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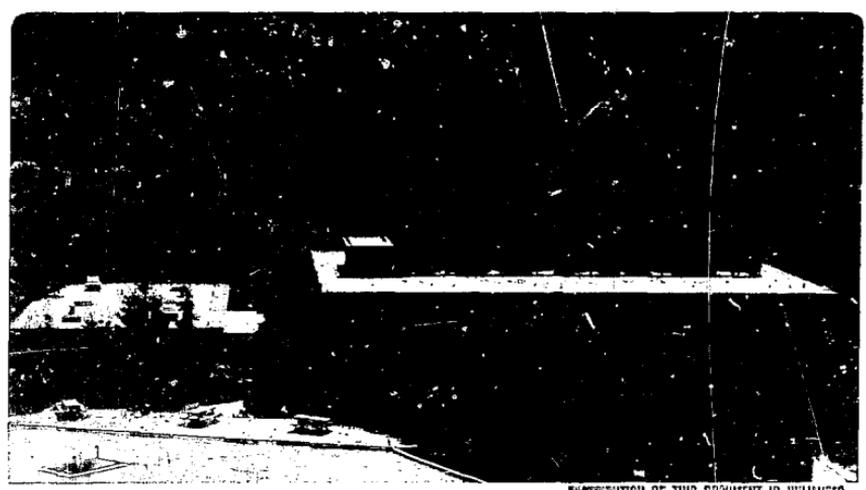
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MASTER

C.B. Harris, S. M. George, A.L. Harris, and M. Berg

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The Separation of Rapidly and Slowly Varying Intermolecular Forces in Liquids
Using the Temperature Dependence of Coherent Picosecond Stokes Scattering.

by

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Abstract

The temperature dependence of attractive and repulsive force contributions to vibrational line broadening are studied in liquid acetonitrile by using Coherent Picosecond Stokes scattering.

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I. Introduction

Previous studies have established that Raman lineshapes in liquids can be both homogeneously and inhomogeneously broadened (1,2). Recent work (2,3) has also suggested that homogeneous broadening results from rapid (~ 1 ps) collisional processes, which are associated with the repulsive part of the intermolecular potential. In contrast, slow (> 5 ps) processes associated with the attractive part of the potential are believed to cause inhomogeneous broadening.

With a combination of spontaneous Raman spectroscopy and picosecond coherent Raman studies, it is possible to distinguish these two processes. Selective coherent Stokes scattering can measure the homogeneous dephasing time for an inhomogeneously broadened vibration (4). The associated homogeneous linewidth is deconvoluted from the isotropic Raman lineshape to give the inhomogeneous lineshape. The result is an experimental separation of the dynamics associated with the attractive and repulsive parts of the intermolecular potential.

Temperature dependent studies of isotropic Raman lineshapes have been done previously (5,6). However, these studies alone can not distinguish between homogeneous and inhomogeneous processes, and therefore are incomplete probes of liquid dynamics. We have performed picosecond coherent Stokes experiments on the symmetric methyl stretching vibration of acetonitrile over its entire liquid range. These experiments give the first complete test of theories relating to both rapid and slow processes in liquids.

The experimental method has been previously described (2), except for a low depolarization temperature cell which will be described at a later time. Acetonitrile was chosen because it has been well studied by spontaneous Raman (6,7), has a long homogeneous dephasing time (2), and is significantly inhomogeneously broadened (2). In addition, acetonitrile has no vibrational modes below 362 cm^{-1} (8), so dephasing by energy exchange perturbations is not expected (9).

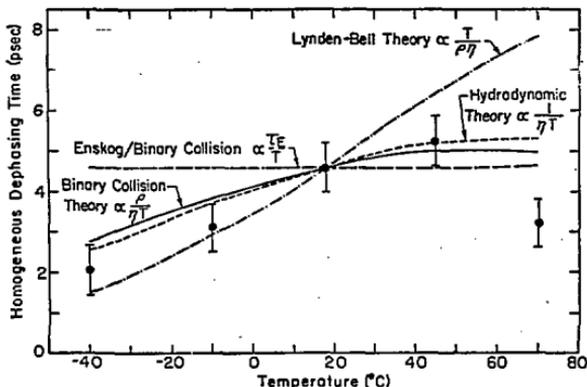


Figure 1: Homogeneous dephasing times for the symmetric methyl stretching vibration of acetonitrile as a function of temperature: Experimental measurements (dots) and theoretical predictions (lines).

