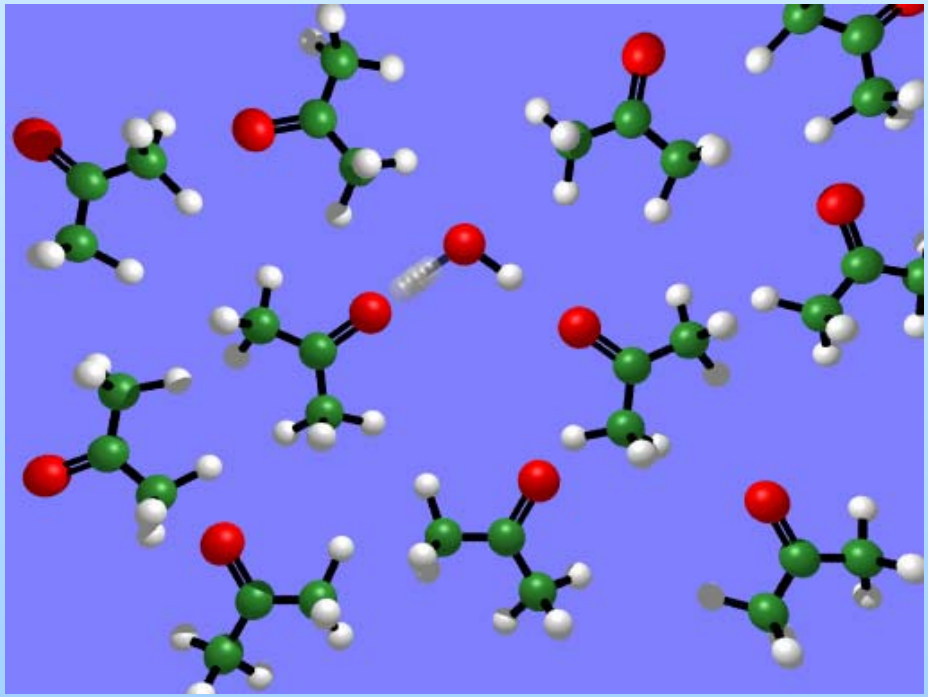
Energy transfer in single hydrogen-bonded water molecules



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Amsterdam, The Netherlands

Outline

I Introduction

II Two-color polarization resolved pump-probe

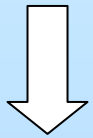
III Dynamics of bulk liquid water

IV Dynamics of embedded H_2O molecules

V Conclusions

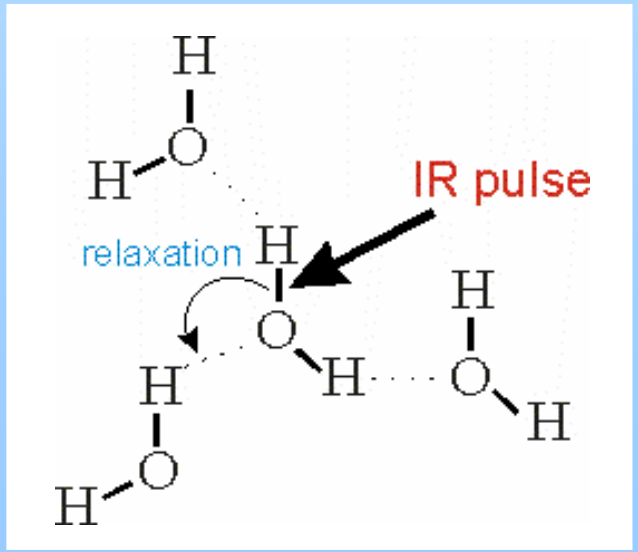
I Introduction

Linear spectral response of water gives little information on the microscopic structure and dynamics



