

Probing Intermolecular Couplings in Simulations of the Two-Dimensional Infrared Photon Echo Spectrum of Liquid Water

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Abstract. Simulations of the 2D-IR photon echo spectrum of the OH stretching vibration in liquid water were presented, explicitly including intermolecular coupling and nonadiabatic effects. Close agreement with the experimental polarization anisotropy was found for surprisingly small intermolecular couplings. Increased sensitivity of the anharmonic two-dimensional OH stretching potential causes the fast spectral diffusion dynamics.

Introduction

The unique properties of liquid water ultimately originate from the correlations and intermolecular couplings in the extended hydrogen bond network. Two-dimensional photon echo spectroscopy of the OH stretch vibration has proven the most direct probe of fluctuations and correlations in the local structures. The recent experimental observation of extremely fast memory loss in pure water [1,2] is still pending a full understanding of the underlying mechanisms and theoretical description due to difficulties in treating the resonant energy transfer in the liquid.

Here, we present our most recent simulation results [3] using numerical integration of the Schrödinger equation to calculate two-dimensional photon echo and polarization anisotropy response of the OH stretch vibration in liquid water. This is the first work explicitly treating intermolecular vibrational coupling and anharmonic effects, as well as fluctuations of the transition frequencies and dipole moments and their anharmonicities. Relatively small intermolecular couplings are found sufficient to reproduce experimental energy transfer time scales due to rapid fluctuations of the two-dimensional OH stretch potential, distinctly different from one-dimensional stretch potentials as in HOD. These fluctuations also lead to the fast loss of correlations observed in the two-dimensional spectra.

Theory

We use molecular dynamics simulation of 64 H₂O molecules at room temperature in combination with an *ab initio* electrostatic map to obtain local OH stretch frequencies, dipole moments, and anharmonicities of both. The distribution of fundamental frequencies is shown in Fig. 1 (a). We then construct the time-dependent anharmonic vibrational Hamiltonian using the 128 local anharmonic modes (symmetric and asymmetric stretch for 64 molecules) as basis. Intermolecular coupling is included using dipole dipole coupling. To study different coupling regimes, we adjusted the dielectric constant in the dipole dipole coupling term. Statistical analysis of the couplings allows extraction of the average next neighbour coupling κ .

Calculation of the 3rd order vibrational signal requires summation of 6 different Liouville diagrams. The propagation of the time dependent multimode system is performed using numerical integration of the Schrödinger equation [4]. For propagation of the two-particle excitations we use the split operator method, splitting the two-particle Hamiltonian into harmonic and anharmonic parts. Fluctuations and anharmonicities of the transition dipole moments are explicitly treated within the calculated nonlinear response.

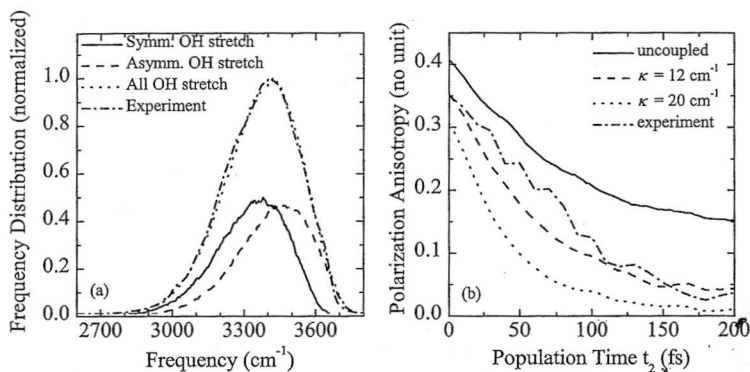


Fig. 1. (a) OH stretch frequency distributions in liquid water generated from all molecular configurations using our electrostatic map; in blue, experimental linear spectrum [5]. (b) Simulated polarization anisotropy for different coupling regimes; in blue, experimental result [2].

Results and Discussion

In Figure 1 (b), we show the simulated polarization anisotropy, calculated from spectrally integrated pump probe signal. The uncoupled system displays a fast initial signal decay due to strong fluctuations of the transition dipole moments accounting for of the signal decay. The remainder of the signal decay is due to fast librational and slow reorientation dynamics. Upon intermolecular coupling, the signal decays speeds up with increasing coupling strength and long lived components vanish entirely. This effect can clearly be assigned to resonant intermolecular energy transfer. Additionally, the initial polarization anisotropy is reduced with increasing coupling strength κ . We find excellent agreement with the experiment for κ as small as 12 cm^{-1} .

The two-dimensional spectra ($\kappa = 12 \text{ cm}^{-1}$) for population times $t_2=0, 100, 200, 500 \text{ fs}$ are displayed in Fig. 2. At $t_2=0$, two peaks corresponding to the fundamental transition and excited state absorption are observed. Both are stretched along the diagonal, indicating initial inhomogeneity of the OH stretch ensemble. As a function of t_2 , both peaks become vertical on different time scales across the spectrum; no single time scale of loss of correlations can be extracted. The red side of the spectrum shows faster dynamics where correlations decay on a 100 fs time scale, whereas on the blue side of the spectrum correlations persist up to 200 fs. These findings are in close agreement with our recent experimental results [2].

The fast loss of correlations is not dominated by energy transfer but rather due to rapid fluctuations of the two-dimensional OH stretching potential in H₂O, leading to mixing between states for fundamental and overtone states. This effect is distinctly different from one-dimensional OH stretching potentials as in HOD. It results in increased sensitivity of the fundamental transitions leading to fast loss of correlations in the two-dimensional spectra. Similarly, strong fluctuations of the transition dipole moments lead to modulations of the intermolecular couplings, opening up many energy transfer pathways, ultimately allowing rapid energy transfer and, consequently, some contribution to memory loss from spatial averaging.

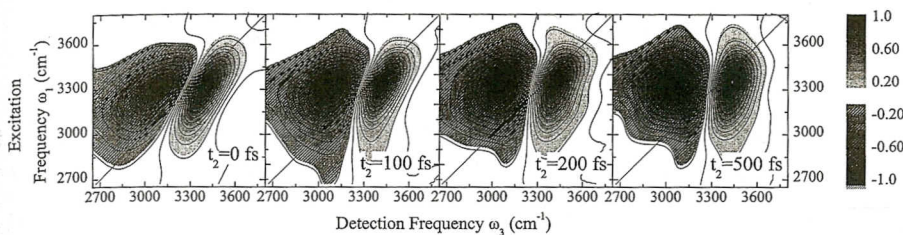


Fig. 2. Simulated 2D-IR spectra of the OH stretch vibration in liquid water for $\kappa = 12 \text{ cm}^{-1}$.

Conclusions

We presented simulations of the two-dimensional photon echo spectra and polarization anisotropy of the OH stretch vibration in liquid water. Our new simulation procedure using numerical integration of the Schrödinger equation allows explicit treatment of intermolecular vibrational coupling for the first time. Average next neighbour couplings of only 12 cm^{-1} were found fully sufficient to reproduce experimental energy transfer time scales. The simulated two-dimensional spectra are in close agreement with recent experimental results.

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