Multi-Dimensional IR Spectroscopy of Acetic Acid Dimers and Liquid Water

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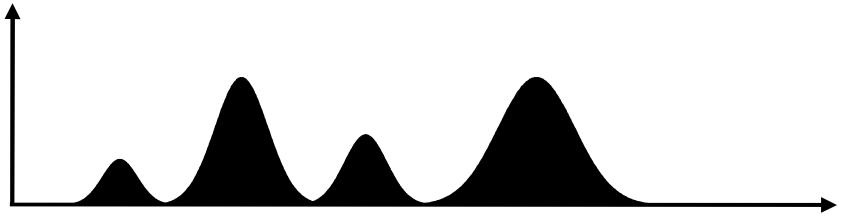
Outline

- Multi-dimensional spectroscopy
- Couplings in acetic acid dimers
- Structural dynamics in pure water

From Linear to Multi-Dimensional Spectroscopy

Linear spectroscopy

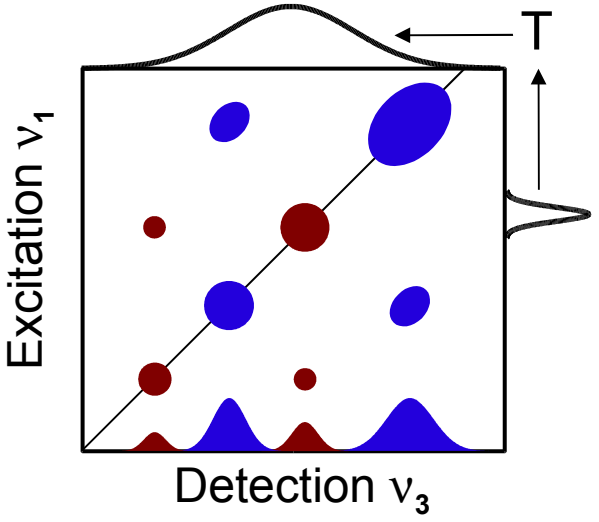


Which transitions couple to each other?

What is the broadening mechanism?

How fast are the dynamics?

