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Stochastic Theory of Vibrational Dephasing and Transient CARS Lineshapes

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Considerable progress has been made in recent years in studies of the dynamics of vibrational excitations in liquids[1]. Before the advent of picosecond spectroscopic methods, vibrational dephasing was studied through measurements of the isotropic Raman lineshape $I_0(\omega)$. This lineshape is proportional to the Fourier transform of the vibrational correlation function $\langle\hat{q}(t)\hat{q}(0)\rangle$, where $\hat{q}$ is the coordinate of the relevant vibrational mode, and $\langle\cdots\rangle$ indicate a trace over the equilibrium density matrix[2]. The distinction is traditionally made between homogeneous and inhomogeneous contributions to spectral lineshapes. Although these two limits are well defined, the classification of realistic line broadening mechanisms into these two categories is not always possible. Consider a molecule coupled to a bath with time scale $1/\Lambda$. If Λ is much smaller than the observed line width, the line is inhomogeneously broadened. As Λ is increased, the lineshape will change, and only when Λ is much larger than the observed linewidth, will a Lorentzian, homogeneously broadened line emerge. For intermediate Λ, the line cannot be classified as either homogeneously or inhomogeneously broadened. Stochastic[2] and microscopic[3] models, which are valid for arbitrary Λ and interpolate between these limits, allow a more realistic calculation of spectral lineshapes in liquids. A fundamental question concerning the time-resolved CARS spectroscopy in liquids is, under what conditions does the experiment provide more microscopic information than is contained in $I_0(\omega)$. Particular attention has been given to whether coherent transient CARS spectroscopy can distinguish between homogeneous and inhomogeneous broadening mechanisms[1,4]. In this article, we analyze the information content of coherent CARS spectra for a general line-broadening mechanism with an arbitrary correlation time $1/\Lambda$. Our model[5,6] interpolates continuously between the limits of homogeneous and inhomogeneous line broadening[7]. We model the molecular liquid as a collection of three-level systems of the type depicted in Fig. 1. $|1\rangle$ and $|2\rangle$ denote vibronic states belonging to the manifold of the ground state, whereas the vibronic state $|3\rangle$ belongs to an electronically excited state. The energy difference between $|2\rangle$ and $|1\rangle$ is $\hbar\Omega_2 + \hbar\Delta(t)$. $\Delta(t)$ is a stochastic process with zero mean arising from the random force exerted on the absorber molecule by its fluctuating environment. The effect of this fluctuating energy is to broaden the spontaneous Raman lineshape for the $|1\rangle$ to $|2\rangle$ transition (proper dephasing). We shall consider two pulse sequences denoted Raman free induction decay (RFID) and Raman echo (RE). The experiments both begin with a pair of time-coincident pulses with frequencies ω_L and ω_S ($\Omega_2=\omega_L-\omega_S$) that excite a coherence between $|1\rangle$ and $|2\rangle$ by stimulated Stokes scattering. There follows a delay period of duration t_D. In the RFID, the system is then irradiated by a probe pulse with frequency ω_{L2} and emission is detected at frequency $\omega_{L2}-\Omega_2$ (Stokes) or frequency $\omega_{L2}+\Omega_2$ (anti-Stokes). In the RE, the system is irradiated with another pair of excitation pulses. After another delay period of duration t, the system is probed with a pulse with frequency ω_{L2}, and the coherent Stokes or anti-Stokes signal is detected. The RFID consists of one pair of excitation pulses, one delay period, and a probe pulse, while the RE consists of two pairs of excitation pulses, two delay periods, and a probe pulse. The pulse sequences are shown in Fig. 2. In both cases, the coherent signal is observed at the direction $k_L-k_S+k_{L2}$. We have calculated the signal for both experiments using the tetradic (Liouville space) scattering formalism[3]. If the pulses are very short (compared with all detuning frequences and relaxation rates), the signals are[6]:

$$S_{RFID}(t_D) = |\chi_{RFID}(t_D)|^2 \tag{1}$$

$$\chi_{RFID}(t_D) = \langle\hat{q}(t_D)\hat{q}(0)\rangle \tag{2}$$

and

$$S_{RE}(t,t_D) = |\chi_{RE}(t,t_D)|^2 \tag{3}$$

$$\chi_{RE}(t,t_D) = \langle\hat{q}(-t)\hat{q}(0)\hat{q}(t_D)\hat{q}(0)\rangle. \tag{4}$$

The averages over the fluctuating energy of state $|2\rangle$ in (2) and (4) can be carried out in a straightforward manner if $\Delta(t)$ is taken to be a Gaussian variable[2,6]. In this case χ_{RFID} and χ_{RE} are given by

$$\chi_{RFID}(t_D) = \exp[-g(t_D)] \tag{5}$$

$$\chi_{RE}(t,t_D) = \exp[-2g(t) - 2g(t_D) + g(t+t_D)], \tag{6}$$

where

$$g(t) = \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \, \langle\Delta(\tau_1-\tau_2)\Delta(0)\rangle. \tag{7}$$

For illustrative purposes, we shall consider dephasing that is induced by two independent processes that modulate the energy of state $|2\rangle$.

$$\langle\Delta(t)\Delta(0)\rangle = D_1^2\exp(-\Lambda_1|t|) + D_2^2\exp(-\Lambda_2|t|). \tag{8}$$

D_n and Λ_n are respectively the magnitude and inverse time-scale of process n. Substitution of (8) and (7) into (5) and (6) will give general expressions for the li

