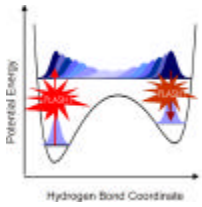
Coherent Vibrational Response of Hydrogen Bonds

Max-Born-Institut

Nils Huse, Karsten Heyne, Jens Dreyer, Erik T. J. Nibbering, Thomas Elsaesser

Max-Born-Institut, Max-Born-Strasse 2A, D-12489, Berlin

http://www.mbi-berlin.de/en/research/projects/2.05/index.html



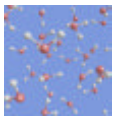
Ultrafast Vibrational Spectroscopy of Hydrogen Bonds

Hydrogen Bond Research Relevance

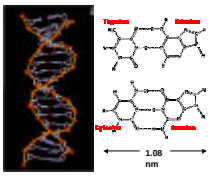
Hydrogen bonds determine structure, function and dynamics

O-H···O

Water : the Medium of life

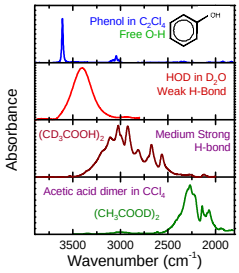


DNA : the Information Storage Unit of life

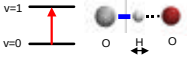


Proteins : the Machinery of life

Infrared Spectroscopy as Tool to Grasp Hydrogen Bond Interactions



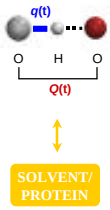
O-H stretching oscillator



O-H/O-D stretching band

- **Red-shift of ν(X-H)**
  - *reduced force constant*
- **Very strong broadening**
  - *anharmonic coupling to low-frequency modes*
  - *Fermi resonances with overtone/combination states*
  - *excitonic (Davydov) coupling*
  - *distribution of bond lengths*
  - *homogeneous broadening*
- **Peculiar bandshape**

Hydrogen Stretching Oscillator Affected by Fluctuating Surroundings



Fluctuating molecular motions in the environment and coupling lead to fluctuating force on hydrogen bond

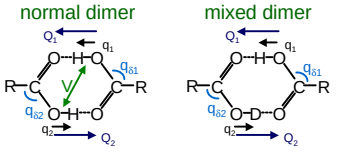
Time scale of fluctuations:

~ 20 fs (10^{-14} s) - 10 ps (10^{-11} s)

H_2O

Vibrational motions are "perturbed": Dephasing, damping and relaxation

Acetic Acid Dimer: Model System for Intermolecular Hydrogen Bonds



O-H stretching mode:

$q_u = (1/\sqrt{2})\,[q_1 - q_2]$

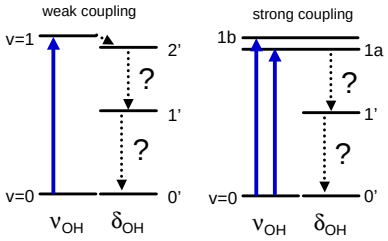
O···O low frequency modes:

$Q_g = (1/\sqrt{2})\,[Q_1 + Q_2]$

$Q_u = (1/\sqrt{2})\,[Q_1 - Q_2]$

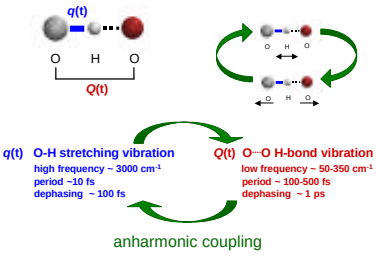
- Anharmonic coupling of O-H stretching and low-frequency modes.
- Excitonic coupling V of the two O-H stretching oscillators (Davydov coupling).
- Fermi resonances of v=1 level of O-H stretching vibration with overtone and combination vibrational levels (O-H bending and C-O stretching modes)
- Theory: Witkowski, Maréchal (1968), Henri-Rousseau (late 1990s)

Fermi Resonances for Hydrogen Bonded O-H Stretching Vibrations

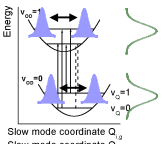


pathways for intramolecular energy redistribution?

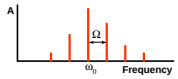
Anharmonic Couplings of Hydrogen Stretching Oscillator to Other Modes Affects Spectral Line Shapes and Dynamics



Anharmonic coupling only:



Absorption: 1 series of lines.

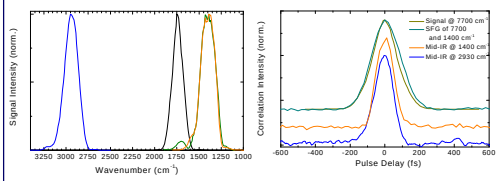


Experimental Methodology

Ultrafast infrared spectroscopy of hydrogen bonded systems

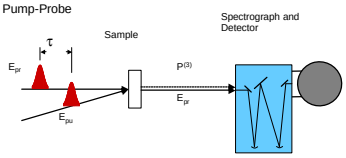
- **Pump-Probe Spectroscopy**
  - *anharmonic couplings between vibrational normal modes*
  - *coherent low-frequency hydrogen bond wavepacket motions*
  - *population kinetics of hydrogen stretching oscillator*
  - *intramolecular energy redistribution*
  - *vibrational cooling*
- **Photon Echo Spectroscopy**
  - *anharmonic couplings between vibrational normal modes*
  - *coherent modulations by multi-level systems*
  - *homogeneous dephasing*
  - *spectral diffusion*

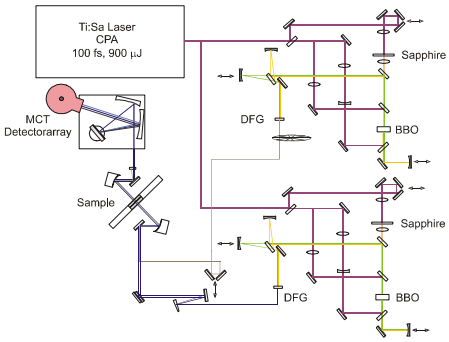
Examples of Femtosecond Mid-IR Pulse Spectra and Auto/Cross-Correlations



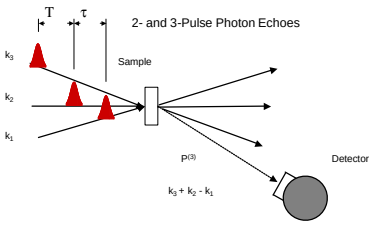
Femtosecond Mid-IR Pump-Probe Spectroscopy

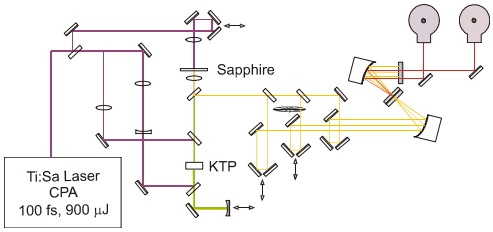
Two-Colour Pump-Probe





Femtosecond Mid-IR Photon Echo Spectroscopy





further information: ***http://www.mbi-berlin.de/de/research/projects/2.05/subprojects/Subproject1/index.html***

and e-mail: ***elsasser@mbi-berlin.de nibberin@mbi-berlin.de dreyer@mbi-berlin.de***

collaborations with: ***Research Group J. Manz/O. Kühn, Freie Universität Berlin, Germany ;***

Research Group S. Mukamel, University of California at Irvine, Irvine, CA, USA