

Local structure and dynamics of liquid acetone by heterodyned 2D IR spectroscopy

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Abstract. Vibrational energy flow and dynamical structures in neat liquid acetone and isotopic mixtures from 2D-IR spectra, photon echoes and transient gratings of its carbonyl modes, show ultrafast reorientation and energy transport.

Introduction. Multiple pulse two-dimensional IR spectroscopy promises to obtain snapshots of molecular structures in the condensed phase.[1] Here we show that it exposes the dynamics of the local structure of liquids: results for liquid acetone are obtained. The liquid responds like a molecular excitonic system undergoing structure fluctuations. Isotope dilution with acetone-2-¹³C allowed measurement of the coupling between molecules. New heterodyned 2D transient grating experiments reveal the dynamics of intermolecular energy transfer.

Experimental Methods. Femtosecond IR pulses (120 fs, 1 μJ, 1715 cm⁻¹) were generated by mixing the signal and idler beams of an 800 nm pumped OPA in an AgGaS₂ crystal. The output was split into three equal beams (wavevectors k_1 , k_2 , and k_3 ; each 300 nJ) and a local oscillator beam (k_{LO} ; 3 nJ) which was combined with the signal field in the phase-matched direction $k_s = -k_1 + k_2 + k_3$, and focused into a single channel HgCdTe detector. The time interval between k_1 and k_2 is τ , T is the interval between k_2 and k_3 , and t is the interval between k_3 and k_{LO} . Photon echo experiments are done by scanning τ and t with $T = 0$. In transient grating experiments, T and t are scanned while keeping $\tau = 0$.

Results and Discussion. For the 50:50 isotope mixture the 2D spectrum shows the ¹²C=O and ¹³C=O stretches of acetone molecules as diagonal peaks. The cross peaks between the two isotope distributions are present but quite weak. For the 3% mixture, the 2D spectrum, shown in Fig. 1(a), exhibits a diagonal peak corresponding to the ¹³C=O stretch, while the corresponding ¹²C=O diagonal peak shows a strongly attenuated echo field at the ¹²C=O fundamental frequency. Pronounced off-diagonal peaks are now observed, characteristic of the existence of intermolecular coupling between ¹³C=O acetone molecules with their surrounding ¹²C=O acetone molecules. Figure 1(b) and (c) show slices through the magnitude and real part of the 2D spectrum at $\omega_i = 1671$ cm⁻¹, taken at two polarization conditions (XXXX) and (XYYX) for (k_1, k_2, k_3, k_{LO}) . The off-diagonal peak retains its phase and has similar intensity in the two polarizations, indicating that the coupling is from neighbors having nearly parallel or anti-parallel C=O groups.

A recent Monte Carlo simulation suggests that the nearest neighbors in liquid acetone can be classified into two groups: one is around 4 Å separation in a side-by-side anti-parallel orientation. The other, near 5.3 Å, is in a head-to-tail parallel

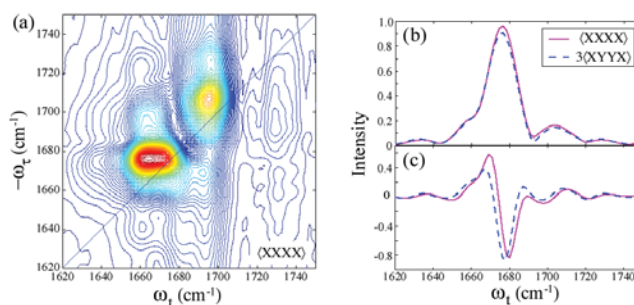


Fig. 1. (a) The absolute magnitude 2D photon echo spectrum of liquid acetone isotopic mixture containing 3% acetone- ^{13}C . Sections through the magnitude (b) and real part (c) of the 2D spectra at $\omega_t = 1671 \text{ cm}^{-1}$, taken at (XXXX) and (XYYX) polarization conditions.

arrangement [2]. The transition dipole contributions to the intermolecular coupling are -3.3 and -4.4 cm^{-1} respectively for these two arrangements. Our measurements of the cross peaks are consistent with both these predictions. The polarization condition $(-\pi/4, \pi/4, \pi/2, 0)$ eliminates signal from aligned molecules and can be used to investigate coupling to molecules of different orientations.