2D spectroscopy

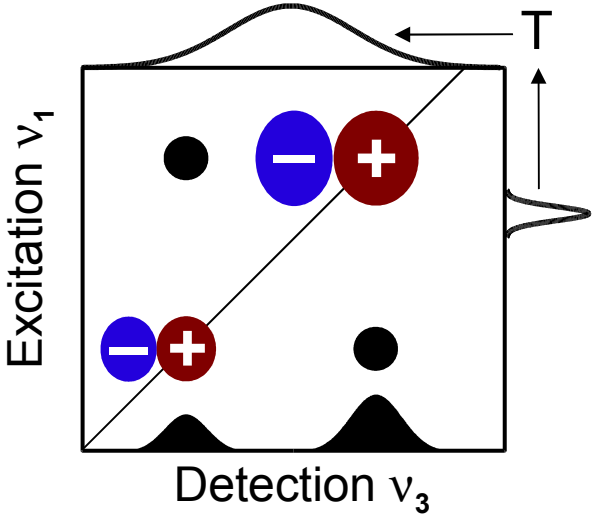


Signals of anharmonic oscillators

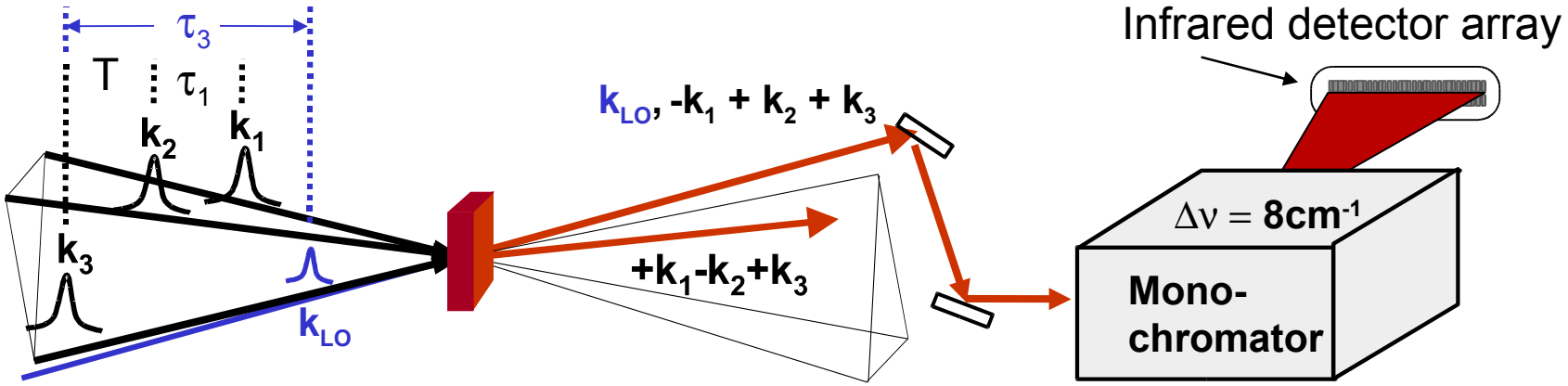
Fundamental transition

Excited state absorption

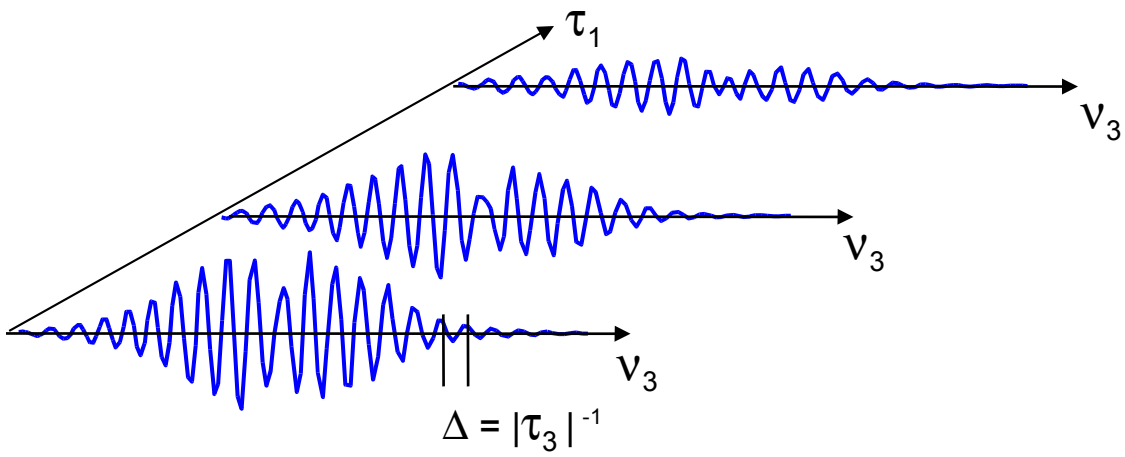
Cross peaks → coupling



Heterodyne Detected Photon Echoes



Spectrograms for different delays of τ_1



Field extraction

$S(\tau_1,\nu_3)$

$\Downarrow$

$E(\tau_1,\nu_3)$

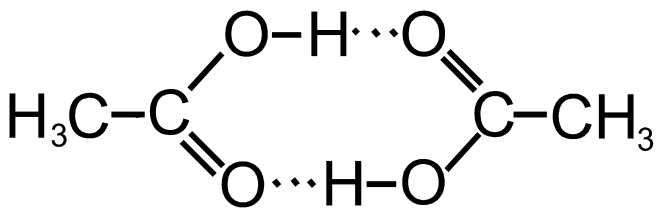
