

Nonlinear Vibrational Response of Coupled Anharmonic Systems — Towards the 2D IR Spectrum of H₂O

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The recent experimental observation of extremely fast memory loss in pure water¹ is still pending a full understanding of the underlying mechanisms and theoretical description, mainly due to difficulties in treating the resonant energy transfer in the pure liquid. We present a new method of numerical propagation of the vibrational dipole moments that allows for nonlinear signal calculations, fully treating the coupled fluctuating Hamiltonian and Non-Condon effects. This approach will, for the first time, allow us to calculate two-dimensional infrared (2D IR) spectra of the OH-stretching vibration in pure water.

We use molecular dynamics (MD) simulations in combination with an ab initio electrostatic map² to gain the fully anharmonic, fluctuating vibrational Hamiltonian and transition dipole moments. We then numerically propagate initially excited dipole moments in the molecular basis according to the different Liouville pathways necessary to calculate the 3rd order signal.^{3,4}

As a first application, we studied the effect of intermolecular coupling on nonlinear vibrational response using the OH stretching mode in pure HOD as a model system. A constant volume SPC/E water MD trajectory of N = 64 molecules with 0.5 fs time steps at room temperature is generated using the GROMACS-3.3.1 program.⁵ We employ the following Hamiltonian as a function of the MD time step τ for N coupled local modes, using the electrostatic map² of HOD to extract transition frequencies and dipole moments of the OH stretch.

$$\hat{H}(\tau) = \sum_m \varepsilon_m(\tau) \hat{B}_m^\dagger \hat{B}_m + \sum_{m \neq n} J_{mn}(\tau) \hat{B}_m^\dagger \hat{B}_n + \sum_{mn, m'n'} V_{mn, m'n'}(\tau) \hat{B}_m^\dagger \hat{B}_n^\dagger \hat{B}_m \hat{B}_{n'} + \int dr \hat{P}(r) \cdot E(r, \tau) \quad (1)$$

The first two terms describe the free Boson system, where ε_m is the transition frequency of mode m . The intermode coupling J_{mn} is calculated using resonant dipole-dipole coupling. The last term describes the interaction with the optical fields. The third term contains both diagonal (intramolecular) and off-diagonal (intermolecular) anharmonicities. The off-diagonal anharmonicities, in this model, arise from anharmonicities in the transition dipole moments (see Equ. 2) affecting the resonant dipole dipole coupling.

$$\hat{\mu}(\tau) = \sum_m \mu_m(\tau) (\hat{B}_m^\dagger + \hat{B}_m) + \sum_m \Delta\mu_m(\tau) \hat{B}_m^\dagger (\hat{B}_m^\dagger + \hat{B}_m) \hat{B}_m \quad (2)$$

Here, μ_m is the 0→1 fundamental transition dipole moment and $\Delta\mu_m$ is the anharmonicity of the 1→2 transition dipole moment. The propagation of initially excited dipole moment is performed using numerical integration of the Schrödinger equation ($\hbar = 1$).

$$\hat{G}(\tau_2, \tau_1) = -i\Theta(\tau_2 - \tau_1) \prod_{\tau=\tau_1}^{\tau_2-\Delta\tau} \exp(-i\hat{H}(\tau)\Delta\tau) \quad (3)$$

\hat{G} propagates the system from τ_1 to τ_2 , $\theta(\tau)$ is the usual Heaviside function, $\Delta\tau = 1$ fs. The nonlinear vibrational signal is calculated in the impulsive limit by dipole interactions (Equ. 2) and propagations (Equ. 3) following the six necessary Liouville pathways.^{3,4}

The matrix exponential in Equ. 3 is calculated exactly for single particle excitations. Propagation of the two-particle excitations needed for the excited state absorption diagrams,⁴ however, poses some difficulties. The large size of the symmetrized two-particle basis being $N(N+1)/2$ makes the calculation of the matrix exponentials in Equ. 3 computationally extremely expensive. On the other hand, the two-particle diagram contains all the anharmonicities and a very high precision for this propagation is required. We propose a new method of calculating these matrix exponentials. We split the two-particle Hamiltonian into harmonic and anharmonic part and employ the split-operator method⁶ to calculate the total propagator.

