

Multi-dimensional IR spectroscopy of acetic acid dimers and liquid water

N. Huse^{}, B. D. Bruner[#], M. L. Cowan[#], J. Dreyer^{*}, E. T. J. Nibbering^{*},
R. J. D. Miller[#], and T. Elsaesser^{*}*

^{*} Max-Born-Institut fuer Nichtlineare Optik und Kurzzeitspektroskopie, Max-Born-Str. 2A, 12489 Berlin, Germany, phone: +49-30-6392-1401, fax: +49-30-6392-1429, e-mail: huse@mbi-berlin.de, www.mbi-berlin.de

[#] Departments of Chemistry and Physics, University of Toronto, 80 St. George St., Toronto, ON, Canada M5S3H6, phone: +1-416-978-0366, fax: +1-416-978-0366, e-mail: mcowan@lphys.chem.utoronto.ca, lphys.chem.utoronto.ca

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Hydrogen bonding, i.e., the formation of a weak bond between a hydrogen donor (an O-H group) and a hydrogen acceptor group plays a key role in the microscopic structure of protic liquids, proteins and DNA. Ubiquitous water forms a multitude of hydrogen bonding geometries with various coupling strengths. The O-H stretching vibration which is particularly sensitive to hydrogen bonding, displays complex relaxation and dephasing dynamics and spectral diffusion in water¹. In contrast, cyclic dimers of carboxylic acids have a well-defined hydrogen bond geometry - a structural motif that resembles DNA base pairs. This geometry manifests in a broad O-H stretching band that shows a complex envelope with a pronounced spectral substructure².

We have investigated the line broadening mechanisms of the O-H stretching band of acetic acid dimers and of liquid H₂O with two-dimensional infrared (2D IR) photon echo spectroscopy. A recently developed diffractive optic (DO) technique³ was employed to measure the complex 2D IR spectra. This technique uses a DO to create two passively phase-locked beam pairs, the two pump pulses and the probe pulse/local oscillator. The latter is automatically overlapped in space with the echo signal and the signal is heterodyne detected by spectral interferometry⁴. The interferograms show a phase stability of better than $1/150$.

Acetic acid dimers in CCl₄ form cyclic dimers (concentration 0.2M) containing two O-H...O hydrogen bonds. In this structure we dissected two important coupling mechanisms, i.e. Fermi resonance coupling between the O-H stretching $v=1$ level and several combination/overtone levels as well as anharmonic coupling to low-frequency dimer modes⁵. Quantum chemical calculations reveal that these two coupling mechanisms are of similar strength. However, coherent couplings due to Fermi resonances dominate the linear as well as the 2D spectrum. Fermi resonances also determine the fast initial dephasing dynamics of the O-H stretching 0-1 coherence which has a decay time of 200 fs. Coherences in low frequency dimer modes dephase within several picoseconds and strongly influence later dephasing dynamics.

In contrast, liquid H₂O with its large distribution of rapidly fluctuating hydrogen bond structures displays an ultrafast loss of inhomogeneity within 50 fs and is accompanied by strong spectral diffusion. Subsequent population relaxation of the O-H stretching mode occurs with a 200 fs time constant and an efficient picosecond energy redistribution within the hydrogen bond network, suggesting a mechanism that stabilizes biological systems in water.

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