II. Homogeneous Processes

The experimental homogeneous dephasing rates, which reflect fast dynamic processes, are shown as a function of temperature in Figure 1. Also shown are several theoretical predictions for the dephasing rates. All the theoretical predictions have been normalized to give the experimental result at 18°C.

The isolated binary collision (10) and hydrodynamic (11) models give the best fit to the data. Although these are very different physical models, their predictions are too similar to be distinguished by these experiments. Lynden-Bell's model (12) predicts a larger variation in dephasing rate, and does not fit the data as well. A variation of the isolated binary collision model which uses the Enskog collision time has been proposed by Schroeder, et al. (6) to account for temperature dependent isotropic Raman data. When inhomogeneous broadening is properly taken account of however, this model predicts the wrong temperature dependence for the homogeneous dephasing rate. None of these theories can completely account for the drop in dephasing time at 70°C.

III. Inhomogeneous Processes

In contrast to the homogeneous linewidth, the inhomogeneous linewidth reflects relatively slow processes. Based on an experimental comparison of inhomogeneous broadening of symmetric methyl stretching vibrations in various liquids, George, Auweter and Harris suggested that inhomogeneous broadening is caused by slowly decaying density fluctuations (2). This model leads to the prediction that the inhomogeneous linewidth is given by:

$$LW \propto \bar{\rho} \sqrt{k_B T \kappa_T} \quad (1)$$

where $\bar{\rho}$ is the number density, k_B is Boltzmann's constant, T is the temperature, and κ_T is the isothermal compressibility.

Schweizer and Chandler (3) have proposed that long range attractive forces (dispersion and dipole-dipole) provide the coupling between the local density and the vibrational frequency. Their model leads to the formula:

$$LW \propto \frac{\langle \Omega_A \rangle}{\sqrt{\bar{N}}} \sqrt{k_B T \kappa_T \bar{\rho}} \quad (2)$$

where \bar{N} is the average number of nearest neighbors, and $\langle \Omega_A \rangle$ is the attractive contribution to the gas-to-liquid frequency shift. $\langle \Omega_A \rangle$ is found by subtracting the theoretically calculated repulsive contribution from the experimentally observed frequency shift.

Figure 2 compares the predictions of these two models to experimentally measured inhomogeneous linewidths. Both models correctly predict the temperature dependence of the inhomogeneous linewidth, except at 70°C. Because there is little change in the strength of the attractive interaction,

the two models are almost identical over the temperature range studied. Almost all of the variation in inhomogeneous linewidth can be attributed to changes in the amount of density fluctuation.

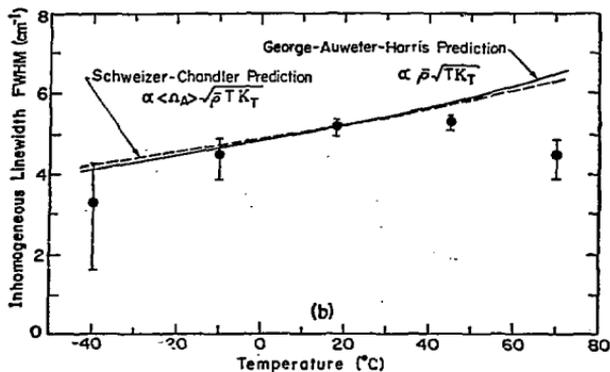


Figure 2: Inhomogeneous linewidth for the symmetric methyl stretching vibration of acetonitrile as a function of temperature: Experimental measurements (dots) and theoretical predictions (lines).

IV. Conclusions

None of the theories for homogeneous or inhomogeneous broadening correctly explains the observed behavior at 70°C. We are currently exploring the possibility that this is due to more rapid decay of the density fluctuations at higher temperatures. If this hypothesis is true, this is the first direct observation of "spectral diffusion" in a liquid.

We have shown that liquid dynamics has fast and slow components, which change significantly with temperature. The variations in the fast and the slow processes have opposing results, leading to little observed change in the isotropic Raman lineshape. The agreement between experiment and theory supports the association of the repulsive and attractive portions of the intermolecular potential with rapid and slow processes, respectively. This is the first experimental study to resolve the temperature dependent effects of the repulsive and attractive forces in a liquid.

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