Fourier transform

$\Downarrow$

$E(\nu_1,\nu_3)$

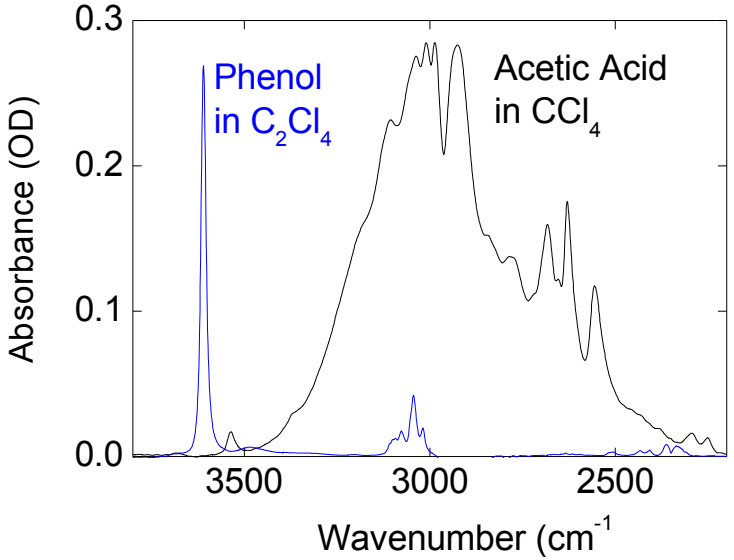
Acetic Acid Dimers

Cyclic acetic acid dimer

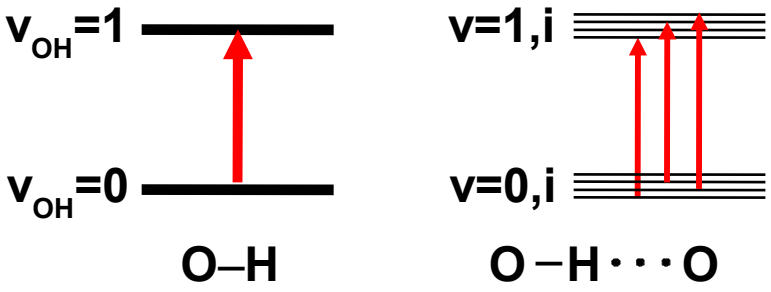


well-defined geometry

OH-stretching vibration



2 levels vs. multi-level structure

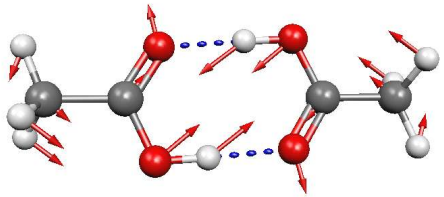


- red-shift of ν(o-H)
- very strong broadening
- structured bandshape

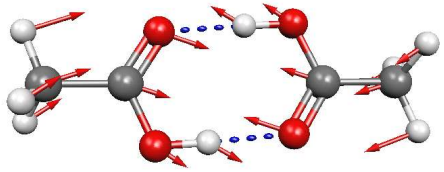