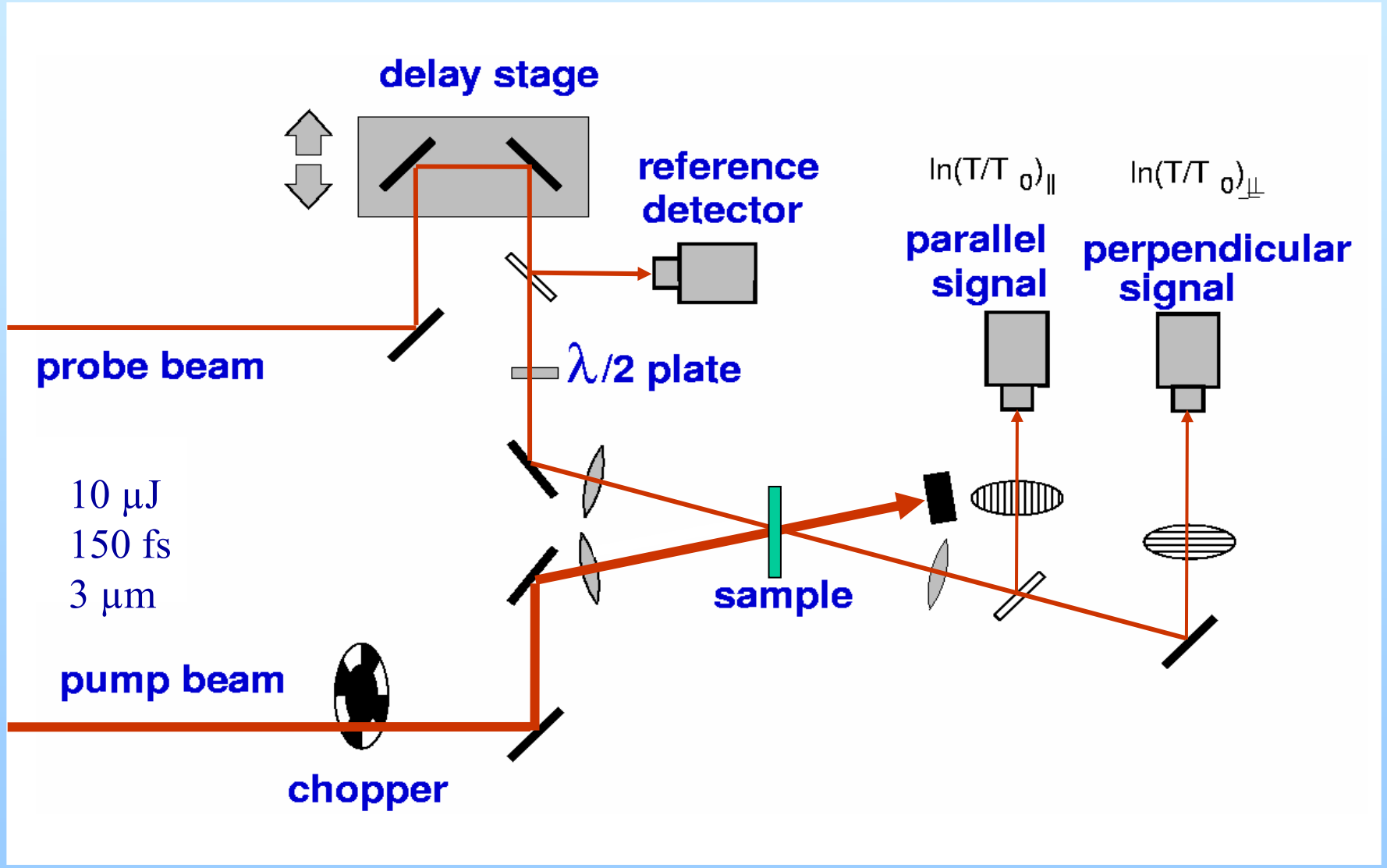
Nonlinear time-resolved mid-IR spectroscopy

H. Graener, G. Seifert, and A. Laubereau, PRL 66, 2092 (1991)

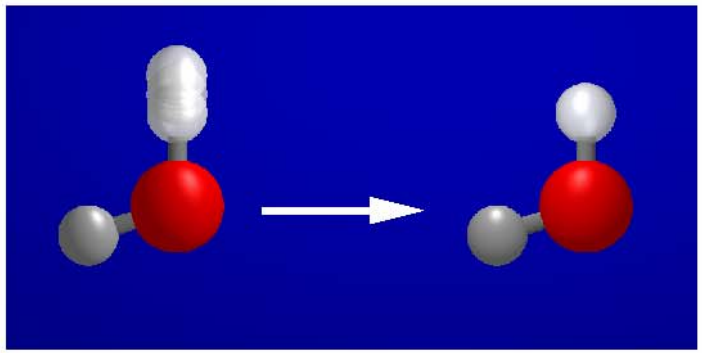


- Energy transfer and relaxation
- Motion (reorientation) of water
- Hydrogen-bond dynamics

