

## Critical Test of Vibrational Dephasing Theories in Liquids by Use of Selective, Coherent, Picosecond Stokes Scattering

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A picosecond coherent probing technique is used to determine the homogeneous vibrational linewidth in liquids. Isotope effects on the symmetric  $\text{CH}_3$ -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.<sup>1,2</sup> This technique overcomes the problem of inhomogeneous broadening and allows homogeneous linewidths to be determined in liquids with unknown inhomogeneity.<sup>3</sup>

Many theoretical models for vibrational dephasing in liquids and solids have been proposed.<sup>4-10</sup> The major approaches are based on energy exchange mechanisms,<sup>4</sup> hydrodynamic theories,<sup>5</sup> and binary-collision models.<sup>6,7</sup> These theories predict functional dependences on macroscopic properties such as temperature  $T$ , density  $\rho$ , and viscosity  $\eta$ , 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  $T$ ,  $\rho$ ,  $\eta$ , 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  $\text{CH}_3$ -stretching vibration in methanol and acetone.

Isotope substitution allows vibrational frequencies to be correlated with calculated normal

modes.<sup>11</sup> To a very high order of approximation, the potential function is insensitive to isotopic substitution<sup>11</sup>; 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 mode-locked Nd:glass laser. After amplification and frequency doubling the pulses had a duration of  $\approx 5$  psec and a spectral bandwidth (full width at half maximum) of  $\approx 4.0 \text{ cm}^{-1}$ , yielding a bandwidth product of  $\approx 0.6$ , 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  $\text{CH}_3$ -stretching vibrations were excited by stimulated Raman scattering and probed by coherent Stokes Raman scattering.<sup>1</sup> From the experimental probing geometry a selectivity  $\delta\nu \geq 0.3 \text{ cm}^{-1}$  ( $T_2/2 \leq 18$  psec) was obtained, indicating that the collinear Stokes probing technique could detect a homogeneously broadened line as narrow as  $0.3 \text{ cm}^{-1}$ .<sup>2</sup> 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 to 2.7 psec for inhomogeneously broadened vibrational linewidths.

The coherently scattered Stokes probe signal and the excitation Stokes spectrum were separat-

ed 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  $d_4$ -methanol and  $d_6$ -acetone, both with 99.5 at. % D, were used. Figure 1 shows the coherently scattered Stokes signal of the symmetric  $\text{CH}_3$ -stretching vibration of acetone ( $\bar{\nu}=2925\text{ cm}^{-1}$ ) as a function of probe pulse delay. On the average, we obtained a dephasing time of  $T_2/2=1.5\pm 0.5$  psec for acetone. The dephasing curve of the symmetric  $\text{CD}_3$ -stretching vibration in deuterated acetone ( $d_6$ -acetone) is also shown in Fig. 1. For  $d_6$ -acetone, the average of several runs was  $T_2/2=1.65\pm 0.5$  psec. Therefore, the ratio of the dephasing times,  $T_2^d/T_2^h$ , for deuterioacetone/protoacetone is approximately equal to 1.

For the symmetric  $\text{CH}_3$ -stretching vibration of methanol ( $\bar{\nu}=2836\text{ cm}^{-1}$ ), we observed an average of  $T_2/2=1.2\pm 0.5$  psec. This result is shorter than the result obtained by Laubereau, Wochner, and Kaiser<sup>1</sup> under similar conditions. 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  $\text{CH}_3$ -stretching vibrations of methanol as was previously reported by Carman *et al.*<sup>12</sup> 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  $\text{CH}_3$ -stretching vibrations were excited. Nonlinear 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  $\text{CD}_3$ -stretching vibration in  $d_4$ -methanol we determined an average of  $T_2/2=1.3\pm 0.5$  psec, giving a ratio of  $T_2^d/T_2^h\approx 1$ . The experimental results are compiled in Table I.

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.

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

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

where  $\tau_c$  is the elastic collision time,  $\omega$  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,  $\mu$ , and the mass factor  $\gamma$  appearing in the repulsive experimental interaction potential. According to Fischer and Laubereau,<sup>6</sup> the mass of the  $\text{CH}_3$  group, not the mass of the total molecule, is used to determine the reduced mass of the  $\text{CH}$ -stretching vibration. This leads to

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

where  $m_C$  is the mass of the carbon atom,  $m_H$  is the mass of the hydrogen or deuterium atom,

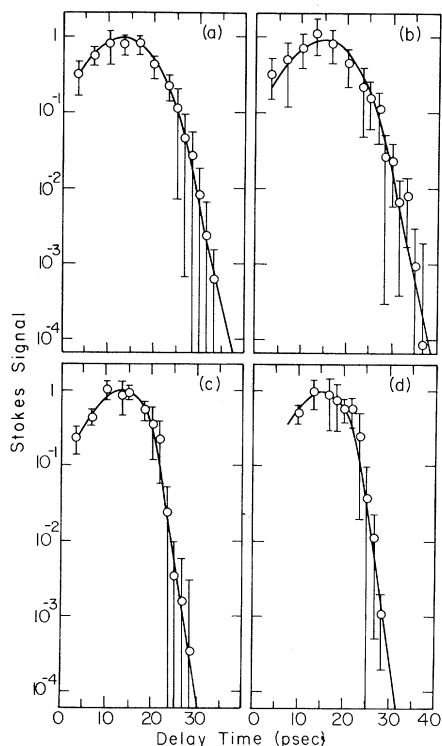


FIG. 1. Coherent Stokes signal as a function of delay time  $t_D$ . (a)  $h_6$ -acetone, (b)  $d_6$ -acetone, (c)  $h_4$ -methanol, (d)  $d_4$ -methanol.

