0}{2}\right)^{-1} \text{Re} \int_0^\infty dt \exp(-st)$$

$$\times \text{Tr}_v \left\{ S^-(0) \left[\left\langle \exp\left(i\int_0^t dt'\,(\omega_0 + \Delta\omega(t')) S_z^x\right) \right\rangle S^+(0) \right] \right\}$$

$$= Z \, \text{Re} \int_0^\infty dt \exp\left[-(s - i\omega_0)t\right] \left\langle \exp\left(i \int_0^t dt'\, \Delta\omega(t')\right) \right\rangle, \tag{5}$$

where Z is a temperature-dependent prefactor, and we have used in the last step the matrix representations of Liouville operators in carrying out the trace operation.

Assuming (as did Dattagupta 1977) that the fluctuations in the environment cause $\Delta\omega(t)$ to 'jump' instantaneously from one value to another with a probability governed by a stationary Markov process, the lineshape in the strong collision model can be expressed as

$$I_d(\omega) = Z \, \text{Re} \, [\{\mathcal{U}^0(p + \nu)\}^{-1} - \nu], \tag{6}$$

where $p = s - i\omega_0$, ν is a parameter which defines the mean rate of 'jump' of $\Delta\omega(t)$ from one value to another, and

$$\mathcal{U}^0(p + \nu) = \int_{-\infty}^{+\infty} d(\Delta\omega)\, p(\Delta\omega)\, [p + \nu - i\,\Delta\omega]^{-1}, \tag{7}$$

$p(\Delta\omega)$ specifying the stationary distribution of the continuous random variable $\Delta\omega$. A special case of (6) when the frequency can take only two values yields the results of the exchange model of dephasing (Harris *et al* 1977, 1978; Shelby *et al* 1979). We shall assume for $p(\Delta\omega)$ a Gaussian distribution:

$$p(\Delta\omega) = (4\pi\,\sigma^2)^{-1/2} \exp\left[-(\Delta\omega)^2/4\,\sigma^2\right]. \tag{8}$$

This choice is dictated by two reasons: (i) in the limit of a large number of possible frequency values, the central limit theorem applies and (ii) the stationary frequency distribution in the KM is also given by (8) and therefore, the comparison of the KM with the SCM is facilitated by the chosen form in (8). Equation (7) can then be written as

$$\mathscr{U}^0 (p + \nu) = \frac{\sqrt{\pi}}{2\sigma} \exp{(x^2)} \operatorname{erfc}{(x)}, \tag{9}$$

where erfc (x) denotes the complementary error function of its argument x defined as

$$x = (p + \nu)/2\sigma. \tag{10}$$

Substitution of (9) into (6) completes the solution to the vibrational lineshape in the SCM.

The normalized correlation function $C_d^{SCM}(t)$ in the strong collision model, may be obtained directly from the inverse Laplace transform of (6). This task, however, is to be performed numerically, a route that is usually time-consuming and marred by truncation errors. Instead, we find it more suitable to adopt the following scheme (for a similar technique, see also Eagles and McClung 1973). The correlation function is taken to obey a Volterra equation

$$\frac{d}{dt} C_d^{SCM}(t) = - \int_0^t dt' \, K(t') \, C_d^{SCM}(t - t'), \tag{11}$$

where the kernel $K(t)$ has the structure

$$K(t) = K^0(t) \exp{(-\nu t)}, \tag{12}$$

and $K^0(t)$ obeys an equation similar to (11) in terms of the *known* function $C^0(t)$:

$$\frac{dC^0(t)}{dt} = - \int_0^t dt' \, K^0(t') \, C^0(t - t'), \tag{13}$$

$$C^0(t) = \int_{-\infty}^{+\infty} d(\Delta\omega) \, p(\Delta\omega) \exp{(i\,\Delta\omega t)}$$

$$= \exp{(-\sigma^2 t^2)}. \tag{14}$$

It may be easily verified by taking repeated Laplace transforms and using the convolution theorem that the set of equations (11)—(14) is entirely equivalent to the derived expression (6) for the lineshape in the SCM. The numerical method

(Eagles and McClung 1973) then consists in solving (13) for $K^0(t)$, determining $K(t)$ from (12), and finally evaluating $C_d^{SCM}(t)$ from (11).