Two-color polarization-resolved pump-probe



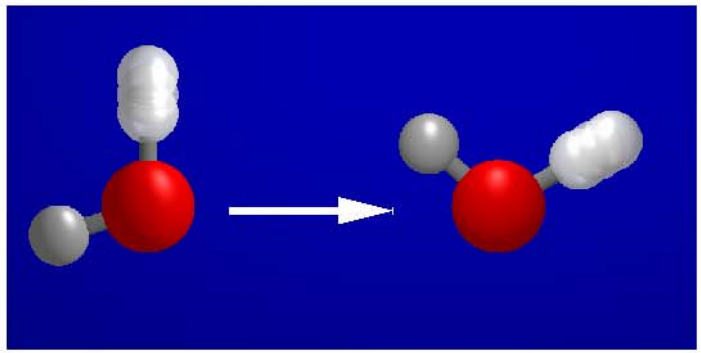
Vibrational relaxation
Spectral diffusion



$$S = \ln(T/T_0)_{\parallel} + 2 \cdot \ln(T/T_0)_{\perp}$$

$$\propto \exp(-\tau/T_1)$$

Reorienation
Resonant energy transfer



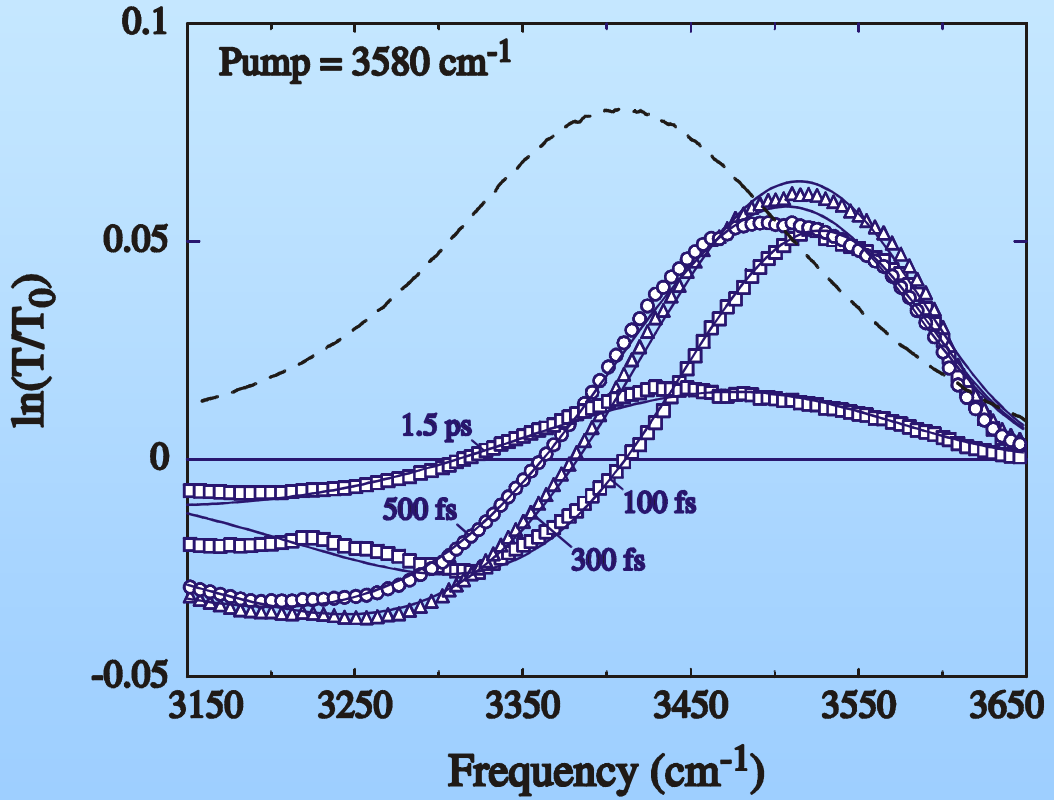
$$R = \frac{\ln(T/T_0)_{\parallel} - \ln(T/T_0)_{\perp}}{S}$$

$$\propto \exp(-\tau/\tau_{or})$$

III Dynamics of bulk liquid water

Spectral hole burning of $HDO:D_2O$

R. Laenen et al. Phys. Rev. Lett. 80, 2622 (1998); G. Gale et al. PRL **82**, 1068 (1999);
S. Woutersen et al. PRL **83**, 2077 (1999); H.J. Bakker et al. JCP **116**, 2592 (2002)