$$\exp(-iH^{(2)}\Delta\tau) = \exp(-iH_0^{(2)}\Delta\tau)\exp(-iV\Delta\tau) \quad (4)$$

Here, $H^{(2)}$ denotes the full two-particle Hamiltonian, and $H_0^{(2)}$ is the harmonic part (first two terms in Equ. 1) and V is the anharmonic part (third term in Equ. 1) of $H^{(2)}$. The harmonic exponential can be calculated exactly from factorization of the single-particle propagators, and $V\Delta\tau$ is small enough to allow 1st order Taylor expansion of the exponential with good accuracy. The split operator method gives good accuracy provided small enough time steps.⁷ The calculated 3rd order response functions were averaged over 200 trajectories for each required combination of excitation pulse polarizations.

In Figure 1 (a), we show the impulsive pump probe signal for parallel and crossed parallelization of the pump and probe pulses, with and without intermolecular coupling. The signal was spectrally integrated over the whole OH band. In Figure 1 (b), we plot the polarization anisotropy, calculated from these pump probe transients. The signal of the uncoupled system shows two contributions, an early damped oscillation (oscillation period ~ 70 fs, damping constant ~ 35 fs, amplitude ~ 0.025) due to librational modulation and a slower reorientation of the transition dipoles with a time constant of ~ 950 fs. Switching on the intermolecular coupling, we observe these two processes to be negligible and the signal is now dominated by intermolecular energy transfer.

The main interest of this study is the effect of the intermolecular coupling on the nonlinear signal, and in particular the 2D spectra, when entering the coupling regime observed for pure H₂O.¹ Therefore, we adjusted the one free parameter in the model, that is the dielectric constant ϵ in the resonant dipole dipole coupling, to reproduce the anisotropy decay of ~ 80 fs observed in H₂O.^{1,8} The resulting ϵ is ~ 40 which is about two times smaller than the value expected for water.⁹ This, however, can be well understood from single-mode character of our HOD model system that provides only half as many accepting modes per unit volume. For this value of ϵ , we extract an average next neighbor coupling of 25 cm^{-1} .

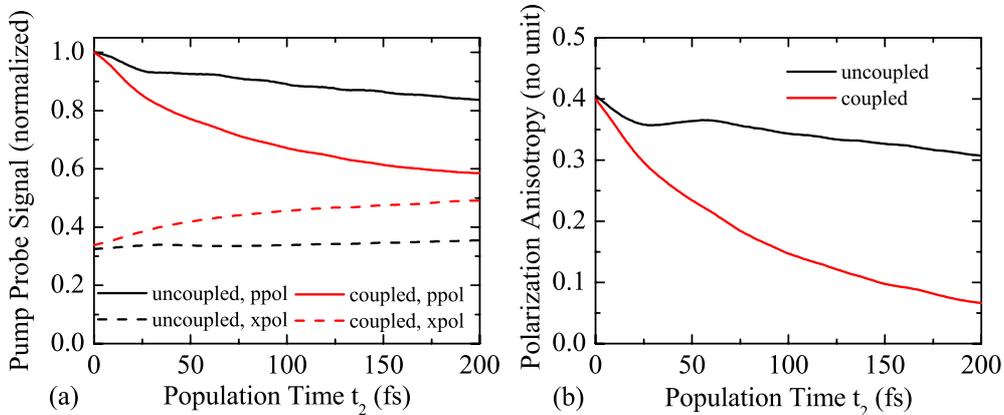


Figure 1. (a) Spectrally integrated, impulsive pump probe signal, parallel (solid) and crossed (dashed) polarization for the uncoupled (black) and coupled (red) system. (b) Transient polarization anisotropy of the OH-stretching vibration. Upon coupling (red), resonant energy transfer dominates the signal decay, librational modulation and reorientation dynamics become negligible.

