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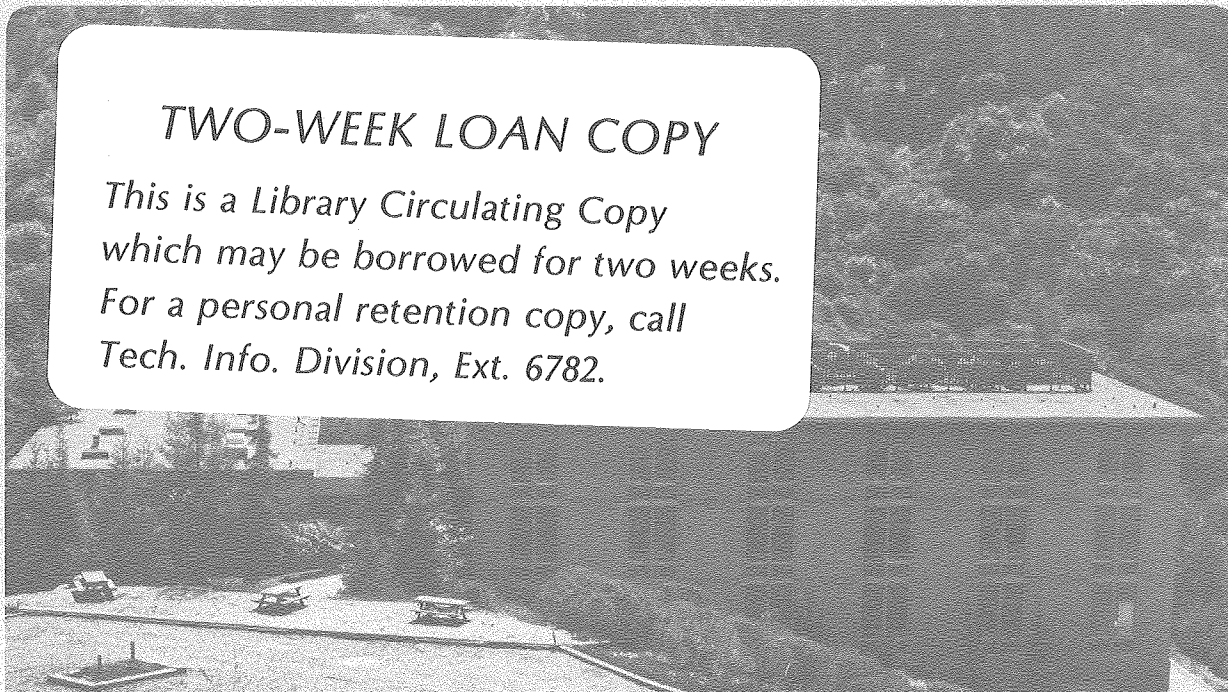C. B. Harris, H. Auweter and S. M. George

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A Critical Test of Vibrational Dephasing Theories in Liquids

Using Selective Coherent Picosecond Stokes Scattering

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Abstract

A picosecond coherent probing technique is used to determine the homogeneous vibrational linewidth in liquids. Isotope effects on the symmetric CH_3-stretching vibration in methanol and acetone provided a sensitive test for various vibrational dephasing theories. Theories based on binary-collision or hydrodynamic models do not correctly account for the observed isotope effect. Exchange theory is shown to be qualitatively consistent with the results.

Although theories abound, the exact mechanism for vibrational dephasing in condensed phases has remained elusive because definitive experiments have not been performed. Vibrational dephasing times are generally derived from spontaneous Raman or infrared vibrational linewidths, which are assumed to be homogeneous. Unfortunately, intermolecular interactions give rise to a distribution of vibrational frequencies, i.e., to inhomogeneous broadening, which seriously impairs the linewidth investigations. A recently developed picosecond probing technique is able to extract the homogeneous linewidth from an inhomogeneously broadened vibrational band.[1,2] This technique overcomes the problem of inhomogeneous broadening and allows homogeneous linewidths to be determined in liquids with unknown inhomogeneity.[3]

Many theoretical models for vibrational dephasing in liquids and solids have been proposed.[4-10] The major approaches are based on energy exchange mechanisms [4], hydrodynamic theories [5], binary collision models [6,7]. These theories predict functional dependences on macroscopic properties such as temperature T, density ρ and viscosity η, and on microscopic properties such as the vibrational frequency and the mass of the atoms involved in the vibration. To our knowledge, no systematic picosecond time-domain investigation of vibrational dephasing times in liquids has been performed as a function of T, ρ, η or isotopic composition. Therefore, the vibrational dephasing mechanism in liquids has not yet been established. In this publication, we present an experimental test for the various proposed vibrational dephasing mechanisms by determining the isotope effect on the dephasing time of the symmetric CH_3-stretching

vibration in methanol and acetone.