We are now in a position to compare the preceding result of the SCM with the one obtained in the KM. In the latter, $\Delta\omega(t)$ is assumed to be a stationary Gaussian-Markov process so that (Kubo 1962)

$$\langle \exp(i\int_0^t \Delta\omega(t')dt')\rangle = \exp[-\int_0^t (t-\tau)\langle \Delta\omega(\tau)\Delta\omega(0)\rangle d\tau], \tag{15}$$

in which $\quad \langle \Delta\omega(\tau)\,\Delta\omega(0)\rangle = \langle (\Delta\omega)^2\rangle \exp(-\tau/\tau_c), \tag{16}$

where the correlation time τ_c may be identified as ν^{-1} if the KM is interpreted as a weak collision model (§ 1). Assuming further that the stationary distribution of $\Delta\omega$ is governed by the same probability function as in equation (8), we have

$$\langle (\Delta\omega)^2\rangle = 2\,\sigma^2. \tag{17}$$

Therefore, the lineshape function in the KM is given from (15—17) by

$$I_d(\omega) = Z\,\mathrm{Re}\int_0^\infty dt\,\exp(-pt)\,C_d^{KM}(t), \tag{18}$$

where $\quad C_d^{KM}(t) = \exp\left\{-2\sigma^2\nu^{-2}[\exp(-\nu t)-1+\nu t]\right\}. \tag{19}$

In figures 1a-1c, we present a comparative study of the computed values of $C_d^{SCM}(t)$ and $C_d^{KM}(t)$ plotted for three different values of the Kubo parameter $(\sigma\tau_c)$. We find that the results differ significantly at long times, especially for *larger* values of $\sigma\tau_c$.
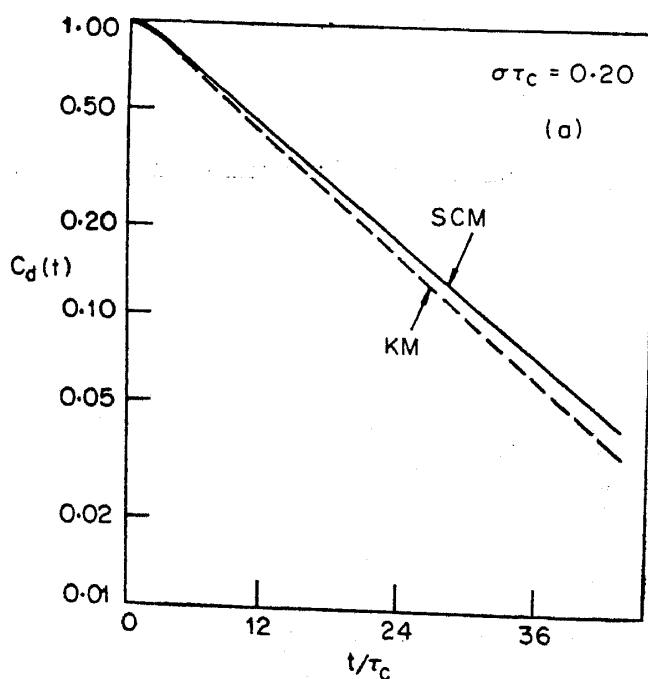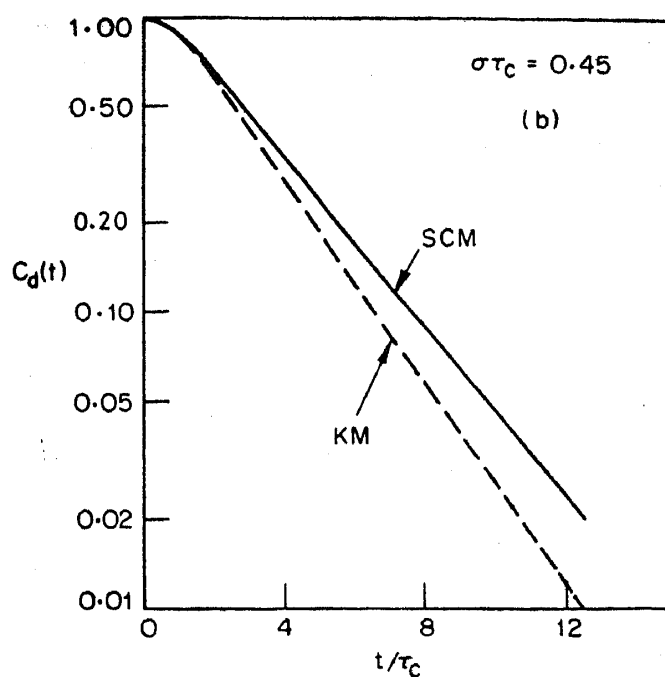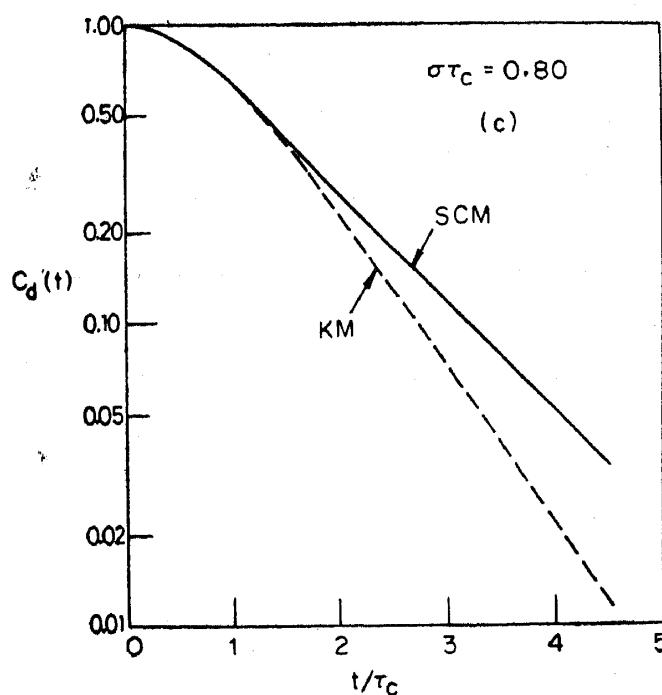