Acetic Acid Dimers

Cyclic acetic acid dimer

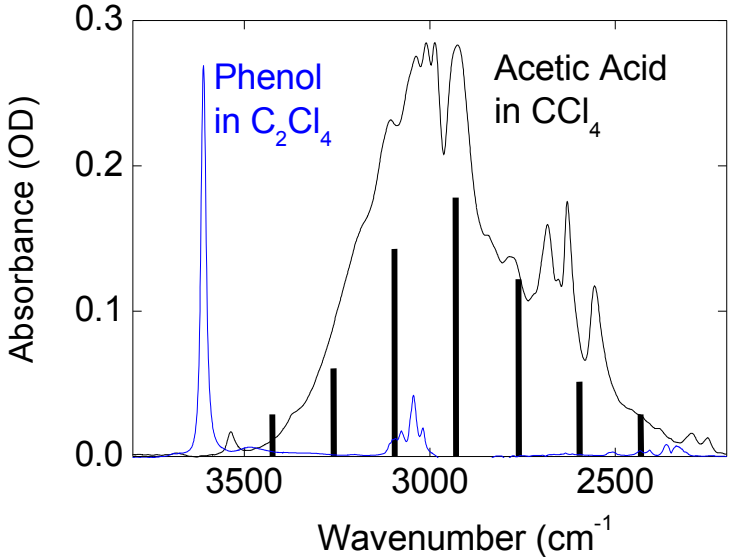
ip bending
148 cm^{-1}



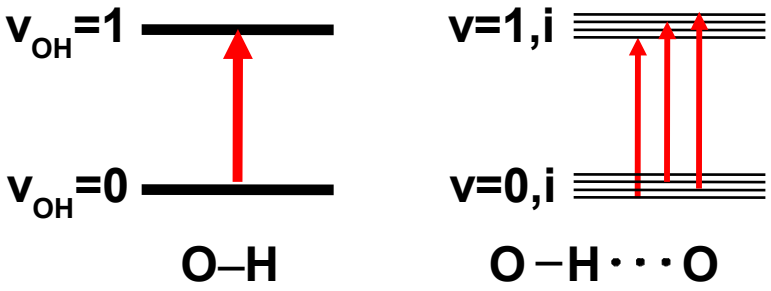
ip stretching
-143 cm^{-1}



OH-stretching vibration



2 levels vs. multi-level structure

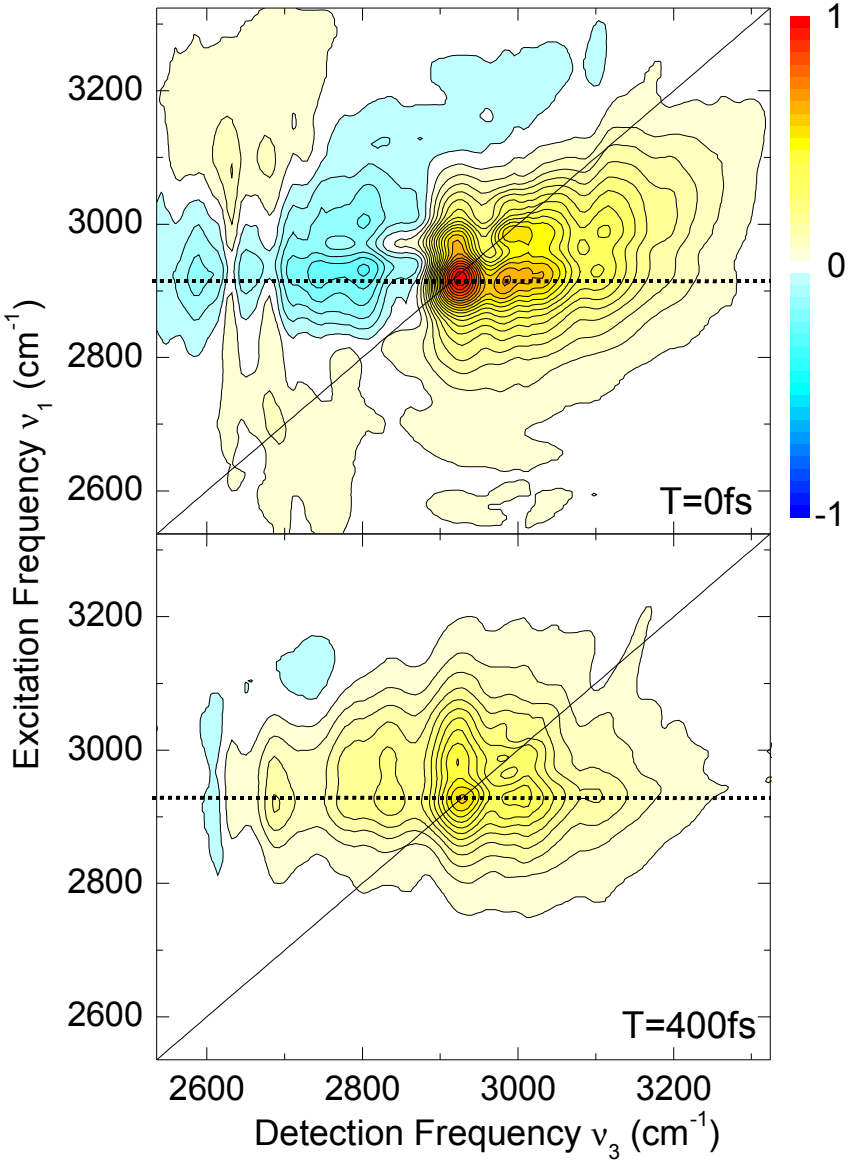


Broadening mechanism:

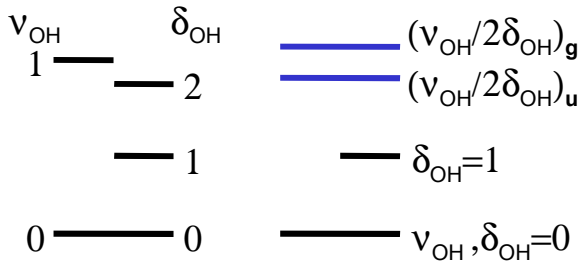
- anharmonic coupling to low-frequency modes
- Fermi resonances?