Isotope substitution allows vibrational frequencies to be correlated with calculated normal modes [11]. To a very high order of approximation, the potential function is insensitive to isotopic substitution [11]; therefore, the effect of isotopic substitution and especially the effect of deuteration on the vibrational dephasing time presents a critical test for the frequency and effective mass dependence of theoretically predicted dephasing times.

The experiment was performed with single picosecond pulses selected from the rising edge of pulse trains emitted from a stabilized, passively-modelocked Nd:glass laser. After amplification and frequency doubling the pulses had a duration of $\lesssim 5$ psec and a spectral bandwidth (FWHM) of ≈ 4.0 cm^{-1}, yielding a bandwidth product of ≈ 0.6, which indicates that the pulses were essentially bandwidth-limited. Each pulse was split into an excitation pulse and a properly delayed probe pulse. The polarization of the probe pulse was rotated such that the probe pulse was polarized perpendicularly with respect to the excitation pulse. The excitation and probe pulses were recombined collinearly in a 10 cm sample cell. The CH_3-stretching vibrations were excited by stimulated Raman scattering and probed by coherent Stokes Raman scattering.[1] From the experimental probing geometry a selectivity $\delta v \gtrsim 0.3$ cm^{-1} ($T_2/2 \lesssim 18$ psec) was obtained, indicating that the collinear Stokes probing technique could detect a homogeneously broadened line as narrow as 0.3 cm^{-1}.[2] Furthermore, we have measured $T_2/2$ values of 0.7 psec in dimethylsulfoxide and 2.7 psec

in acetonitrile. These $T_2/2$ values indicate that the linewidths
of dimethylsulfoxide and acetonitrile are inhomogeneously broadened,
and demonstrate that our experimental configuration can measure
$T_2/2$ values from at least 0.7 psec to 2.7 psec for inhomo-
geneously broadened vibrational linewidths.

The coherently scattered Stokes probe signal and the excita-
tion Stokes spectrum were separated and simultaneously detected
on the target of a two-dimensional optical multichannel analyzer.
This detection technique and its features will be described
elsewhere.

Spectroquality methanol and acetone, as well as
methanol-d_4 and acetone-d_6, both with 99.5 atom
% D   were used. Fig. 1 shows the coherently scattered Stokes
signal of the symmetric CH_3-stretching vibration of acetone
($\tilde{\nu}$ = 2925 cm^{-1}) as a function of probe pulse delay. On the
average, we obtained a dephasing time of $T_2/2$ = 1.5 ± 0.5 psec for
acetone. The dephasing curve of the symmetric CD_3-stretching
vibration in deuterated acetone (d_6-acetone) is also shown in
Fig. 1. For d_6-acetone, the average of several runs
was $T_2/2$ = 1.65 ± 0.5 psec. Therefore, the ratio of the
dephasing times, T_2^d/T_2^h, for deutero/proto-acetone is approximately
equal to 1.

For the symmetric CH_3-stretching vibration of methanol ($\tilde{\nu} = 2836$ cm^{-1}) we observed an average of $T_2/2 = 1.2 \pm 0.5$ psec. This result is shorter than the result obtained by Laubereau et al. under similar conditions.[1] When we spectrally resolved the Stokes scattering from both the excitation and probing process, however, stimulated Raman gain was observed in both the asymmetric and symmetric CH_3-stretching vibrations of methanol as was previously reported by Carman et al.[12] In addition, we observed that the Stokes spectrum of methanol was much more sensitive to laser intensity than the Stokes spectrum of the other liquids, possibly because both the symmetric and asymmetric CH_3-stretching vibrations were excited. Non-linear frequency modulation was enhanced and could influence the coherence of the initially excited vibrations. Therefore, we used laser pulses near the threshold for stimulated Raman scattering, spectrally observed each shot and discarded any shot that displayed frequency modulation in order to insure that the results would be unaffected. For the symmetric CD_3-stretching vibration in d_4-methanol we determined an average of $T_2/2 = 1.3 \pm 0.5$ psec, giving a ratio of $T_2^d/T_2^h \simeq 1$. The experimental results are compiled in Table 1.