Figure 1a.

Figure 1b.

Figure 1c.

Figure 1. a-c. The vibrational correlation function in the case of pure dephasing in the KM and the SCM for three different values of the Kubo parameter $\sigma \tau_c$.

As the KM neglects the cumulants of order higher than the second (Kubo 1969), the corresponding correlation function decays more rapidly than the one in the SCM. It can be seen from figure 1b that for $\sigma \tau_c = 0.45$, the difference between the values of $C_d^{SCM}(t)$ and $C_d^{KM}(t)$ is $\sim 50\%$ for $t \sim 10\,\tau_c$ (% difference $\equiv 100 \times (C_d^{SCM} - C_d^{KM})/C_d^{KM}$.

To test the applicability of the SCM, we consider now the experimental data on pure dephasing obtained by Shroeder *et al* (1977a) on CH_3CN and CD_3CN. As can be seen from figures (5)—(8) of Shroeder *et al* (1977a), the fit of the data to the KM is not satisfactory at long times. The SCM, on the other hand, gives a better account of the data. In order to highlight this, we single out the data on CH_3CN at 60°C and 0·03 kbar which have been analysed here on the basis of the KM with a value of the Kubo parameter $\sigma\tau_c = 0\cdot21$. Figure 2 shows clearly that the SCM provides a better interpretation of the data for $\tau_c = 0\cdot11$ psec (and hence $\sigma = 1\cdot91$ psec^{-1}).

