Coherent Vibrational Response of Hydrogen Bonds

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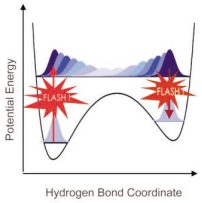
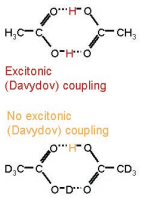
http://www.mbi-berlin.de/en/research/projects/2.05/index.html

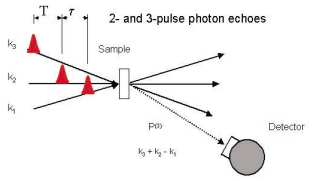


Vibrational Multilevel Quantum Coherences

Acetic Acid Dimers Isotopomers



Femtosecond Mid-IR Photon Echoes monitor Dephasing, Spectral Diffusion and Wave-Packet Motions

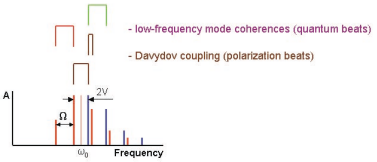


- 2 Pulse Photon Echo: T=0, scan τ
- Transient Grating Scattering: τ=0, scan T
- 3 Pulse Photon Echo: scan τ, scan T
- Echo Peak Shift Measurement:

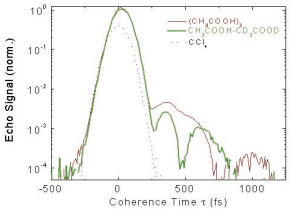
determine $\tau_{max}(T)$ where $\frac{\partial S_{3PE}(\tau,T)}{\partial \tau}=0$

Anharmonic + Davydov coupling V:

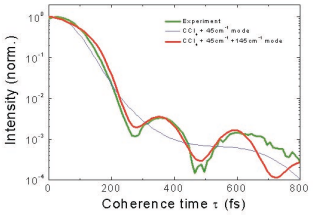
Photon echo: modulations of signals by



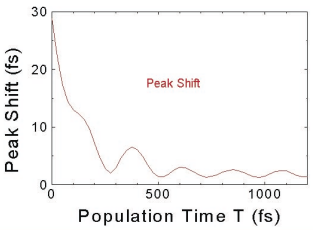
Experimental Two-Pulse Photon Echo Signal @ 2938 cm^{-1}



Calculated Two-Pulse Photon Echo Signal for (CD_3COOH)-(CD_3COOD)



Thee-Pulse Stimulated Photon Echo Peak Shift Signal for (CH_3COOH)$_2$



Conclusions on Acetic Acid Dimer

- Coherent pump-probe and photon echo signals are determined by low-frequency wave packet motions
- Low-frequency vibrations strongly coupled to the hydrogen stretching oscillator are the 50 cm^{-1} τ_{bg} methyl torsion, 145 cm^{-1} δ_{ag} dimer in-plane bending and 170 cm^{-1} ν_{ag} dimer in-plane stretching modes
- Davydov coupling is of minor importance in transient data
- Line broadening dominated by homogeneous process (T_2 ~ 200 fs)
- O-H stretching and O-H bending lifetimes are 200 fs and 250 fs, respectively
- Anharmonic coupling between O-H stretching and O-H bending leads to pronounced absorption changes of bending mode, without involving relaxation induced excess populations

Ab Initio Simulation of Coherent 2D Infrared Spectra

Why 2D ?

- New insights into structural and dynamical properties of molecules and chemical reactions on ultrafast time scales
- Disentanglement of congested 1D spectra
- Direct signatures of intra- and intermolecular couplings
- Direct access to properties of potential energy surfaces (diagonal and off-diagonal anharmonicities)

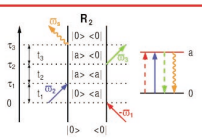
Objective:

- Develop a procedure to calculate multidimensional infrared spectra from first principles

Simulation of 2D infrared spectra

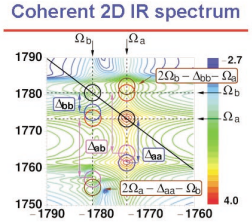
- Select coordinates
  - ⇨ local internal coordinates or normal modes
- Anharmonic couplings between vibrational modes and dipole derivatives
  - ⇨ numerical differentiation of analytical harmonic force constants (to 4th order) and dipole moments (to 2nd order) provided by ab initio calculations (e.g. DFT/B3LYP)
- Vibrational exciton Hamiltonian
  - ⇨ anharmonic molecular eigenstates, eigenvectors and transition dipole moments
- Third order nonlinear response functions
  - ⇨ time domain approach using sum over states
- 2D IR correlation spectra
  - ⇨ signals for selected wave vectors as a function of 2 variables (time, frequency)

Nonlinear response functions
Connection to quantum chemistry



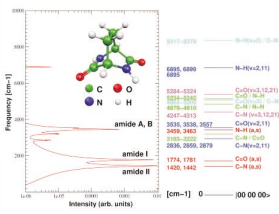
$$R_{ijkl}(t_1,t_2,t_3)=P(0)$$
$$\times\Theta(t_1)\mu_{0a}\exp(+i\Omega_{0a}t_1)\exp(\Gamma t_1)$$
$$\times\Theta(t_2)\mu_{0a}\exp(-i\Omega_{0a}t_2)\exp(\Gamma t_2)$$
$$\times\Theta(t_3)\mu_{a0}\exp(-i\Omega_{a0}t_3)\exp(\Gamma t_3)$$
$$\times\mu_{0a}\times\langle f_{a0}|J_{a0}k_{0a}|f_{0a}\rangle$$

Coherent 2D IR spectrum

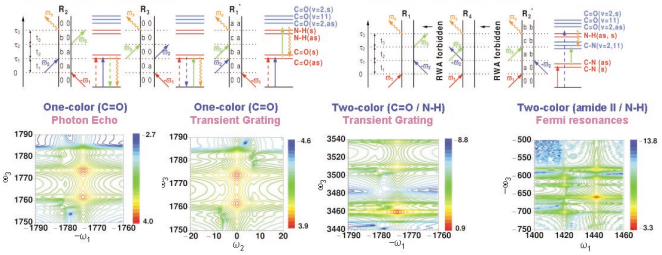


Diagonal peaks: Overtone peaks (diagonal)
Cross peaks: Combination band peaks (off-diagonal), Overtone peaks (off-diagonal)

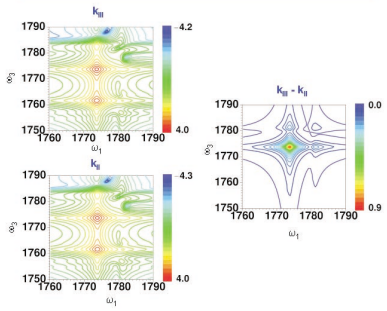
A Rigid Model Dipeptide



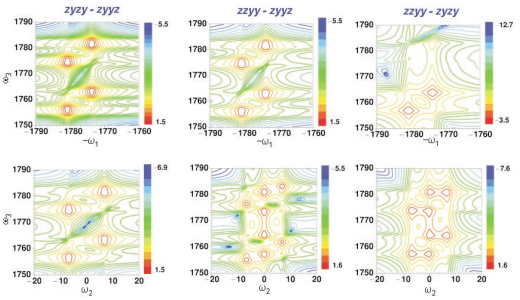
$k_I = -k_1 + k_2 + k_3$ $\quad$ $k_{II} = +k_1 - k_2 + k_3$



Linear combinations of wavevectors
⇨ eliminates overtone peaks



Polarization configuration of pulses
⇨ eliminates diagonal peaks



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

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