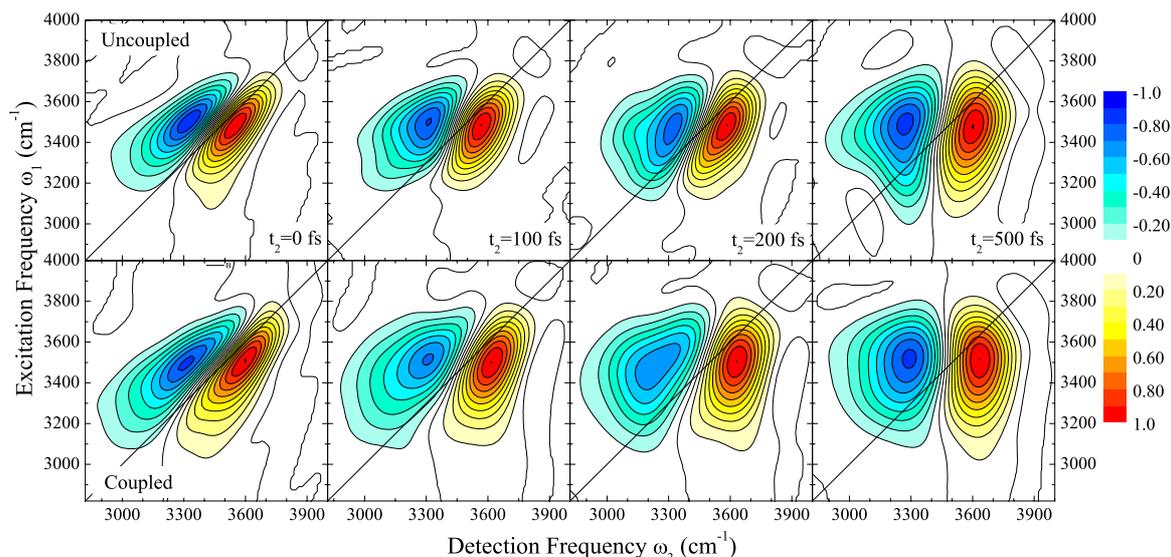


Figure 1. 2D IR spectra of the OH stretch in pure HOD at population times $t_2 = 0, 100, 200, 500$ fs. The coupled system shows slightly broader spectral response, as well as moderately faster decay of frequency correlations.

In Figure 2, we compare the 2D IR spectra of the uncoupled and coupled system for population times $t_2 = 0, 100, 200,$ and 500 fs. For both systems, we see an initial inhomogeneity corresponding to an initial distribution of molecular environments. The spectra of the uncoupled system evolve with t_2 , exhibiting an averaging of sites on a ~ 500 fs time scale. This agrees well with the intermediate time scales observed in experimental studies system of isolated OH oscillators in a water environment.^{10,11} Upon coupling, we observe two effects. (1) All spectra broaden slightly. This effect is already observed in the linear spectra (not shown) where the coupling leads to an additional broadening of ~ 80 cm^{-1} . (2) The spectral diffusion dynamics speed up moderately. We observe ~ 300 fs spectral diffusion time. Therefore, we conclude that the resonant energy transfer, even though it contributes, does not dominate the extremely fast spectral diffusion observed in 2D IR spectra of pure water systems.¹

In conclusion, we present a new method of calculating nonlinear vibrational signal of moderately sized, fluctuating anharmonic molecular systems by numerical propagation, fully treating intermolecular coupling and non-Condon effects. This approach allows us to estimate the effect of intermolecular coupling on the nonlinear vibrational response. For a pure HOD model system, we observe 80 fs resonant energy transfer for an average next neighbor coupling of ~ 25 cm^{-1} . This intermolecular coupling leads to moderate decrease in spectral diffusion time scales. The method will allow us to calculate the nonlinear vibrational response of H_2O treating all the above effects for the first time.

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