Heyne et al., J. Chem. Phys. 121 (2004), 902

Fermi Resonances

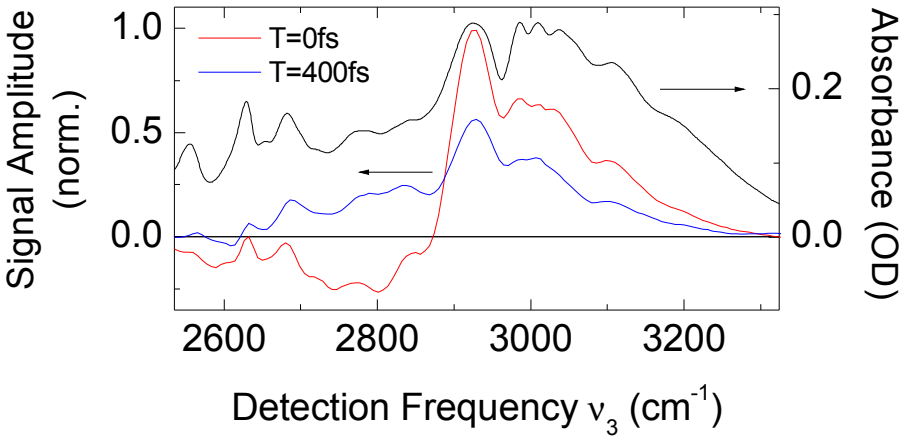


Fermi resonances



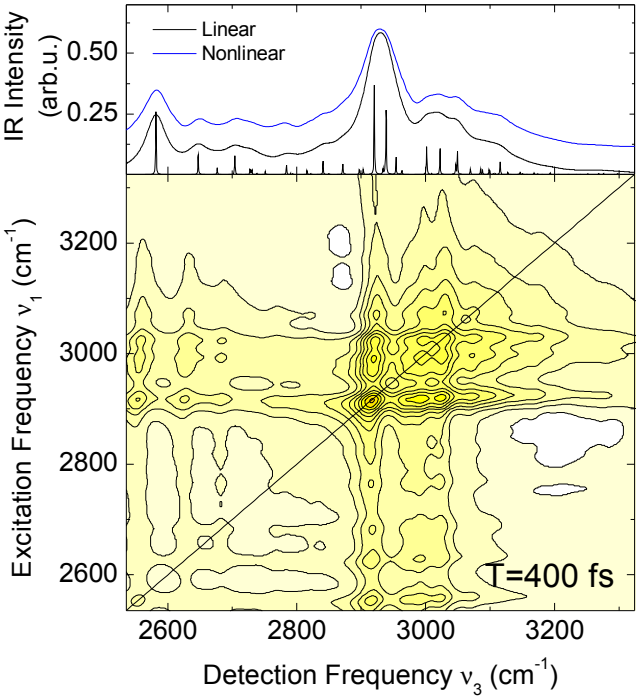
Transitions: ν_{OH}, δ_{OH}, ν_{CO}, $\nu_{C=O}$

Profiles

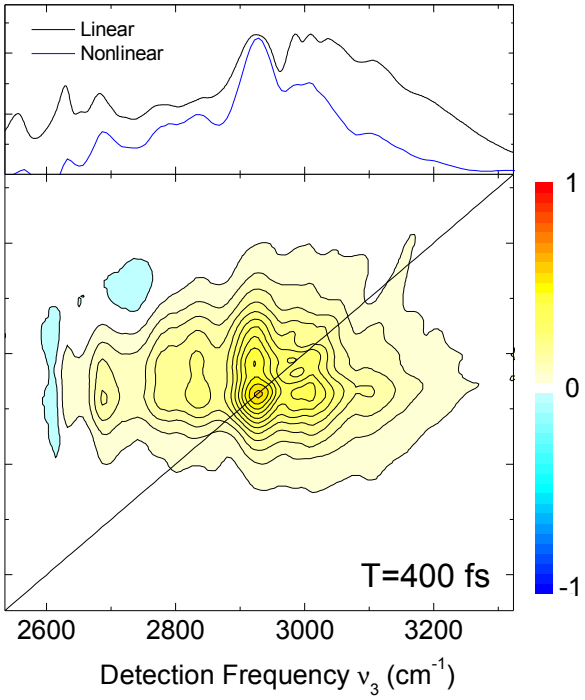


Ab-initio Calculations

Theory



Experiment



Ab-initio calculations:
Fermi resonances
dominate 2D spectra

Cubic coupling constants with i = ν_{bu}OH (cm^{-1})

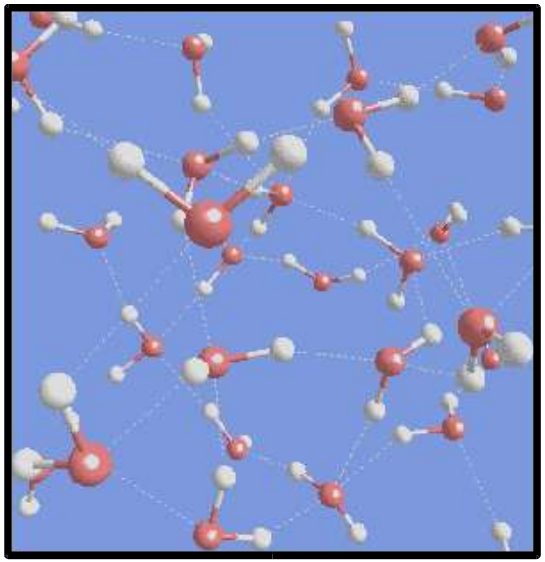
j (a_g)	*k* (b_u)	
δOH	νC–O	-141
νC–O	δOH	-125
δOH	δOH	98
νC=O	νC–O	-85

Dreyer, Int. J. Quantum Chem. (in press)

