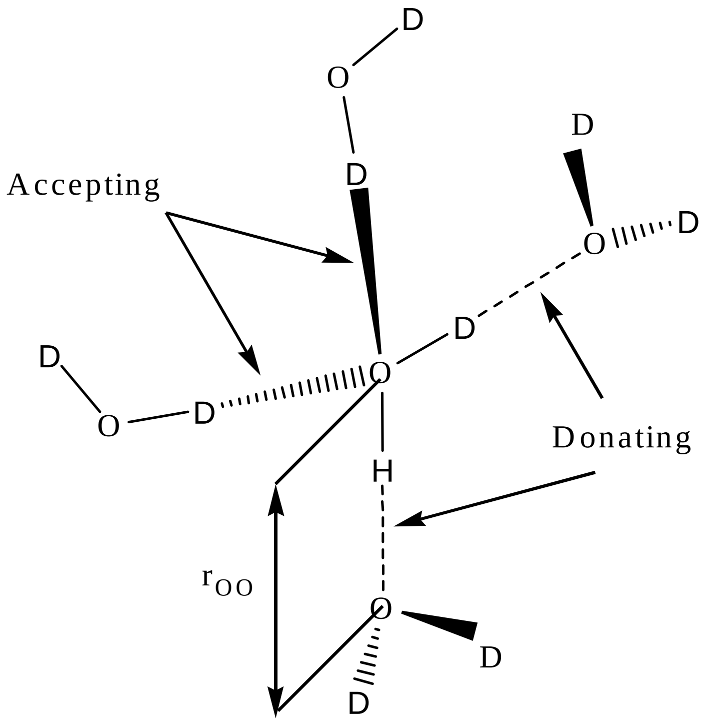
Relation between frequency and H bond length in heavy water
Toward the understanding of the unusual properties of the H bond dynamics in nanoporous media?

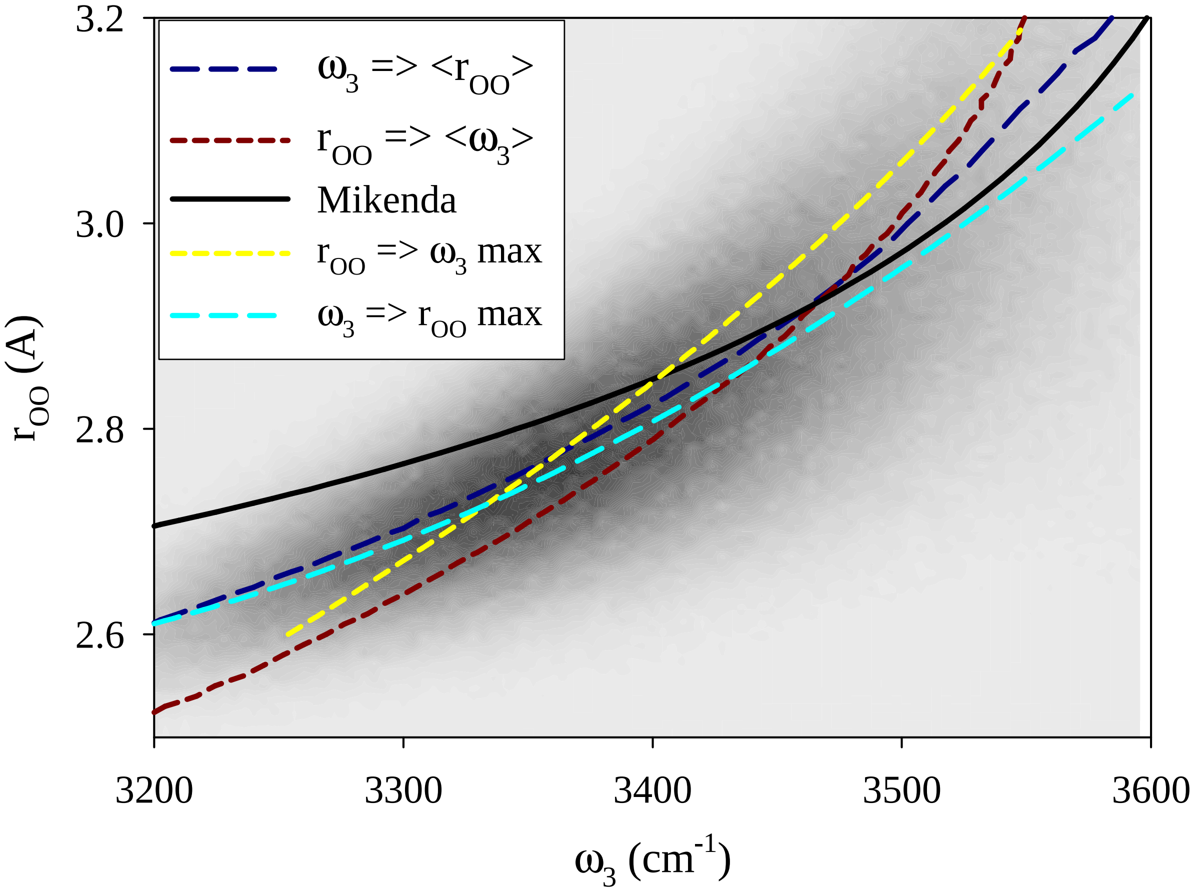
S. Pommeret, R. Musat, J.P. Renault, S. Le Caër
CEA/Saclay,