In order to determine if resonant vibrational energy transfer contributes to the observed dephasing times, we performed isotopic dilution experiments. No change in the dephasing time was observed for concentrations as low as 5% methanol in deuterated methanol.

Our experimental results can be used to test both the binary-collision model [6,7] and the hydrodynamic model [5] for vibrational dephasing in liquids. According to the binary collision theory, the dephasing time T_2 is given by

$$T_2 = \frac{4}{9}\tau_c \frac{M^2}{\mu\gamma^4} \frac{\omega^2 L^2}{k_B T} \tag{1}$$

where τ_c is the elastic collision time, ω is the frequency of the molecular vibration, L is a measure for the range of the repulsive potential, and $k_B T$ is the thermal energy. The combined mass factor is determined by the reduced mass of the vibration, M, the reduced mass of the collision, μ, and the mass factor γ, appearing in the repulsive experimental interaction potential. According to Fischer and Laubereau [6], the mass of the CH_3-group, not the mass of the total molecule is used to determine the reduced mass of the CH-stretching vibration. This leads to

$$\frac{M^2}{\mu\gamma^4} = \left(\frac{3m_C m_H \cos \alpha}{m_C + 3m_H \cos \alpha}\right)^2 \frac{2}{m_C + 3m_H} \left(\frac{m_C + 3m_H \cos \alpha}{m_C}\right)^4 \tag{2}$$

where m_C is the mass of the carbon atom, m_H is the mass of the hydrogen or deuterium atom, respectively, and $\cos \alpha = \sqrt{1/3}$.

Table 1 gives all parameters which are necessary to compute the dephasing times. The collision time τ_c is given by

$$\tau_c = \frac{\rho d^2}{6\eta} \tag{3}$$

where ρ is the density, d is the molecular distance and η is the viscosity. The ratio of the calculated dephasing times T_2^d/T_2^h is equal to 2.5 for methanol and 2.4 for acetone. The result for the vibrational dephasing time in Oxtoby's hydrodynamic theory has been shown to be almost identical to eq. (1) [5]. The only differences are in replacing the molecular radius d/2 by the atomic radius R_i and in an overall factor which is approximately given by the liquid's inverse packing fraction. Thus, the hydrodynamic theory for the vibrational dephasing time gives the same frequency and mass dependence as the isolated binary collision theory.

By comparing our experimental results with the predictions of the binary collision model and the hydrodynamic theory, we conclude that both theoretical approaches cannot correctly account for the isotope effect on the vibrational dephasing time of the symmetric CH_3-stretching vibration in methanol and acetone. We observe that our dephasing times show a much less pronounced dependence on frequency and mass than predicted by these theories.

We note that the absence of an isotope effect on the vibrational dephasing time is in approximate agreement with predictions given by the exchange theory [4]. Since there is no change in the potential function upon isotopic substitution, the product $\delta\omega \cdot \tau$, which determines the dephasing time in terms of the exchange theory, remains nearly unchanged.

In exchange theory, δw is a frequency shift resulting from anharmonic coupling in the <u>intramolecular</u> potential and τ is given by $\tau = W_+^{-1} \exp(-E_i/kT)$, where W_+ is the intermolecular scattering rate for a low frequency mode coupling into a vibration, $\exp(-E_i/kT)$ is the Boltzmann factor, and E_i is the energy of the low frequency mode. Deuteration reduces low frequency mode frequencies by approximately 20%, which increases the Boltzmann factor by approximately 25%. This causes $T_2/2$ to increase <u>or</u> decrease a <u>small</u> amount depending on whether or not the system is in fast ($|\delta w \tau| < 1$), slow ($|\delta w \tau| > 1$) or intermediate exchange ($|\delta w \tau| \cong 1$). The results are qualitatively consistent with the exchange theory, although temperature dependent measurements of the dephasing time are necessary to verify this mechanism.