Liquid Water

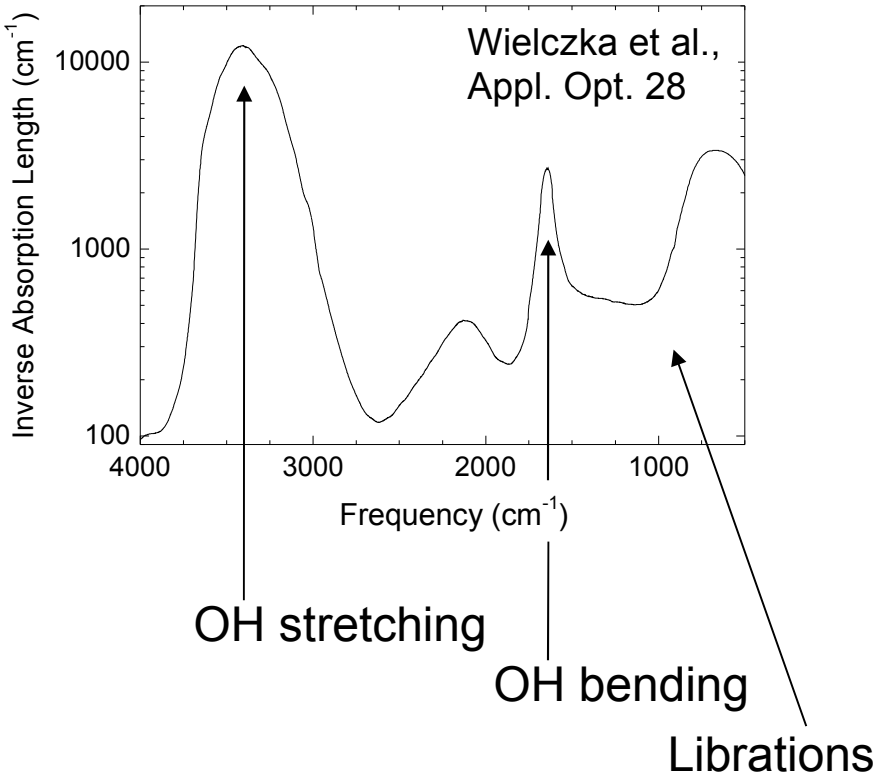
Hydrogen bonds determine the structure and other properties of water

MD simulation of water
(from Parinello group)



Fluctuating geometry

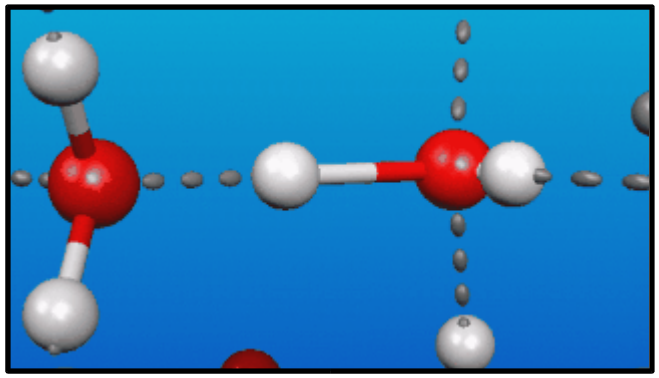
Linear absorption spectrum



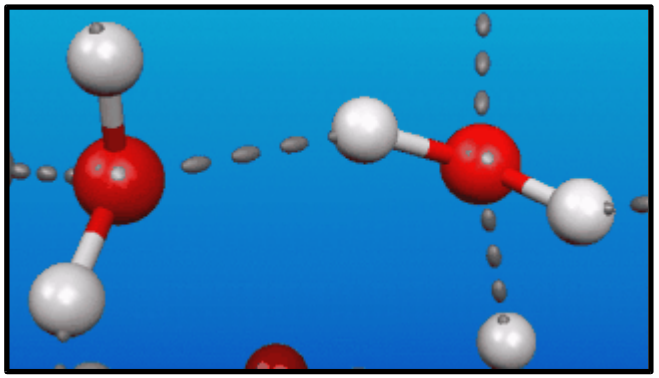
HOD in D_2O:

Stenger et al., *Phys. Rev. Lett.* **027401** (2001)
Stenger et al., *J. Phys. Chem A* **105** (2001), 2929