S. Bratos, J.-Cl. Leicknam
Université Pierre et Marie Curie – Paris 6,

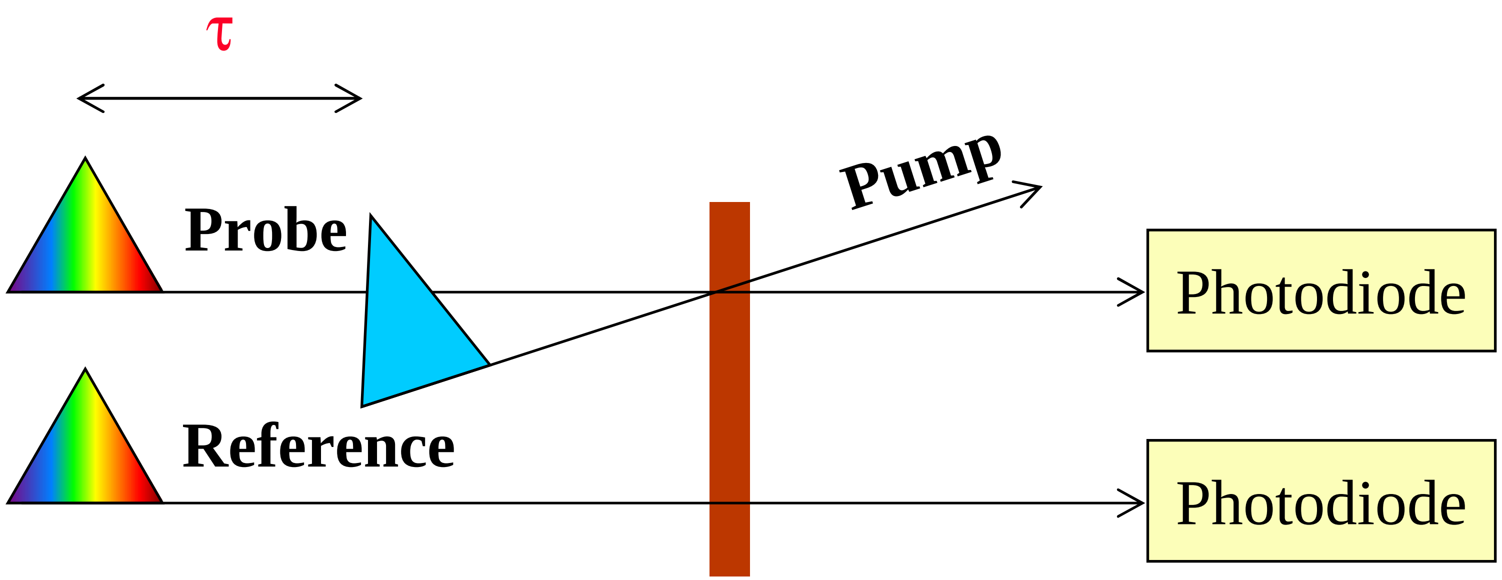
R. Righini, J. Palmer
University of Florence

