PROBING INTERMOLECULAR COUPLINGS IN SIMULATIONS OF THE 2D-IR PHOTON ECHO SPECTRUM OF LIQUID WATER

ALEXANDER PAARMANN, R. J. DWAYNE MILLER, *Institute for Optical Sciences and Departments of Physics and Chemistry, University of Toronto, Toronto, ON,M5S 3H6, Canada.*; TOMOYUKI HAYASHI, SHAUL MUKAMEL, *Department of Chemistry, University of California, Irvine, California 92697-2025, USA.*.

Two-dimensional infrared photon echo and pump probe studies of the OH stretch vibration provide a sensitive probe of the correlations and couplings in the hydrogen bond network of liquid water. We present simulations of the nonlinear vibrational response of liquid water using numerical integration of the Schrödinger equation with a Hamiltonian constructed to explicitly treat intermolecular coupling and non-adiabatic effects. The simulated two-dimensional spectra are in close agreement with our recent experimental results [a]. The high sensitivity of the OH stretch vibration to the bath dynamics is found to arise from intramolecular effects due to mixing between states in the two-dimensional anharmonic OH stretching potential. Surprisingly small intermolecular couplings reproduce the experimentally observed intermolecular energy transfer times.

[a] D. Kraemer, M. L. Cowan, A. Paarmann, N. Huse, E. T. J. Nibbering, T. Elsaesser, and R. J. Dwayne Miller, PNAS, **105** , 437, (2008).