TABLE I. Parameter values, IBC-model  $T_2$  times, and experimental  $T_2$  results.

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

and  $\cos\alpha = 1/\sqrt{3}$ .

Table I gives all parameters which are necessary to compute the dephasing times. The collision time  $\tau_c$  is given by

$$\tau_c = \rho d^2 / 6\eta, \quad (3)$$

where  $\rho$  is the density,  $d$  is the molecular distance, and  $\eta$  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).<sup>5</sup> The only differences are in replacement of 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 (IBC).

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  $\text{CH}_3$ -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.<sup>4</sup> Since there is no change in the potential function upon isotopic substitution, the product  $\delta\omega\tau$ , which determines the dephasing time in terms of the exchange theory, remains nearly unchanged.

In exchange theory,  $\delta\omega$  is a frequency shift resulting from anharmonic coupling in the intramolecular potential and  $\tau$  is given by  $\tau = W_+^{-1} \times \exp(-E_i/kT)$ , 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 or decrease by a *small* amount depending on whether or not the system is in fast ( $|\delta\omega\tau| < 1$ ), slow ( $|\delta\omega\tau| > 1$ ), or intermediate exchange ( $|\delta\omega\tau| \approx 1$ ). 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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## Ion-Acoustic Double Layers

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It is found, by means of numerical simulations, that an ion-acoustic instability ( $v_d < v_{te}$ ) results in the formation of double layers in a sufficiently long system. Anomalous resistivity generated by the ion-acoustic instability causes the buildup of a dc potential which in turn accelerates electrons further to enhance the original instability leading to the formation of double layers.

Anomalous resistivity and double layers have long been important subjects in both laboratory and space plasmas.<sup>1-5</sup> Because of the highly nonlinear aspect of double layers, existing theories deal only with the steady-state solutions.<sup>1, 2</sup> In order for double layers to be a reality, however, one must prove that they can be reached from a realistic initial condition. Computer simulation is the most powerful tool to study this dynamical process. The necessary condition for the formation of double layers obtained from the previous simulations,<sup>3, 4</sup> the steady-state theory,<sup>1</sup> and laboratory experiments<sup>5, 6</sup> is that the electron drift velocity exceed the electron thermal velocity ( $v_d > v_{te}$ ), or double layers are a result of two-stream (Buneman) instability.

There are, however, observations<sup>7</sup> which support the existence of double layers (electrostatic shocks) along the auroral field lines where the electron drift speed is much less than the electron thermal speed. The low-intensity field-aligned current may be able to excite electrostatic ion-cyclotron waves or ion-acoustic waves, but cannot excite two-stream instability.<sup>8</sup>

In this Letter we show that, contrary to the earlier conclusion, double layers can be formed even if the electron drift speed is less than the electron thermal speed. This is proved by means of extensive one-dimensional particle simulations to be discussed. The underlying physical picture for this new process is the following: Suppose the system under consideration is sufficiently long. Then, no matter how small, the anomalous resistivity may be caused by an ion-acoustic in-

stability, and the dc potential buildup associated with the localized resistivity in the system becomes large enough to accelerate electrons further. The acceleration in turn should enhance the original instability so that the anomalous resistivity and dc potential are further enhanced by a bootstrap action. Therefore, a new stage of the instability will take place which would not happen in a short system where little effective acceleration occurs.

In order to study this process in detail, we have performed one-dimensional particle simulations with the system length  $L = 1024\lambda_D$ ,  $512\lambda_D$ , and  $256\lambda_D$ , and  $128\lambda_D$  where  $\lambda_D$  is the initial electron Debye length which is equal to computational mesh size. Initially the density is uniform and the electron velocity distribution is assumed to be a drifting Maxwellian.  $T_e/T_i = 20$ ,  $M_i/M_e = 100$ , and  $v_d$  (electron drift speed)  $= 0.6v_{te}$ . A smaller drift speed at  $v_d = 0.3v_{te}$  and  $L = 1024\lambda_D$  is also tried with the other parameters remaining the same. Periodic boundary conditions are used throughout the calculations. No external potential is applied across the system.

Figure 1 shows the results of  $L = 1024\lambda_D$  and  $v_d = 0.6v_{te}$  for the electron and ion phase-space distributions, Figs. 1(a) and 1(b), the electron and ion density profiles in real space, 1(c) and 1(d), and the potential profile, 1(e), at  $t\omega_{pe} = 960$  when the localized structure (double layer) has fully developed. In Fig. 1(e), a large potential jump comparable to the thermal energy,  $e\Delta\phi/T_e \approx 1$ , can be seen across the double layer. Along with the potential jump, large density discon-