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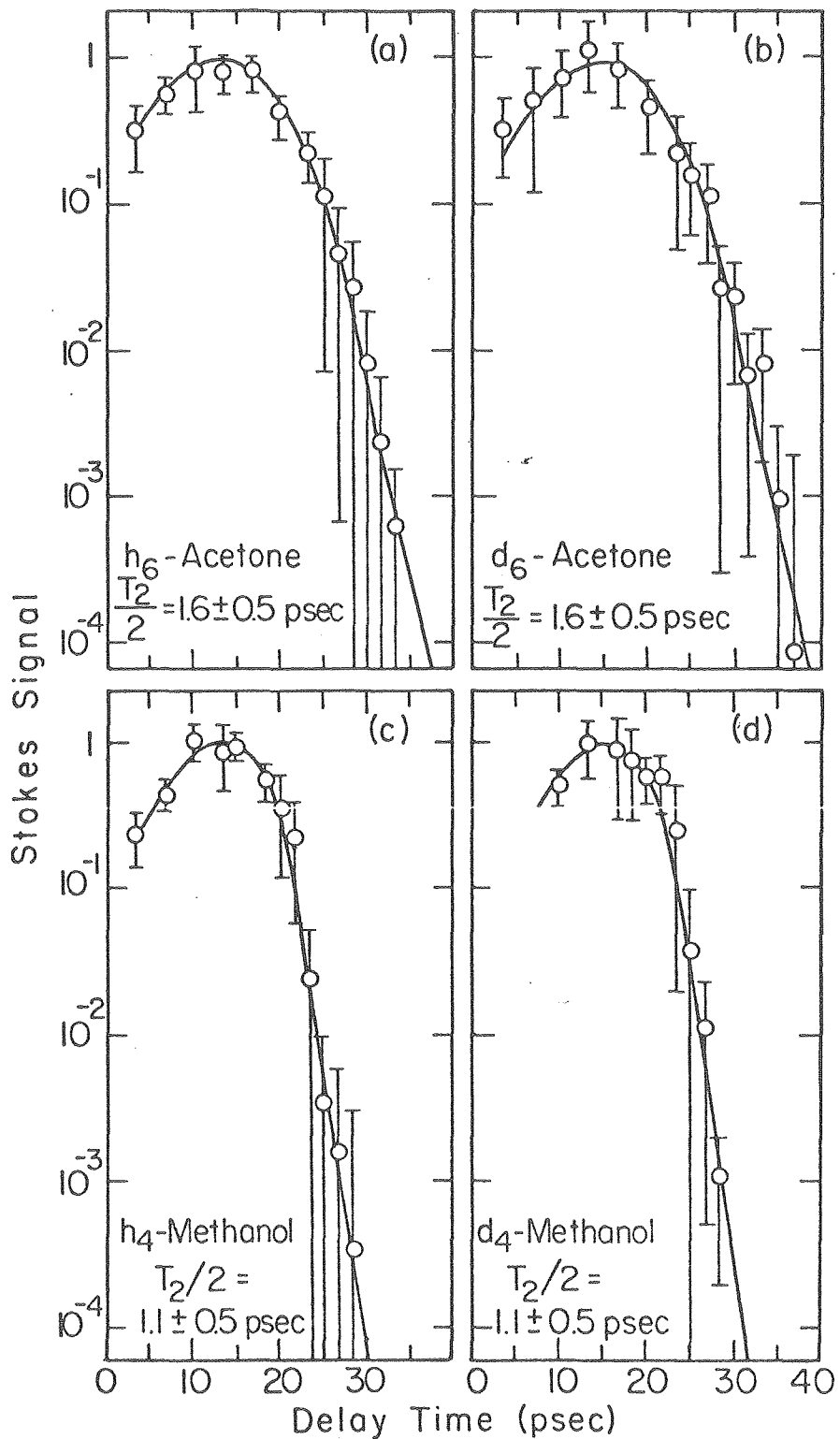(12) R. L. Carman, M. E. Mack, F. Shimizu, and N. Bloembergen, Phys. Rev. Lett. $\underline{23}$, 1327 (1969).

Table 1:

	$\tilde{\nu}[cm^{-1}]$	$\rho[g/cm^3]$	$\eta[cP]$	$\tau_c[10^{-13}s]$	T_2(IBC) (psec)	T_2(exptl) (psec)
Methanol	2836	0.7914	0.597	0.37	0.55	2.4
Methanol-d_4	2074	0.888	0.597	0.41	1.39	2.6
Acetone	2925	0.7899	0.327	0.99	2.31	3.0
Acetone-d_6	2108	0.8722	0.327	1.09	5.62	3.3

Figure Caption

Figure 1: Coherent stokes signal as a function of delay time t_D.
        (a) h_6-acetone
        (b) d_6-acetone
        (c) h_4-methanol
        (d) d_4-methanol

Figure 1