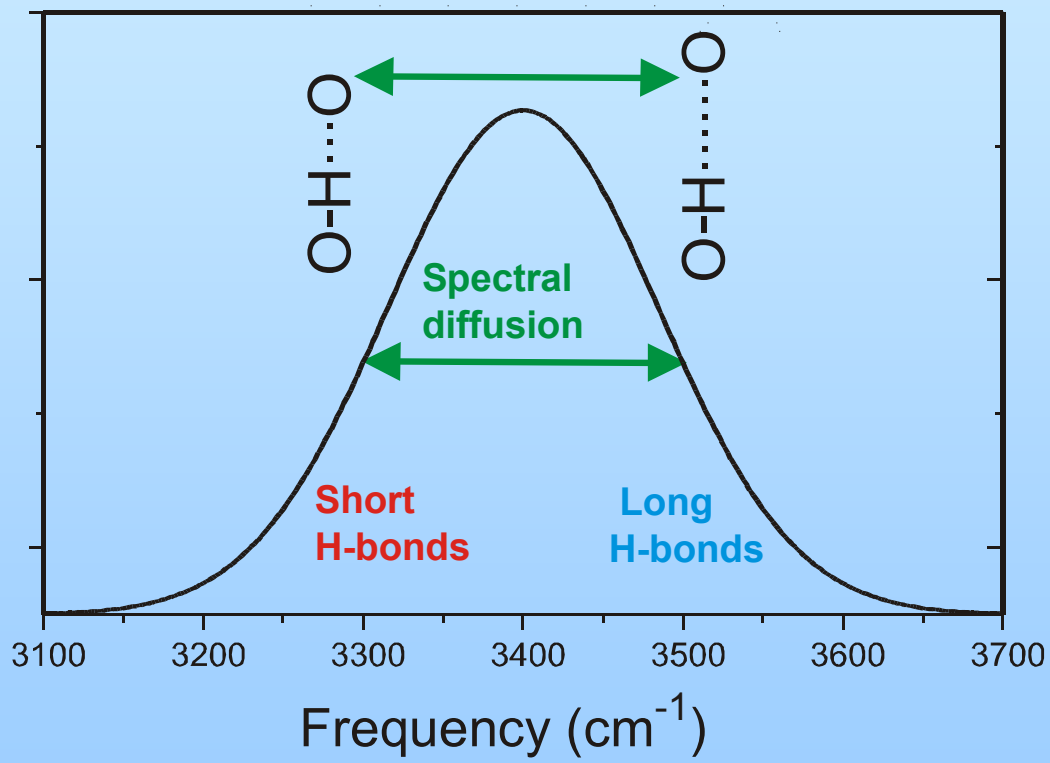
(Heterodyne) photon echo spectroscopy of $HDO:D_2O$

J. Stenger et al. Phys. Rev. Lett. **87**, 027401 (2001); J. Stenger et al. J. Phys. Chem. A **106**, 2341 (2002);
C.J. Fecko et al. Science **301**, 1698 (2003); S. Yeremenko et al. Chem. Phys. Lett. **369**, 107 (2003)

Spectral diffusion:

Fast component: $\tau_c \sim 100$ fs (librations, H-bonds)

Slow component: $\tau_c \sim 700$ fs (H-Bonds)



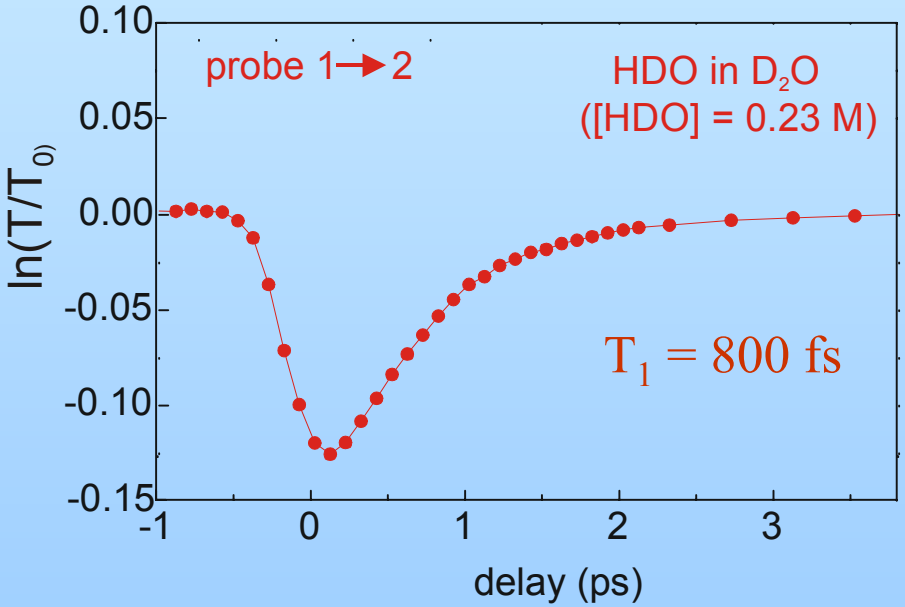
Suggests that hydrogen bond oscillation would be overdamped.

