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Contents

Femtosecond Dephasing Processes of Molecular Vibrations

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Dynamical and static interactions in molecular liquids may be deduced from Raman and infrared spectra. In a limited number of cases the shape of the spectral band is understood by a definite line-broadening mechanism. Many realistic liquids, on the other hand, show complicated structures with non-Lorentzian asymmetric and partially overlapping bands. In addition, the spectral bandwidth may be considerably broader than 10 cm^{-1} corresponding to molecular time constants of less than 1 ps. The high time resolution now available in femstosecond coherent anti-Stokes Raman spectroscopy /1-3/ gives the possibility to study various line-broadening mechanisms on the time scale of the molecular interaction.

In the present experiments we applied a femtosecond laser system allowing tunable excitation of vibrational modes between 300 cm^{-1} and 3000 cm^{-1}. The laser pulses derived from a femtosecond unidirectional ring dye laser (pulse duration t_p = 80 fs) serve as the exciting and probing laser pulses at frequencies ω_L /4/. A standard synchronized tunable picosecond dye laser supplies the Stokes pulses at ω_S. Coherently scattered anti-Stokes light at $\omega_{AS} = 2\omega_L - \omega_S$ is detected as a function of the time delay between probing and exciting pulses (of perpendicular polarization). The high time resolution of the experimental system is readily demonstrated in Fig.1 showing the coherent anti-Stokes signal obtained from the OD-stretching mode of liquid D_2O. The full circles are experimental data taken at a sample temperature of 65°C. These data points are close to the experimental response function determined

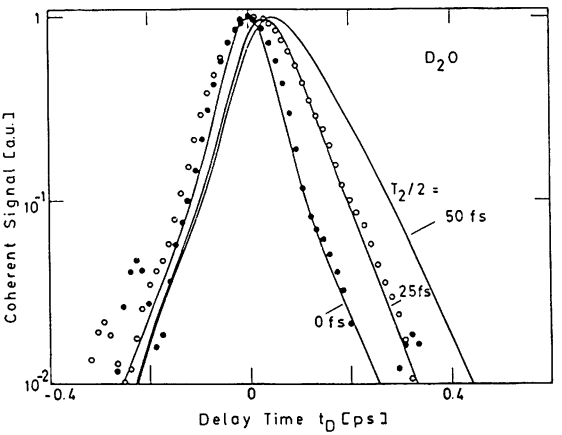

Fig. 1 Time-resolved coherent Raman signal from the OD vibration of liquid D_2O at 21°C (open circles) and 65°C (closed circles). The solid curves are calculated using a decay time $T_2/2$ of 0fs, 25fs, or 50fs.

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by a cross-correlation experiment. A different signal is obtained when the sample is held at a lower temperature of 21°C (open circles). Now the decay of the signal is delayed. The solid curves are calculated using the experimental response function and decay times of $T_2/2$ = 0, 25 fs, and 50 fs. We interpret the experimental data as follows: At low temperatures the coherent experiment studies the hydrogen bonded D_2O molecules. These complexes have a somewhat lower vibrational frequency than the non-bonded D_2O. We tentatively assign the dephasing time $T_2/2$ = 25 fs to these D_2O complexes. When the sample is heated the hydrogen-bonded complexes break up and the experiment probes the liquid of "monomeric" molecules. A very rapid decay of the signal is observed which is not resolved in our experiment.

Interesting information is obtained when studying the CH_3-stretching modes of liquid methanol. The spontaneous Raman spectrum of methanol shows two strong bands at 2835 cm^{-1} and 2943 cm^{-1}. In addition there are large shoulders around the two major lines. Time-resolved coherent Raman scattering gives the result presented in Fig.2 (solid points). The signal exhibits a pronounced beating structure superimposed to an exponential decay. The solid curve of Fig.2 was calculated using homogeneous dephasing times for the two Raman-active modes. This curve fits the experimental points quite well. In order to take into account the possibility of inhomogeneous broadening, the calculation was repeated with an inhomogeneous contribution of 25% and 50% to the Raman linewidth (see broken curves of Fig.2). These curves noticeably deviate from the experimental data points. We conclude that the CH-stretching modes of methanol are predominantly homogeneously broadened.

Results on the molecular interactions are obtained when measuring the CH-stretching modes of liquid acetonitrile. In Fig.3a the coherent signal decay is shown over three orders of magnitudes. At later delay times the signal follows the exponential decay representing homogeneous dephasing with T_2 = 1.74 ps. At earlier delay times the experimental data deviate from the exponential slope. This fact is apparent from Fig.3b where the signal is multiplied by $\exp(2t_D/1.74ps)$. An overshoot of the signal is seen at early delay times of up to 1.5 ps. Our first attempt was to fit the experimental decay curve by a Kubo line-shape model with an exponential decay of the frequency correlation function /5/. A ready agreement between theory and experiment was

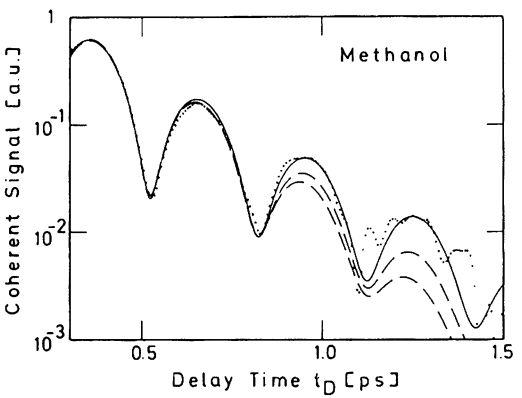

Fig. 2 Coherent signal of liquid methanol (points) and calculated curves assuming homogeneous dephasing (solid curve) and inhomogeneous line-broadening (broken curves) for 25% and 50% inhomogeneous contributions.

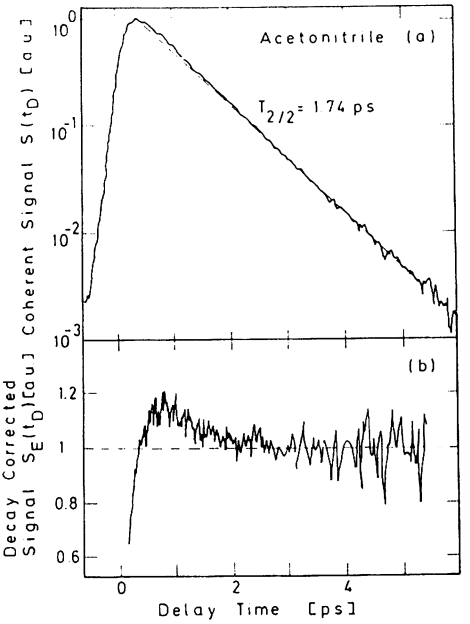

Fig. 3 Coherent signal from liquid acetonitrile. Intermolecular interactions show up by the overshoot of the signal at early delay times.

only obtained with a more elaborate theory, taking into account the close packing of the molecules in the liquid and the attractive part of the molecular interaction /6/.

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