Ultrafast Timescales in Liquid Water



O-H stretching vibration

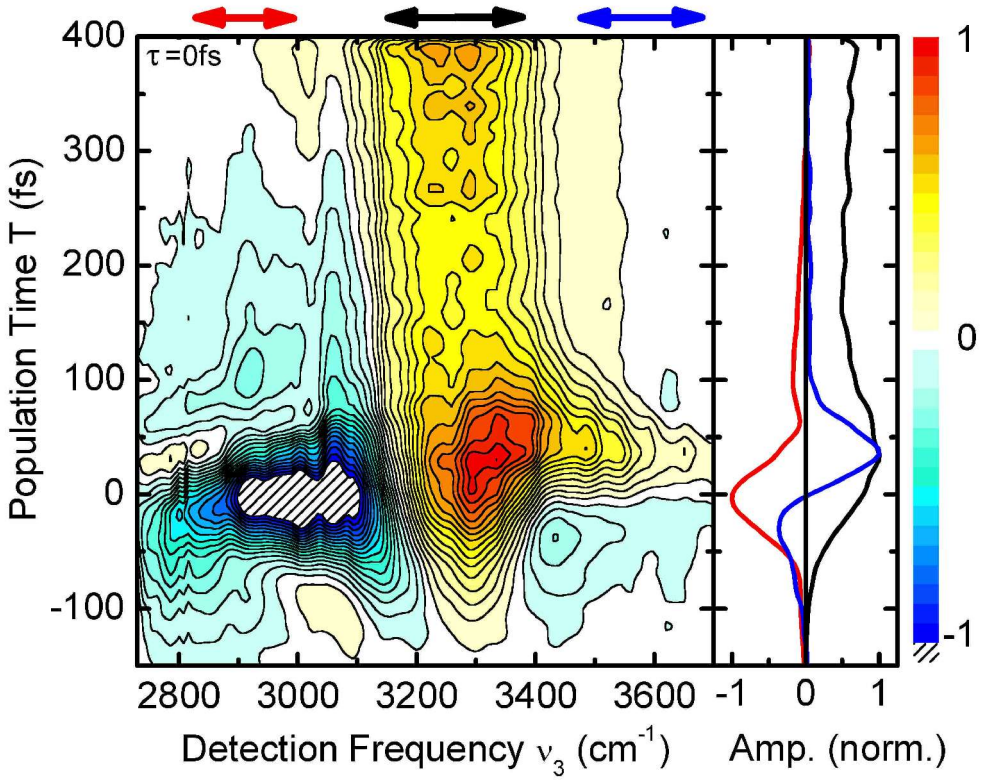


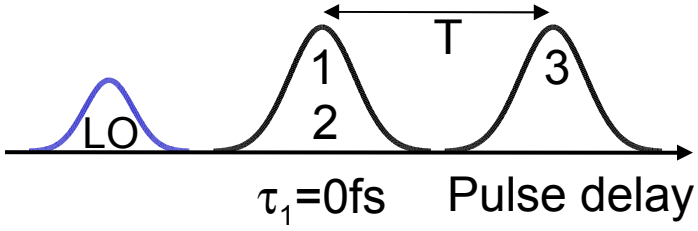
Librations

O-H stretching modes (3400 cm^{-1})	~ 0.01 ps
O-H bending mode (1650 cm^{-1})	~ 0.02 ps
Fast librations (≤1500 cm^{-1})	~ 0.03 to 0.1 ps
Vibrational lifetimes	~ 0.2 ps

Microscopic dynamics of hydrogen bonds is ultrafast.