3. Dephasing and depopulation in the SCM

In this section we would like to deal with a situation in which the effects of dephasing and depopulation are simultaneously present. The physical idea behind our model is the following. Vibrational relaxation is viewed to occur as a result of 'fluctuations' in the environment of the active molecule, the origin of which, at a microscopic level, can of course be traced to basic intermolecular interactions. Now, the environment is a system with a large number of degrees of freedom, and therefore, may be assumed to possess negligible memory. Accordingly, the fluctuations in the environment may be taken to be short-lived and hence modelled as *instantaneous* 'collisions' which perturb the active molecule. Each collision may induce pure dephasing through an alteration in the frequency-separation of the two levels involved in the transition, as described in §2. Additionally, a collision is expected also to have a finite probability of causing a direct transition between the two levels thereby giving rise to population relaxation. Thus, if the vibrational state immediately prior to a collision is $| + \frac{1}{2} \rangle$ in the pseudo-spin language, population relaxation implies that the state is changed
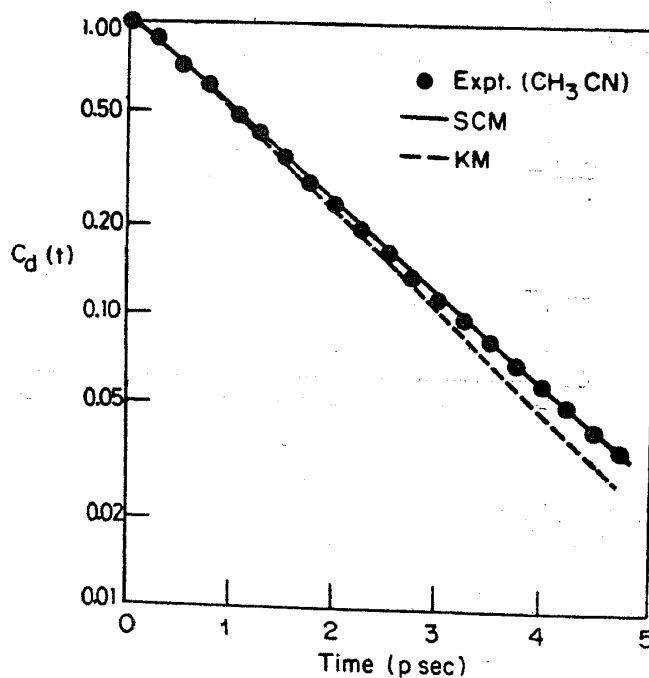

Figure 2. Experimental data on pure dephasing in CH_3CN at $T = 60°C$ and $P = 0\cdot03$ kbar (Schroeder *et al* 1977a) and comparison with the KM and the SCM for values of the parameters $\sigma\tau_c = 0\cdot21, \tau_c = 0\cdot11$ psec.

to $(C_+ | + \frac{1}{2} \rangle + C_- | - \frac{1}{2} \rangle)$ immediately after a collision, where $C_\pm$ are arbitrary amplitude factors. It is evident that such a process can be incorporated in the present model by adding to the Hamiltonian in equation (3), a term of the form $\sum_i \mathbf{S} \cdot \mathbf{h}_i \, \delta \, (t - t_i)$ where $\mathbf{h}_i$ is an 'effective' field which depends on the strength of the interaction between the active molecule and its surroundings at the ith collision. The field $\mathbf{h}_i$, in the present formulation, is of course a random variable which should be averaged over in the final expression for the lineshape (see below).

As mentioned in § 1, a model that is very similar in spirit to the one outlined above, in which each collision is viewed to cause simultaneous dephasing and depopulation, has been treated in detail earlier in a different context of collision broadening in atomic spectroscopy (Dattagupta 1977). Borrowing the results of Dattagupta (1977), the lineshape can now be written as a straightforward extension of equation (6):

$$I(\omega) = Z \, \mathrm{Re} \, \{ [\mathcal{U}^0 (p + \nu)]^{-1} - \nu \, (1 - y) \}^{-1}, \tag{20}$$

where the parameter y depends on the averages of certain functions of the magnitude and direction of the field $\mathbf{h}_i$:

$$y = [\sin^2 (h_i/2) \, (2 - \sin^2 \theta_i)]_{\mathrm{av}} + j \, (\sin (h_i) \cos \theta_i)_{\mathrm{av}} \tag{21}$$

The azimuthal angle ϕ_i specifying the orientation of $\mathbf{h}_i$ does not appear in (21) as $\mathbf{h}_i$ is assumed to be cylindrically symmetric.

