EFFECT OF HYDROGEN BONDING ON THE VIBRATIONAL DEPHASING TIME IN GLYCEROL

R. DORSINVILLE, W.M. FRANKLIN, N. OCKMAN and R.R. ALFANO

Ultrafast Spectroscopy and Laser Laboratory, Physics Department,
The City College of New York, New York, New York 10031, USA

The vibrational dephasing of the methyl CH_2 symmetric stretch mode in glycerol was directly measured over an extended temperature range using picosecond coherent Raman pump and probe spectroscopy. The dephasing time was found to increase dramatically as the temperature of the supercooled liquid was lowered. This observation is attributed to the increased hydrogen bonding with decreasing temperature which hinders the dephasing of the CH_2 vibration by reducing molecular motions.

The knowledge of the vibrational and rotational motions of molecules in the condensed state is indispensable for a full understanding of the dynamics and interactions in the microscopic world of matter [1]. A variety of experimental techniques has been employed to probe the dynamics of molecular motions. Recently, picosecond laser spectroscopy [2,3], has become available for directly measuring the kinetics of the vibrational [3,4] and rotational [5] motion of molecules in the condensed state. Much picosecond work on vibrational dephasing in the liquid state has been pioneered by Laubereau and Kaiser [4]. Direct measurement of the dephasing time of vibrations is achieved by first exciting the vibration of molecules by an intense picosecond laser pulse via stimulated Raman [6] or parametric beating [3,4]. A weak probe pulse properly delayed with respect to the pump pulse can directly monitor the dephasing and population of the excited vibrations as function of time [3,4]. There have been several theoretical models proposed to account for dephasing [7–11]. The mechanisms arise from a variety of interactions such as: resonant energy transfer [12], collisions [7], hydrodynamic processes [8], coupling of high- and low-frequency modes [9], bath interactions, fast and slow repulsive and attractive interactions, [10,11], and population changes, to name a few. The dephasing times predicted by these theories [7–11] were found in accord with the experimental results of several simple non-associated, polyatomic liquids.

In this letter, we present experimental data on the first direct measurement on the vibrational dephasing of a strongly associated liquid, glycerol, over an extended temperature range. Experimental evidence is presented that correlates the dephasing interaction in this strongly associated liquid in its supercooled state with the strength of *hydrogen bonding*.

Our experimental arrangement is similar to that of Laubereau and Kaiser [4]. A mode-locked Nd : glass oscillator with single pulse selector is amplified, passed through a KDP crystal producing a 4 ps pulse at 530 nm. This pulse is then divided into a pump and a probe polarized perpendicularly to each other. The pulses traveled collinearly through a 10 cm sample located in a dewar. A two dimensional OMA coupled to a spectrograph was used to measure the probe Stokes signals at different delay times.

The dephasing times of the 2886 cm^{-1} CH_2 vibration as a function of temperature from 300 to 200 K were determined from the decay of the coherent Stokes probe signal as a function of delay time between the pump and probe laser pulses. As shown in fig. 1, the vibrational dephasing time increases as the temperature decreases. An experimental data point is the mean value of at least 15 laser shots. In fig. 2, the dephasing times extracted from temporal profiles are plotted versus the inverse of the temperature. The data are fitted to the equation:
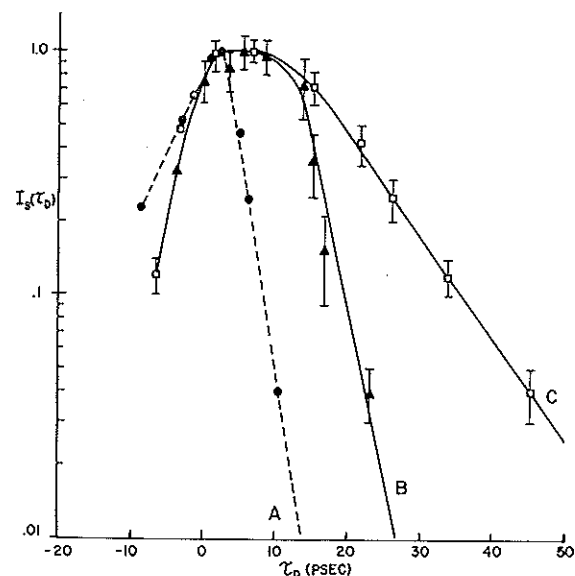
$$T_2 = T_2(0) \exp(E_{AC}/kT) , \qquad (1)$$