The existence of intermolecular coupling is further verified by the results from heterodyned transient grating experiments. Figure 2(a) shows the absolute magnitude spectrum as a function of T for the 3% mixture. A slice through $\omega_t = 1656 \text{ cm}^{-1}$ clearly shows oscillations with a period of 830 fs. These oscillations give rise to a cross peak in the 2D spectrum at $\omega_T = 40 \text{ cm}^{-1}$, corresponding to the isotope shift. Such a cross peak is expected to arise from coupling between isotopomers. Oscillations of 3.3 ps were also found: they were most pronounced in the $^{12}\text{C}=\text{O}$ regions and in the neat liquid. The possible influence of the strong attenuation of the pulse on the form of these oscillations is currently under study.

The transient grating signals in the time domain exhibit significant dependence on the isotope compositions. Figure 2(b) shows the T dependence of the heterodyned transient grating anisotropy for the $^{12}\text{C}=\text{O}$ peak in neat acetone and the $^{13}\text{C}=\text{O}$ peak in the 3% mixture. The anisotropy was obtained by taking the difference between the signals for (XXXX) and (XXYY) polarization conditions, and normalized by the isotropic signal. Clearly neat acetone exhibits faster anisotropy decay. Similar behavior is found in the integrated transient grating signals where neat liquid shows faster decay compared to the 50:50 mixture.

Coupling is also indicated by changes in the linear spectral linewidths as a function of isotopic composition: e.g. the bandwidths of $^{12}\text{C}=\text{O}$ in neat acetone and the $^{13}\text{C}=\text{O}$ in the 3% mixture are 16 cm^{-1} and 10 cm^{-1} , respectively. Integrated three pulse photon echoes of the 50:50 mixture exhibit oscillations and decay slower than those of neat acetone. The correlation function of the $^{13}\text{C}=\text{O}$ peak in the 3% isotope mixture can be measured by heterodyned three pulse photon echo. The extent of excitonic delocalization in the liquid is controllable by varying the isotope concentration. This effect on the correlation function is currently under investigation.

The current results suggest a slowed energy transfer between neighboring molecules in the isotopic liquid due to the energy mismatch. Also plotted in Fig. 2(b) is the expected anisotropy from the rotational correlation time of 0.75 ps

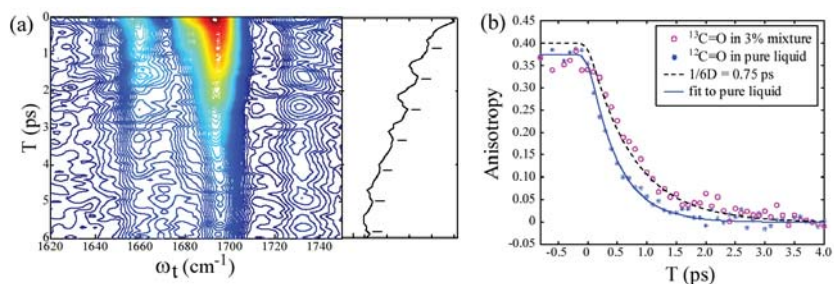


Fig. 2. (a) The absolute magnitude 2D transient grating spectrum of the 3% mixture for the (XXYY) polarization condition. The side panel shows a slice through the spectrum at $\omega_t = 1656 \text{ cm}^{-1}$. (b) Heterodyned transient grating anisotropy of the $^{12}\text{C}=\text{O}$ peak in neat acetone (*) and the $^{13}\text{C}=\text{O}$ peak in the 3% isotope mixture (o).

measured by Rayleigh scattering [3]. The anisotropy decay of the 3% mixture coincides with this curve very well, suggesting it is dominated by molecular reorientation. However in neat acetone the energy transfer (1.5 ps) between acetone molecules influences the decay. For a qualitative picture of the energy transfer, we consider an irreversible energy transfer process between two equivalent vibrators. In the presence of fast and uncorrelated fluctuations of the two levels, the energy transfer rate may be estimated by a Golden rule limit. For a coupling strength of 5 cm^{-1} , the rate is 1.7 ps. The rate slows down to 12 ps when there is a 40 cm^{-1} energy difference between the two levels. Although we do not expect such a simple picture to prevail, the possibility that only a few strongly coupled but not all nearest neighbors participate in the energy transfer process is suggested by this comparison to theory. This point will be addressed by simulations of the coupling and energy fluctuations.

Conclusions. We have measured the complex nonlinear response of liquid acetone in the region of $6 \mu\text{m}$. Isotope dilution studies indicate the presence of intermolecular coupling between parallel or anti-parallel neighbors. Evidence is obtained for delocalization of the C=O mode and irreversible energy transfer among acetone molecules. This transport corresponds to relaxation amongst the partially delocalized states of the liquid. These new and exciting results demonstrate the power of nonlinear methods in revealing structure and dynamics of liquids.

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