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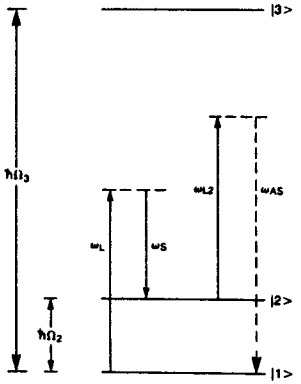

Fig. 1

Energy-level diagram for our model system

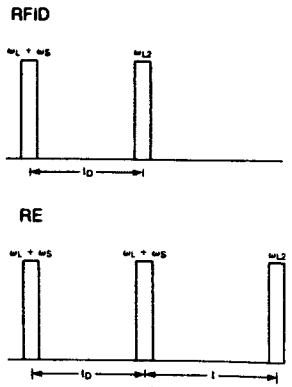

Fig. 2

Pulse sequences for Raman free induction decay and Raman echo experiments.

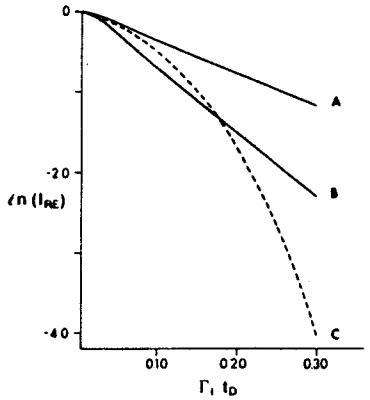

Fig. 3

Raman echo signal, calculated from (6)-(8). $A_1=10^2$, $D_1=D_2=10$. $\Gamma_1=D_1^2/A_1$. A) $A_2=10^{-6}$. B) $A_2=10^{-2}$. C) $A_2=1$. Exponential RE signals will be observed from a system with two dephasing mechanisms if both processes are fast on the experimental time-scale (A), or if one process is fast, and the other is slow on this time-scale (B). Otherwise, the decay will be nonexponential. (C).

and RFID observables for a system with two dephasing mechanisms of arbitrary time-scale and magnitude.

Figure 3 shows logarithmic plots of the RE signal, calculated from (6) - (8). All plots are calculated for $A_1=100$, $D_1=D_2=10$. Plots A, B, and C are calculated respectively for $A_2=10^{-6}$, 100, 1. In all cases, process 1 causes homogeneous line broadening ($A_1/D_1^2 >>1$). In case A, $A_2/D_2<<1$. In this case, the RE signal is nonexponential at very short times but becomes exponential with decay constant $4\Gamma_1$. ($\Gamma_1=D_1^2/A_1$). In case B, process 2 has a time-scale identical to that of process 1 ($A_1=A_2$). In this case, the RE signal is nonexponential at very short times but becomes exponential with decay constant $4(\Gamma_1+\Gamma_2)=8\Gamma_1$. In case C, process 2 has a time-scale that is comparable in magnitude to the time-scale of observation. In this case, the RE signal is nonexponential on the time-scale of observation. Fig. 3 shows that if vibrational dephasing is caused by two different processes with arbitrary time-scales, the observed RE signal is, in general, nonexponential. The signal will be exponential (except at very short times) in two limiting cases. The first such case holds, when the two processes occur on very different time-scales. In this case, one process is "dynamic" on the time-scale of observation, and the other is "static", relative to this time-scale. The line broadening in such a system has homogeneous and inhomogeneous components. The second limiting case that leads to an exponential RE signal occurs, when both processes are "dynamic" on the time-scale of observation. Such a system has a homogeneously broadened line.

In conclusion, we note the following: (i) (2) shows that for weak and short pulses the RFID cannot provide information about the material that is not also present in the low power lineshape function $I_0(\omega)$. This conclusion differs from earlier treatments of this problem [1],[8] (ii) George and Harris [4] have argued that the RFID experiment can be used to measure homogeneous dephasing times of a system with an inhomogeneously broadened Raman lineshape, provided that the initial laser pump pulse is significantly depleted. We have made the distinction between laser pulse depletion, which occurs when the sample is optically dense, and saturation of the material transition, which occurs when the fields are strong. The Bloch-Maxwell equations considered by George and Harris include laser depletion, but they do not include material saturation. We have shown[6] that the experimental observable calculated from these equations cannot show selectivity. Selectivity is defined as the capacity to provide more information than an ordinary lineshape measurement. If these equations are expanded to include material saturation, the information content of the experimental observable will no longer be identical to that of

a low-power lineshape measurement. There are two experimental conditions under which the RFID experiment is not selective: short pulses of arbitrary strength and weak pulses of arbitrary duration. If the experiment is carried out with long, strong pulses, the signal will undoubtedly be characterized by some degree of selectivity. The signal, under these conditions, can be calculated numerically from the complete Bloch-Maxwell equations. (iii) The Raman echo experiment, on the other hand, can be used to go beyond the spontaneous Raman lineshape in obtaining dynamical information, since it is a probe for a four-point correlation function of the dipole operator (similar to the photon echo) [5],[6],[12]. The theory of the Raman echo for a system with an inhomogeneously broadened lineshape was originally developed by Hartmann[9]. Our present treatment generalizes that theory to an arbitrary time-scale of the bath and is valid from the homogeneous to the inhomogeneous broadening limits. Raman echo experiments have been carried out in gases [10] and solids [11] but have not yet been applied to liquids. The Raman echo experiment has the capability of providing significant new information on the dynamics of vibrations in liquids.

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