Relation between frequency and distance





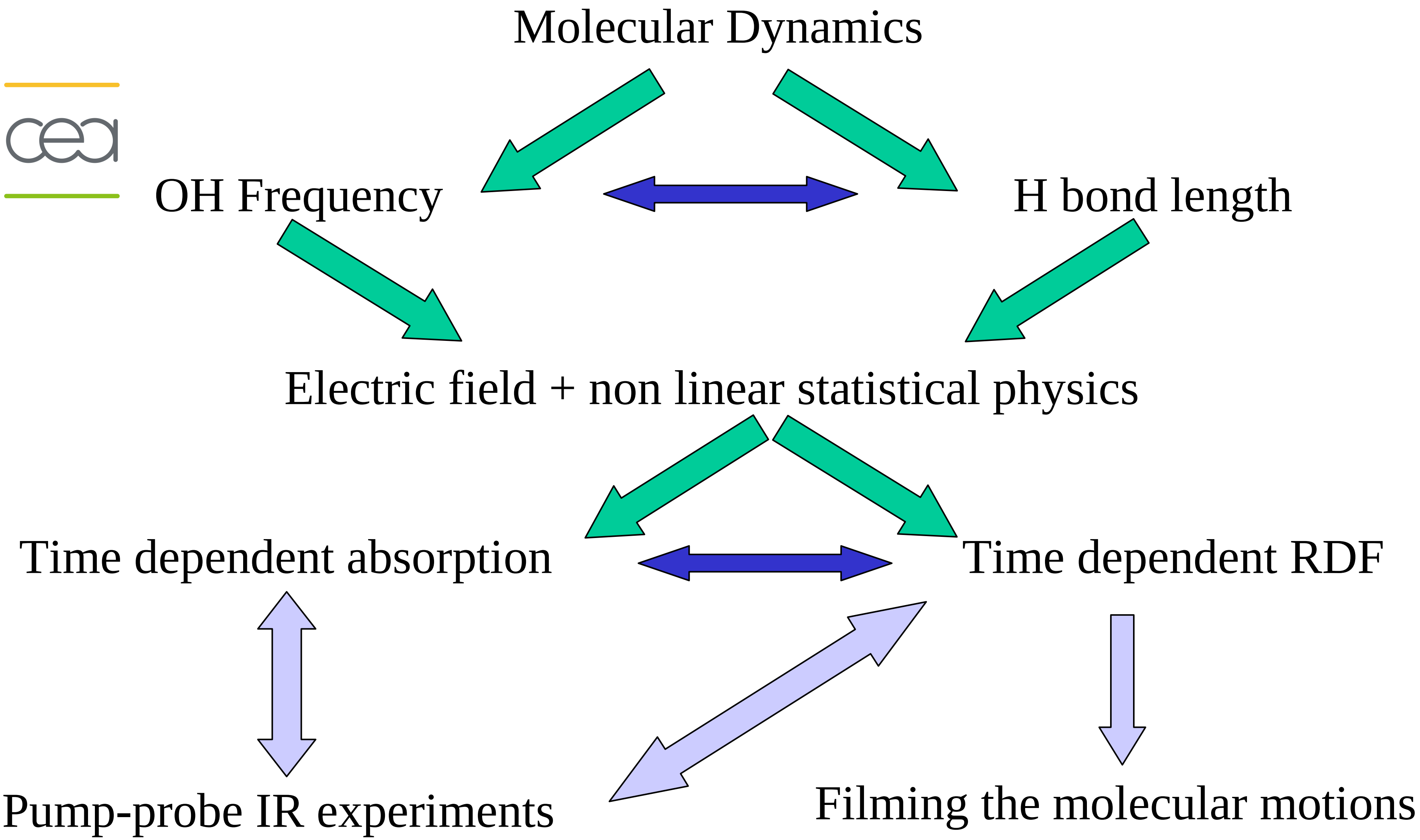
Principle of pump – probe spectroscopy



$$Absorbance = \log_{10}\left(\frac{I_{reference}}{I_{probe}}\right)$$

The time delay between the pump and the probe pulse is often called time

From MD to experiments to molecular motion

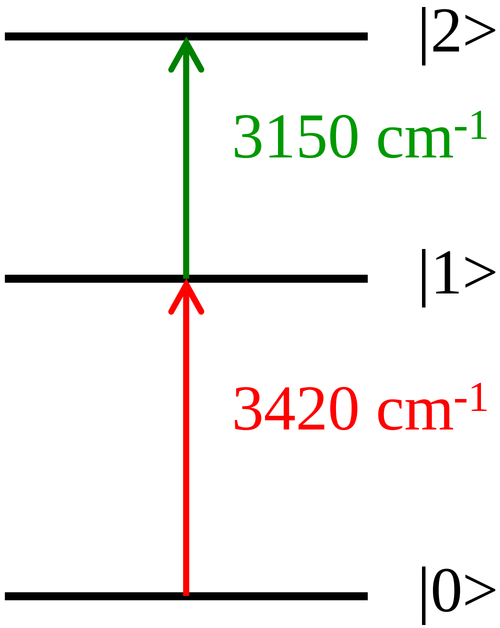


From MD to pump-probe signal

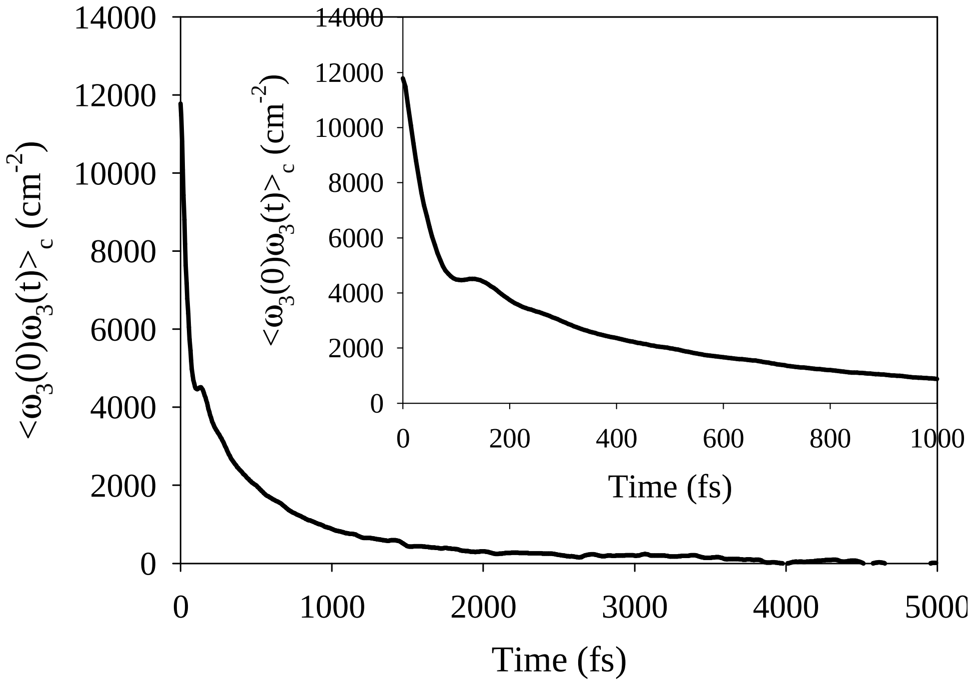
$$S(\Omega_1,\Omega_2,\tau) = \left(2/\hbar^3\right)\mathrm{Im}\int_{-\infty}^{\infty}\int_{0}^{\infty}\int_{0}^{\infty}\int_{0}^{\infty} dt\, d\tau_1\, d\tau_2\, d\tau_3$$

$$\times\left\langle \dot{E}_{2i}(\mathbf{r},t)E_j(\mathbf{r},t-\tau_3)E_k(\mathbf{r},t-\tau_2-\tau_3)E_l(\mathbf{r},t-\tau_1-\tau_2-\tau_3)\right\rangle_E$$