It may be noted from (20) that the case of pure dephasing can be retrieved by 'switching off' the field h and hence y. On the other hand, in a circumstance involving pure depopulation, (or energy relaxation), $\sigma^2 = 0$, and therefore (7), (8) and (20) yield

$$I_p (\omega) = Z \, \mathrm{Re} \, (p + \nu y)^{-1}, \tag{22}$$

which gives rise to a Lorentzian lineshape. The corresponding normalised correlation function in the case of pure depopulation is evidently

$$C_p (t) = \exp (- \nu y t). \tag{23}$$

Our next task is to demonstrate that in the general case in which both dephasing and depopulation are simultaneously operative, the normalized correlation function $C(t)$ (obtained from the inverse Laplace transform of (20)) *does not* equal $G(t)$, where

$$G (t) = C_d (t) \, C_p (t), \tag{24}$$

$C_d (t)$ being given by the solution of (11). This has been performed numerically for different values of the parameters ν and y. First, the h-fields are assumed to be isotropic and hence y is real. Instead of Laplace inversion of (20), $C(t)$ was obtained directly by numerical solution of an inhomogeneous Volterra equation:

$$\frac{dC(t)}{dt} = - \nu y \, C(t) - \int_0^t dt' \, K(t') \, C(t - t'), \tag{25}$$

along with (12)—(14). This route yields more accurate results than the ones obtained by numerical Laplace inversion of (20) (Purniah 1981). Even in this case, discrepancies exist between $C(t)$ and $G(t)$ as shown in figure (3a). Second, y is taken to have an imaginary component also which, as discussed earlier, would arise from an anisotropy in the h-fields (see (21)). In this case, it is more convenient to plot the
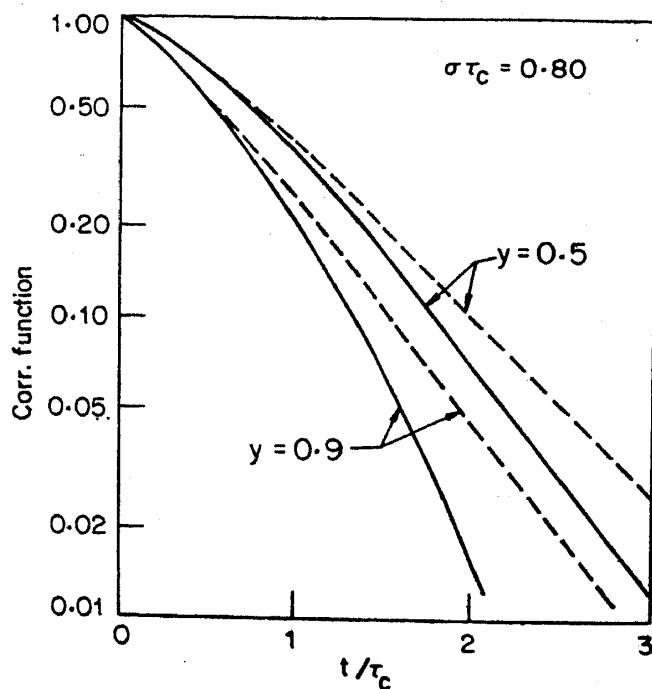