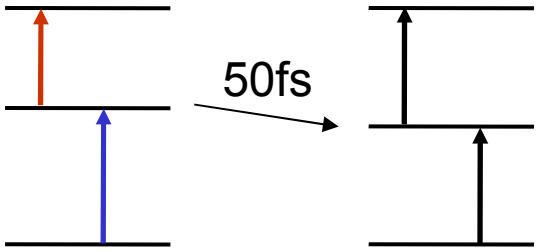
Frequency-Resolved Transient Grating





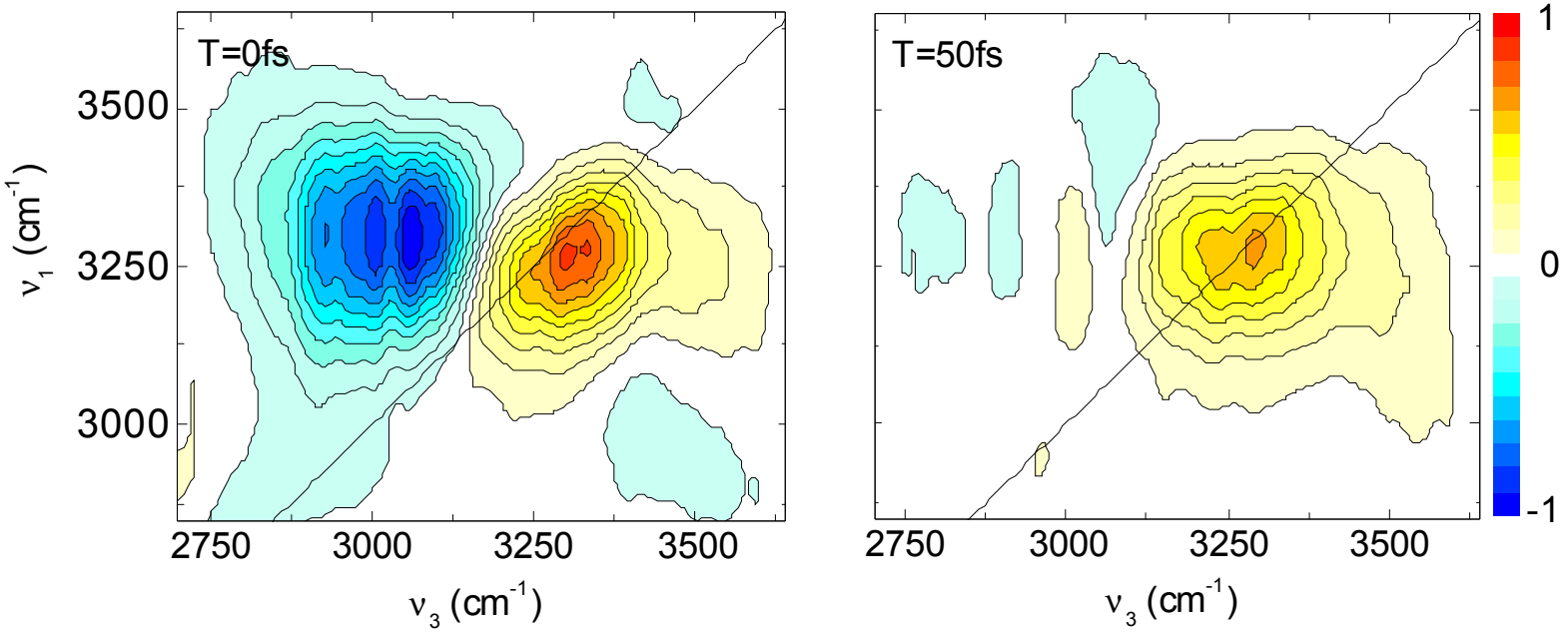
Spectral diffusion
signal decay at the edges within 50 fs

Energy transfer
anisotropy decay in less than 100 fs



Population relaxation
OH stretch lifetime = 190 fs

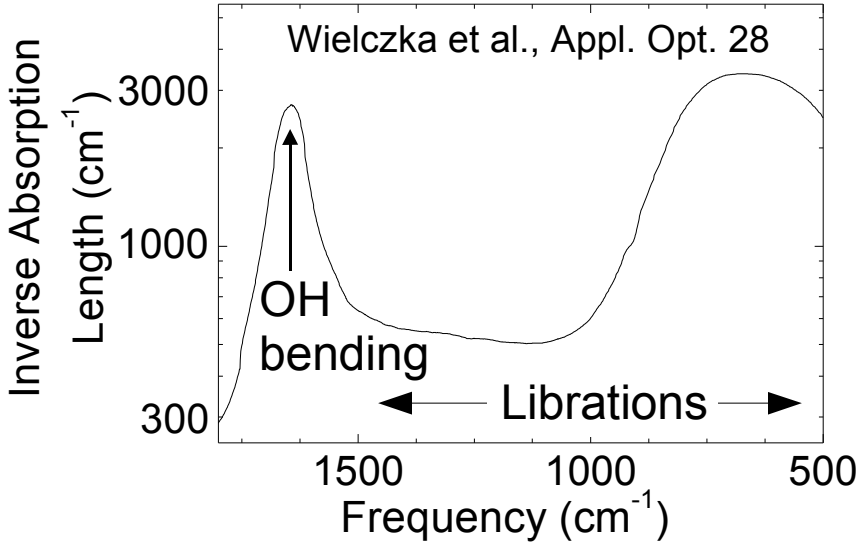
Correlation Spectra of Pure Water



Microscopic origin:

librational modes

with $\omega > \omega$(O...O)



Conclusions

Heterodyne photon echo spectroscopy delivers full information on couplings and line broadening mechanism

Fermi resonances dominate 2D spectra of acetic acid although cubic coupling constants are similar for coupling to low-frequency modes

(Huse et al., submitted)

Loss of inhomogeneity in liquid water within 50 fs due to librational modes of the hydrogen bond network, $T_1 \approx 200$ fs

(Cowan et al., Nature 434 (2005), 199)