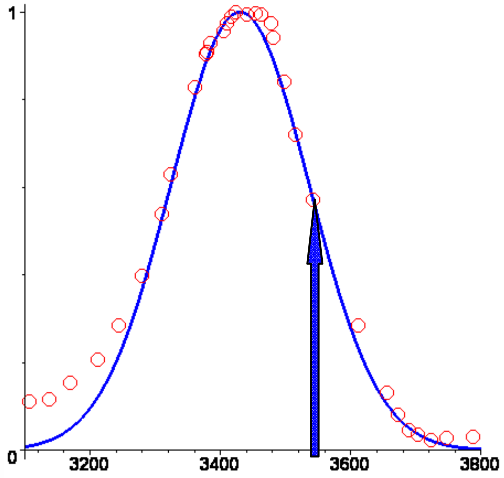
$$\times\left\langle M_l(0)\left[M_k(\tau_1),\left[M_j(\tau_1+\tau_2),M_i(\tau_1+\tau_2+\tau_3)\right]\right]\right\rangle_S$$

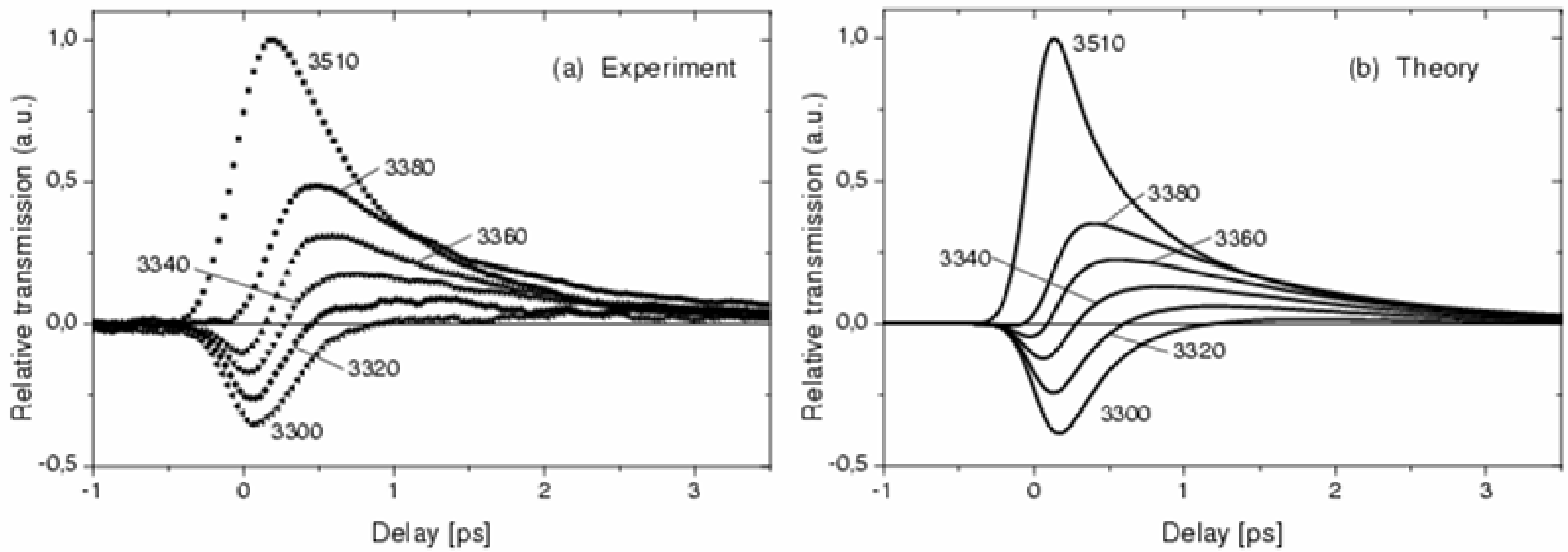


Frequency shift autocorrelation function



Comparison theory experiment (HOD/D_2O)