Figure 3 a. The correlation functions $C(t)$ and $G(t)$ versus time in units of τ_c. The solid curves represent $C(t)$ and the dashed curves represent $G(t)$. Values of y are indicated in the figure.
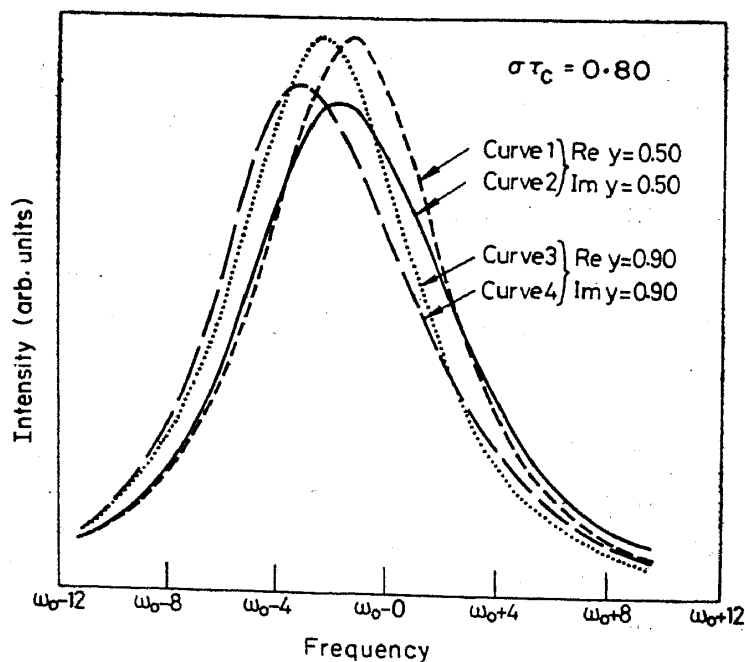

Figure 3 b. Line profiles $I(\omega)$ and $G_{con}(\omega)$ versus frequency. All the curves have been normalised to unity. Curves 1 and 3 are for $G_{con}(\omega)$ and curves 2 and 4 are for $I(\omega)$.

lineshape in the frequency-space. Figure (3b) represents the actual lineshape $I(\omega)$ and the convoluted form $G_{con}(\omega)$ where $G_{con}(\omega) = \int_{-\infty}^{+\infty} I_d(\omega') I_p(\omega-\omega') \, d\omega'$. An interesting feature to note in figure (3b) is that the line profile $I(\omega)$ is not simply shifted as is the case of $G_{con}(\omega)$, but is asymmetric also. Thus the statistical dependence of pure dephasing and depopulation on each other is more pronounced when the h-fields and hence the intermolecular forces are anisotorpic. The above discussion implies that the total linewidths cannot always be taken to be equal to the sum of individual linewidths (due to dephasing and depopulation) in contradiction to the frequently adopted procedure.

4. Concluding remarks

In this paper we have treated the phenomena of dephasing and depopulation associated with vibrational relaxation in molecular systems within a stochastic theory approach. The analysis has been carried out in two distinct stages. First, pure dephasing, which can be imagined to arise on account of random frequency modulations of the vibrational levels, is dealt with in a strong collision model. In this, the vibrational frequency is assumed to 'jump' at random, due to fluctuations in the surroundings of the active molecule, from one value to another among a spectrum of continuous values. The resulting lineshape is shown to provide, in some cases, a better account of the data on pure dephasing than the commonly used Kubo model. An extension of the theory is next made to include the simultaneous occurrence of depopulation effects. Two noteworthy features of the lineshape emerge from the analysis: (a) it is not merely a convolution of the individual lineshapes due to dephasing and depopulation; (b) it is asymmetric as a result of anisotropy in the intermolecular interactions.

We have restricted the present analysis to circumstances in which resonant transfer is not important. Certain nontrivial generalizations of the stochastic theory have to be carried out in order to include also the presence of resonant transfer along with pure dephasing and population relaxation. First, correlation functions of the type $\langle Q_i(0) \, Q_j(t) \rangle$, $i \neq j$ have to be considered. Second, resonant transfer which is essentially a cooperative effect, has to be treated in the pseudo-spin formalism, by including in the Hamiltonian, terms of the form $J_{ij} (S_i^+ S_j^- + S_i^- S_j^+)$ where $S^\pm$ are the usual raising and lowering angular momentum operators. The term J_{ij} represents the strength of the overlap between two active molecules i and j, and is expected to be a random function of time in the fluid phase. Attempts are underway now to investigate the combined effects of dephasing, depopulation and resonant transfer within a stochastic model and the results will be reported elsewhere.

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