Fig.1. Probe Stokes profiles as function of delay time for: (A) ethanol; (B) glycerol (17°C); (C) glycerol (-55°C).
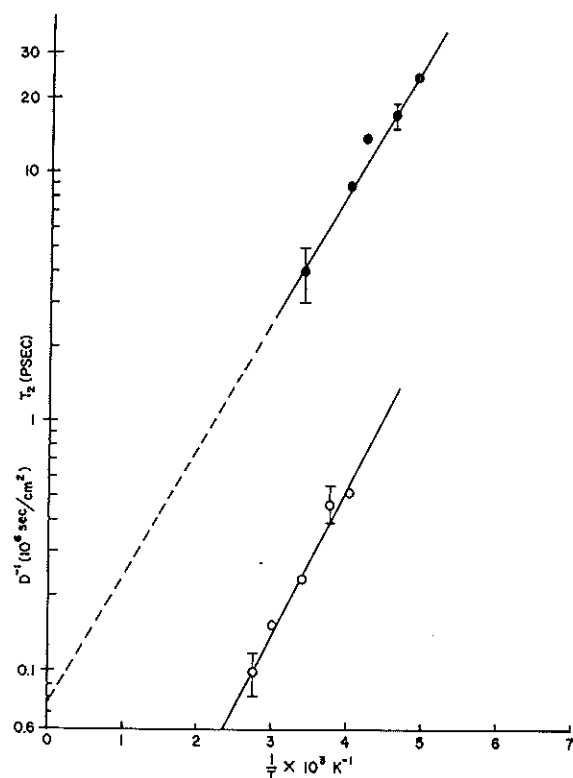

Fig. 2. Dephasing time versus the inverse temperature (•) and inverse of the diffusion coefficient versus the inverse temperature [13] (o).

where T_2 is the dephasing time, E_{AC} is the activation energy, T is the temperature, and k is the Boltzmann constant. The upper solid line in fig. 2 represents the fit to eq. (1) yielding an energy $E_{AC} = 800$ cm^{-1} = 2.5 ± 0.8 kcal/mol and $T_2(0) = 80$ fs.

The glycerol molecule [$C_3H_5(OH)_3$] has three hydroxyl groups per molecule which can hydrogen bond with other glycerol molecules to form a polymeric aggregate network which causes the high viscosity of this liquid. In fig. 2, the reciprocal of the diffusion coefficient, D^{-1}, as a function of temperature is plotted from the data of Larsson and Dahlborg [13]. The D values were extracted from neutron scattering experiments and were interpreted to arise from the motion of the CH_2OH groups inhibited by hydrogen bonding [13]. The salient feature of these curves is that the slopes of T_2 and D^{-1} are parallel. The activation energy [13] from the D^{-1} curve is 3 ± 1 kcal/mol. This is the energy needed to break a single hydrogen bond. The activation energy obtained from T_2 versus T^{-1} in fig. 2 is in excellent agreement with this value. This indicates that the dephasing time, T_2, is inversely proportional to this diffusion coefficient. The infinite temperature dephasing time $T_2(0) = 80$ fs gives a measure of the correlation time of fluctuation without local restrictions.

Various dephasing time models have been introduced to account for the dephasing of the molecular vibrations [7–12]. The collisional [7] and hydrodynamic [8] theories predict a decrease in the time with a decrease in temperature — which is opposite to our observation. The exchange models [9,12] cannot account for the 800 cm^{-1} excitation energy. The slow modulation models [10,11] are concerned with the inhomogeneous linewidths and predict the linewidths to increase with decreasing temperature. The dephasing time measurements obtained from coherent Stokes scattering are a direct measure of the homogeneous linewidths [4,14]. These models have been developed for low-viscosity non-associated liquids. A theoretical treatment applied to high-viscosity associated liquids remains to be formulated.

The dephasing of CH_2 is most likely due to the participation of rotational, rocking, torsions, steric, and other low-frequency modes [9]. Our results strongly suggest that these dephasing interactions of the CH stretch vibrational mode are significantly reduced by

hydrogen bonding [1] which inhibits and restricts these motions [9]. Our conclusions are further supported by the Raman measurements by Wang and Wright [15] showing that the low-frequency modes are inhibited by hydrogen bonding. Upon cooling the sample, the hydrogen bond breakage diminishes causing the formation of large aggregates which slow down local molecular motions and environmental fluctuations. This result accounts for our observed large increase in the vibrational dephasing time with decreasing temperature.

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