Link between distance and pump-probe

$$\Delta g_{OO}(r,t) = -\Delta g_{OO}^{00}(r,t) + \Delta g_{OO}^{11}(r,t)$$

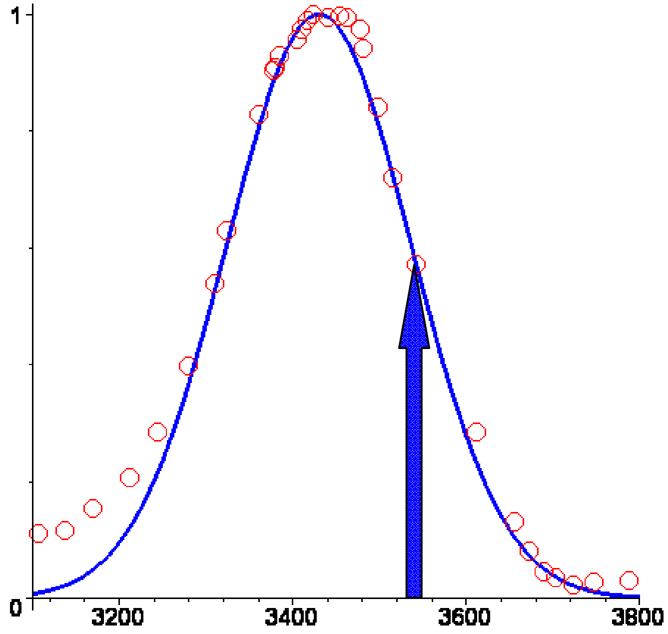
$$\Delta g_{OO}^{mm}(r,t) = \frac{2}{\hbar^2} V \,\mathrm{Re}\left\{ \begin{array}{l} \int_0^\infty d\tau_1 \int_0^\infty d\tau_2 \left\langle \mathbf{E}(\mathbf{r}, t-\tau_1)\mathbf{E}(\mathbf{r}, t-\tau_1-\tau_2) \right\rangle_E \\ \times \left\langle \mathbf{M}_{01}(\tau_1)\mathbf{M}_{10}(\tau_1+\tau_2)\delta_{mm}(\mathbf{r}_1(0)-\mathbf{r}_O(0)-\mathbf{r}) \right\rangle_S \end{array} \right\}$$

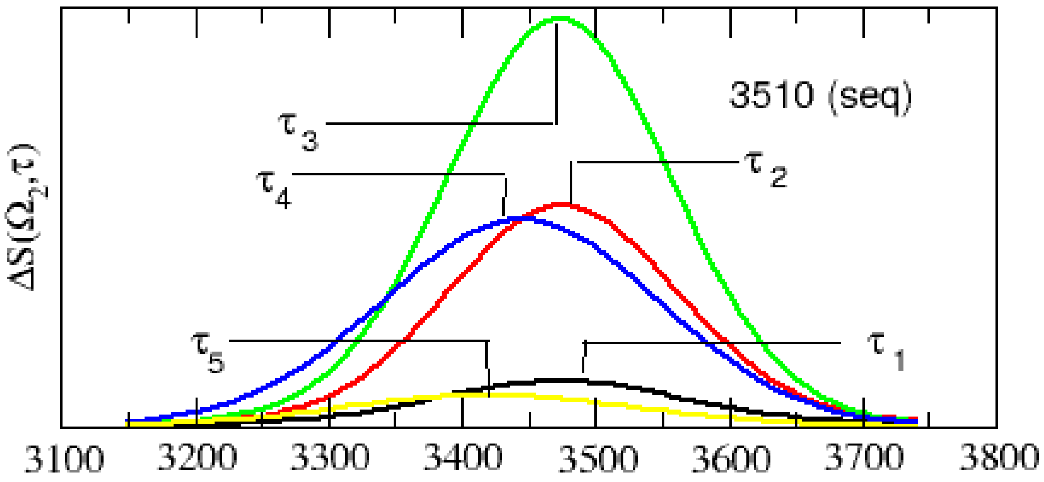
Correlation functions needed:

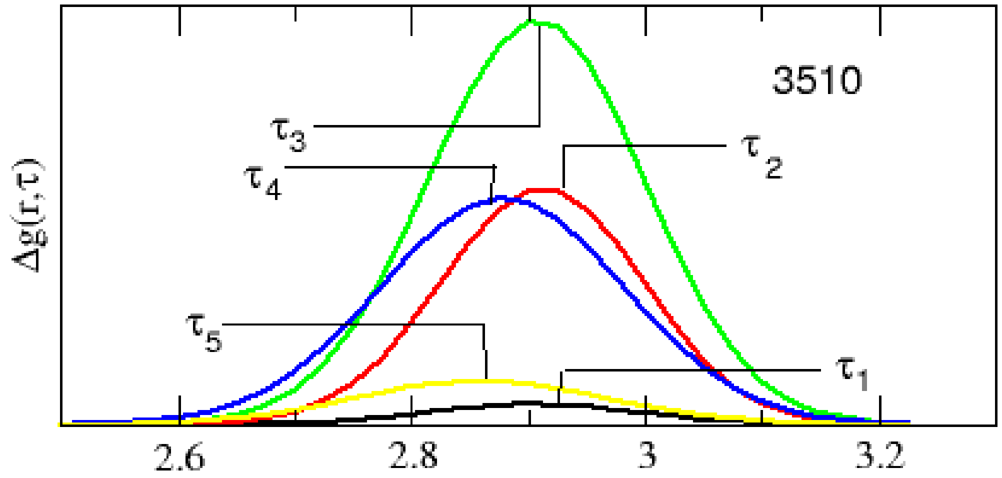
$$\langle \omega(r;t) \rangle = \left\langle \delta(\mathbf{r}_1(0)-\mathbf{r}_O(0)-\mathbf{r})\, \omega(\mathbf{p}^N, \mathbf{r}_O, \mathbf{r}_1-\mathbf{r}_O, \mathbf{r}_2, \ldots, \mathbf{r}_N; t) \right\rangle_S$$

$$\langle \omega(r;t)\, \omega(r;t') \rangle_C = \langle \omega(r;t)\, \omega(r;t') \rangle - \langle \omega(r;t) \rangle \langle \omega(r;t') \rangle$$

