

P. F. Barbara · W. H. Knox  
G. A. Mourou · A. H. Zewail (Eds.)

---

# Ultrafast Phenomena IX

Proceedings  
of the 9th International Conference,  
Dana Point, CA, May 2-6, 1994

With 384 Figures



Springer

# Femtosecond Two-Dimensional Raman Spectroscopy of Liquid Water

S. Palese<sup>1</sup>, J.T. Buontempo<sup>1</sup>, Y. Tanimura<sup>1</sup>, S. Mukamel<sup>1</sup>, R.J.D. Miller<sup>1</sup>, and W.T. Lotshaw<sup>2</sup>

<sup>1</sup>Department of Chemistry and Institute of Optics, University of Rochester, Rochester, NY 14627-0216, USA

<sup>2</sup>General Electric Research and Development Center, P.O. Box 8, Schenectady, NY 12301, USA

**Abstract.** Higher order Raman spectra for water have been calculated, within the Brownian oscillator model, using femtosecond optical Kerr effect (OKE) results to demonstrate the distinctions between the homogeneous and inhomogeneous limits. Experimental results suggest this distribution is inhomogeneously broadened.

Critical to the understanding of condensed phase reaction dynamics is the understanding of a solvent's response to and influence on the system dynamics. Although models of a solvent's vibrational and orientational dynamics can be tested against infrared and Raman studies of the neat solvent, there are ambiguities as the spectral density is usually masked by inhomogeneous broadening. However, valuable information about the solvent nuclear dynamics can be extracted from nonlinear spectroscopies such as infrared and Raman echoes. Using the formalism of Tanimura and Mukamel [1] we have calculated the 3rd, 5th, and 7th order Raman spectra for liquid water employing a multimode Brownian oscillator model to represent the water modes. This model is expected to be appropriate for liquid water because it accounts for nuclear dynamics occurring on a finite time scale, extrapolating continuously between homogeneous and inhomogeneous limits.

The  $\chi^{(3)}$  response function of water was experimentally determined using OKE spectroscopy with pulse widths of 38 fs to provide the spectral density between 1-800  $\text{cm}^{-1}$ . The analytical fit to these results and calculated free induction decay is shown in fig. 1. Using the fit, the higher order Raman responses were calculated in the

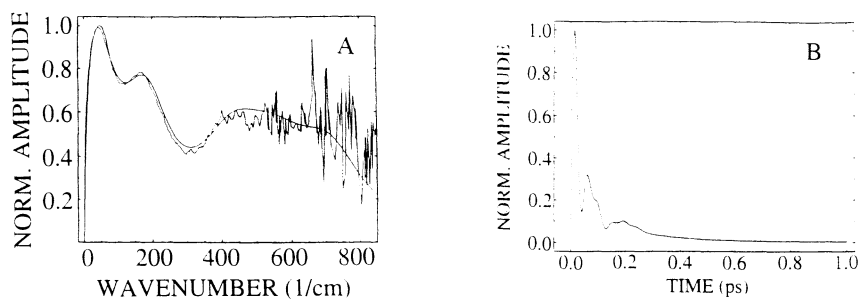


Figure 1. The  $\chi^{(3)}$  nuclear response for water and fit. A) Frequency domain. The imaginary part of the FFT of the heterodyne, out-of-phase OKE response. B) Inverse sine transform of the frequency domain fit.

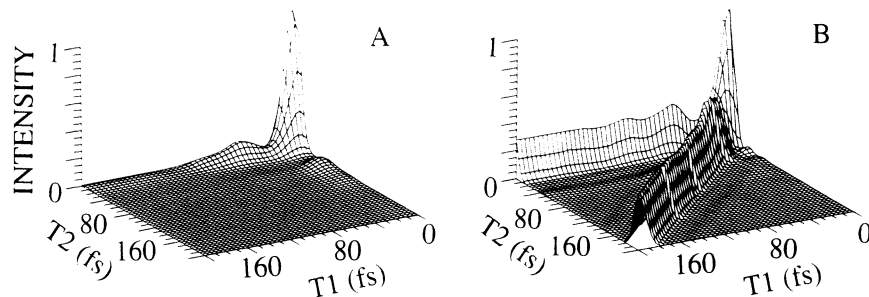


Figure 2. The calculated  $|\chi^{(5)}|^2$  response. A) Homogeneous limit. B) Inhomogeneous limit. A) T1- Excitation delay, T2- Probe delay from second excitation.

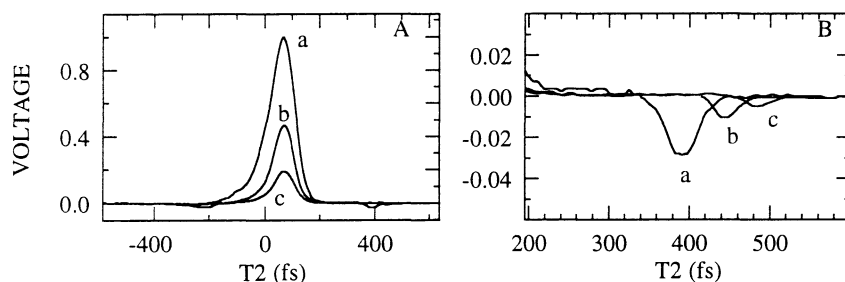


Figure 3. The correlation response collected along the diffracted beam direction (A). T1 = a) 253 fs, b) 303 fs, c) 353 fs. B) Recurrence at  $\approx 2(T1)$  expanded.

homogeneous and inhomogeneous limits. These calculations are shown in fig. 2 for the 5th order ( $\propto \chi^{(5)}$ ) response. The 7th order ( $\propto \chi^{(7)}$ ) response, which is analogous to the Raman echo, shows similar behavior. In 5th order there are clear distinctions between these limits even for a multimode system as complex as the intermolecular modes of water. The most valuable diagnostic, in this regard, is the rephasing of the coherence in the nuclear polarization for the inhomogeneous limit.

Preliminary three pulse grating studies ( $\chi^{(3)}$   $k_D = (k_1 - k_2) + k_{\text{probe}}$ ,  $\chi^{(5)}$   $k_D = (k_1 - k_1') + (k_1'' - k_2) + k_{\text{probe}}$ ) conducted using amplified (300 nJ/pulse) 60 fs pulses suggest that the water distribution is inhomogeneously broadened (fig. 3). The large peak is the  $\chi^{(3)}$  contribution. In this configuration the decay of the recurrence is not due to the homogeneous relaxation time of liquid water, but instead to the temporal overlap of the 1st and 2nd pulses which form the 2nd Raman excitation. However this configuration has superior S/N in discriminating the recurrence relative to collection along the probe direction, due to the presence of a strong background from the two pulse homodyne signals. Even for signal collection along the probe direction mixing between the various orders, because of the square law detector, will lead to an observed decay of the recurrence which is not related to the homogeneous lifetime.

## References

1. Y. Tanimura and S. Mukamel, J. Chem. Phys. **99**, 9496 (1993).