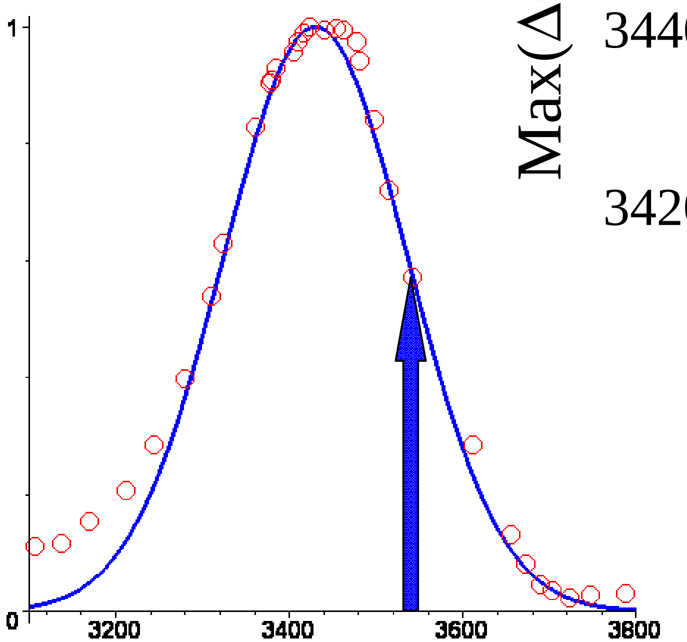
Comparison: transient absorption versus transient RDF

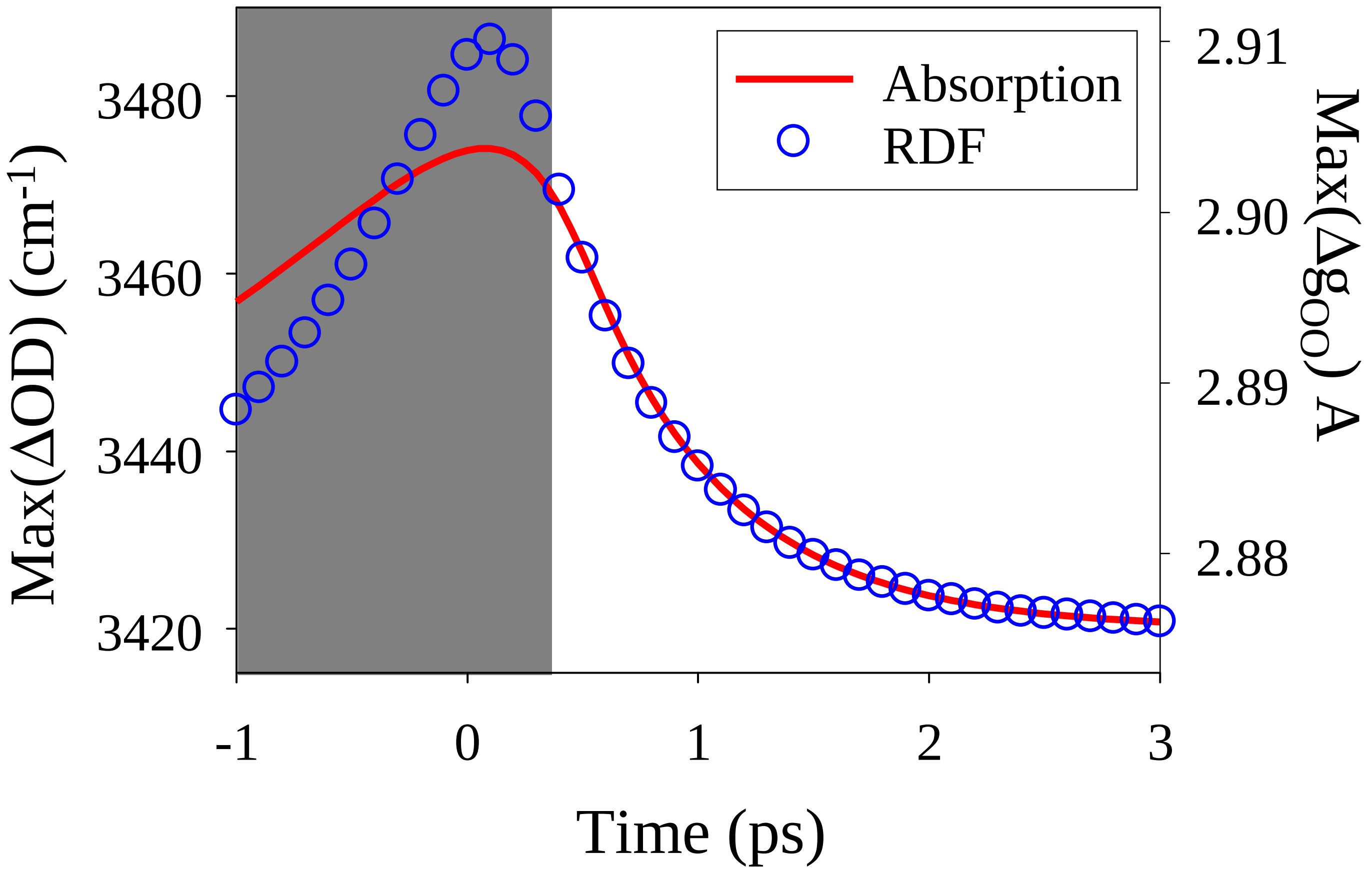






Filming the H bond contraction



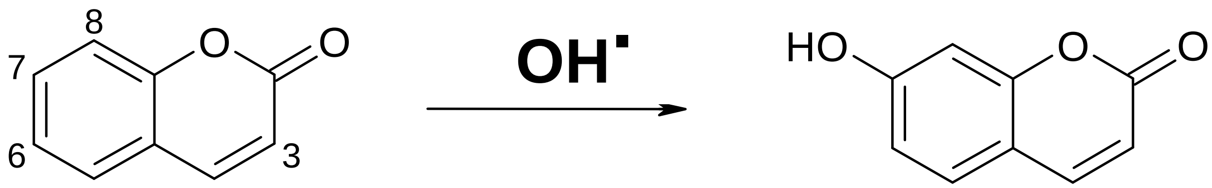


Hole burning dynamic

- For time delay greater than ~ 200 fs the spectral data are indeed representative of the molecular dynamics of water.
  - It is possible to film the molecular motions via IR transient absorption
- For negative and “small” time delay a femtosecond pump – probe experiment does not have any spectral resolution.
  - The IR camera is blind

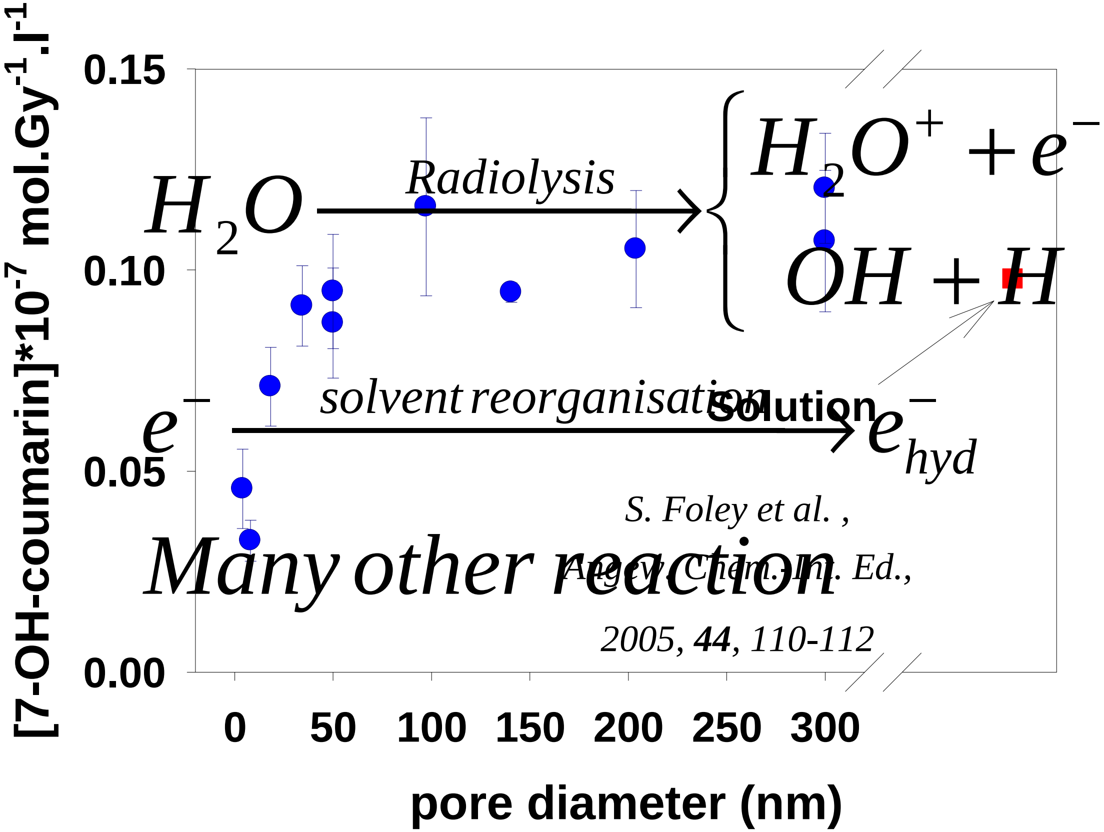
Reactivity in nanoporous media

Hydroxyl radical production

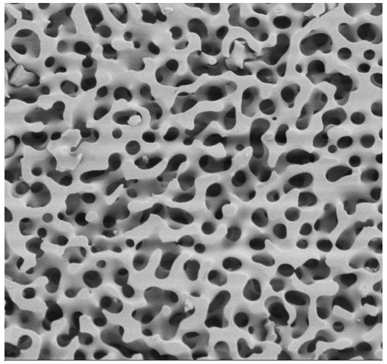


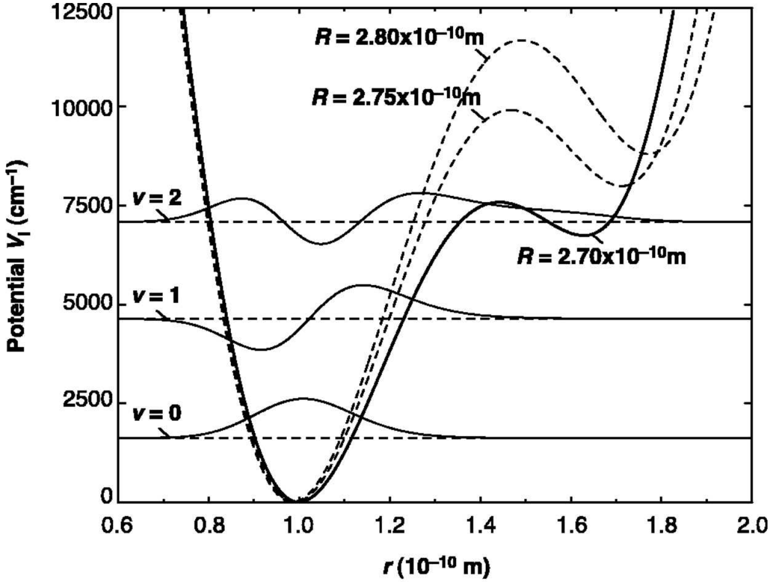
Coumarin
low fluorescence at 410 nm

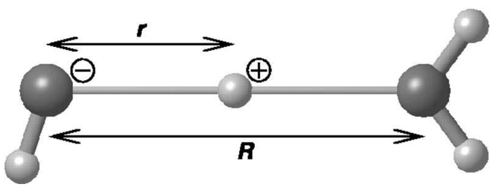
7-hydroxycoumarin
high fluorescence à 456 nm

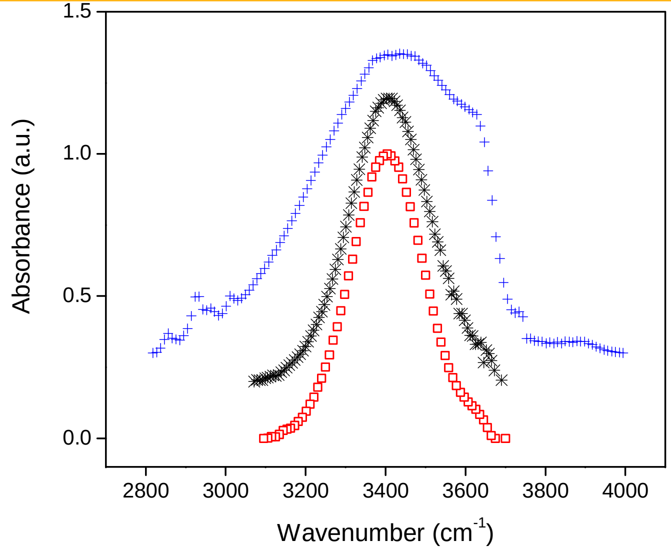


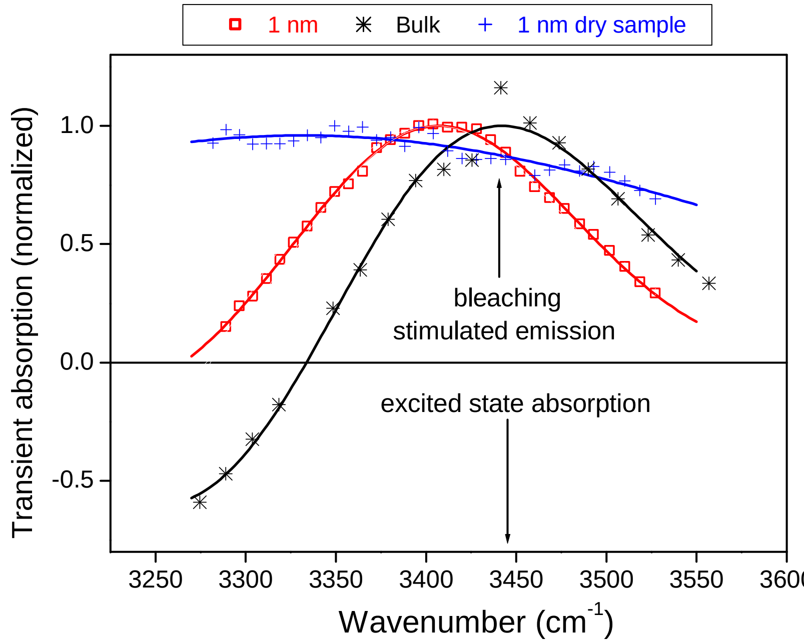
Unusual H bond properties











Conclusion

- Nanoconfinement
  - Changes the reactivity
  - Changes the vibrations
- Possible route to understand those special effects
  - “This indicates that the liquid state cannot be specified by the temperature and pressure alone, but it is also affected by its size in a discontinuous manner: the phase of a liquid in a narrow space can, in principle, be different from that in the bulk.” *Rei Kurita and Hajime Tanaka Phys. Rev. Lett. 98, 235701 (2007)*
  - The dynamics of liquid water are modified in nanoconfined media and induce a significant change of the intramolecular potential that is in favor of a enhanced proton donor character of the first vibrational excited state.

- Thank you for your attention

- Happy birthday to Raluca