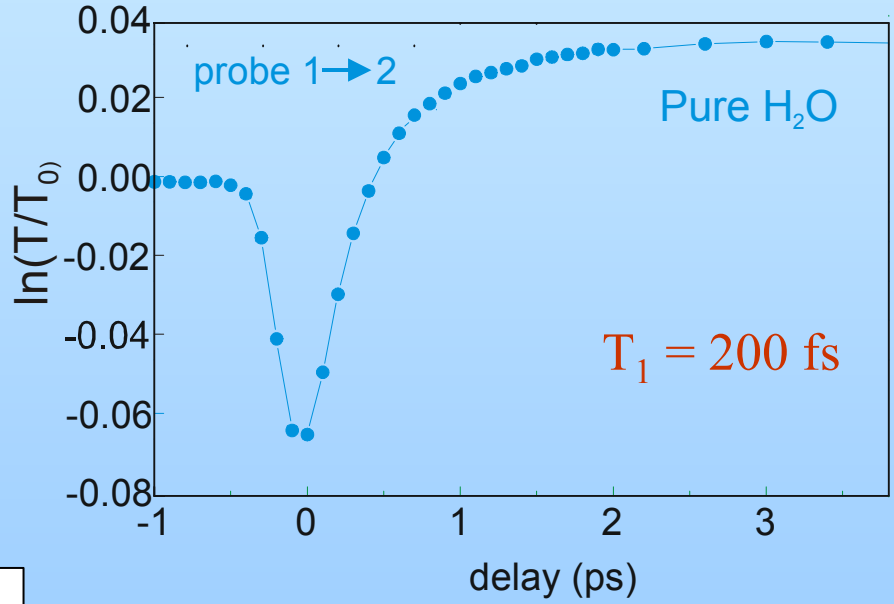
However: hydrogen is strongly damped, but not overdamped!

R. Rey et al. JPCA **106**, 11993 (2002), C.P. Lawrence and J.L. Skinner, JCP **118**, 264 (2003)
C.J. Fecko et al. Science **301**, 1698 (2003)

Vibrational relaxation of pure liquid H_2O

$HDO:D_2O$ good model system for the hydrogen-bond dynamics of H_2O, but:

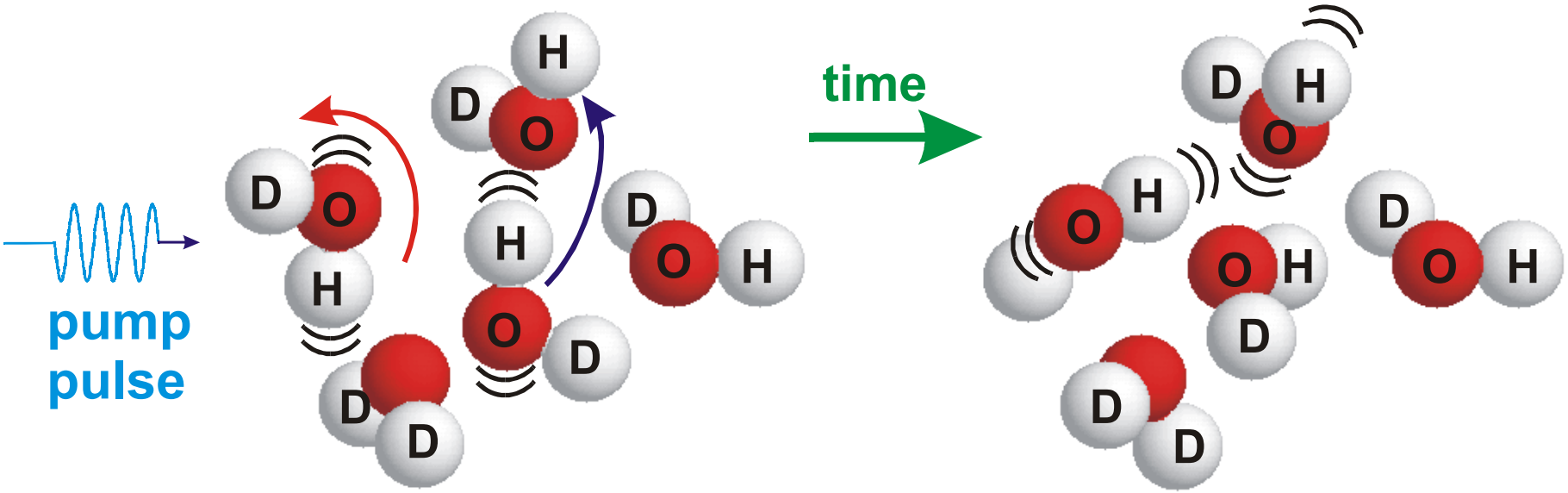




not for the vibrational relaxation of H_2O!

A.J. Lock and H.J. Bakker JCP **117**, 1708 (2002); Z. Wang et al. CPL **378**, 281 (2003);
A. Pakoulev et al. CPL **380**, 404 (2003); H.J. Bakker et al. CPL **384**, 236 (2003)

Depolarization

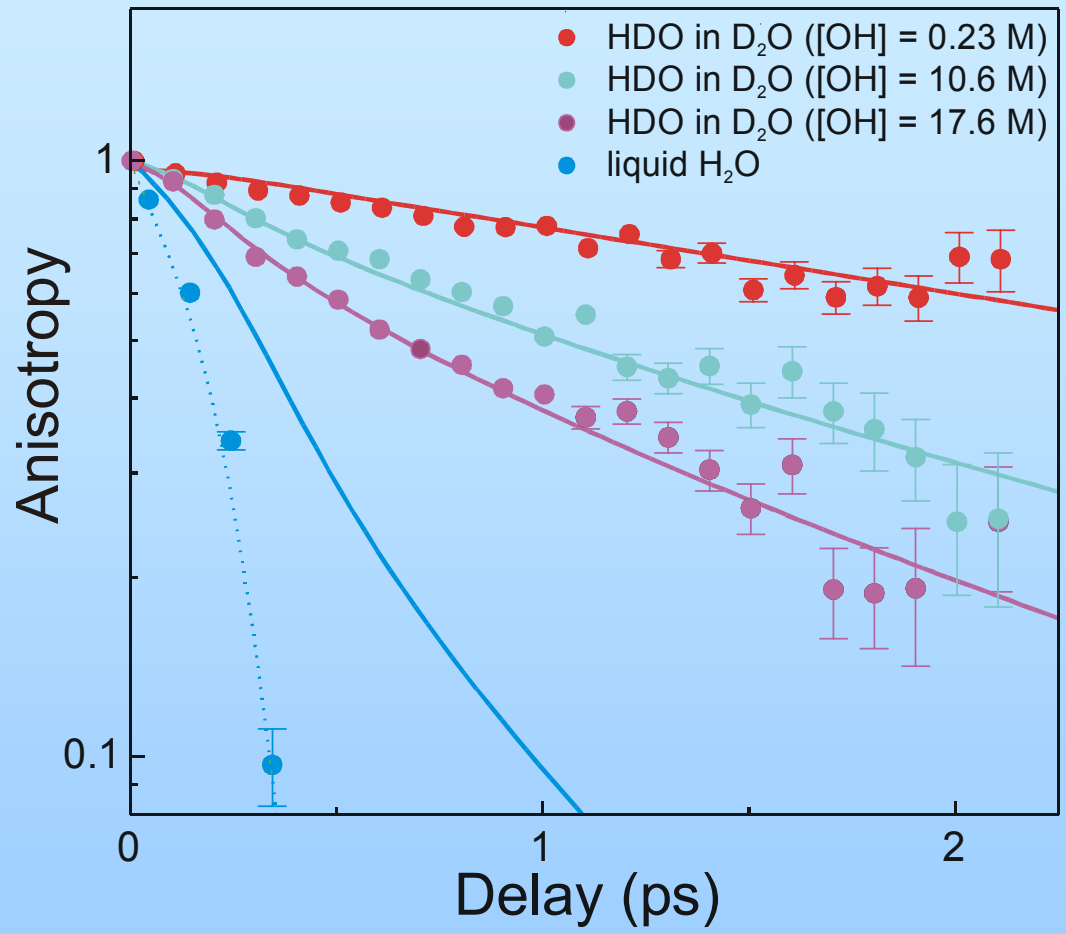


parallel > perpendicular

parallel = perpendicular

⇒decay of anisotropy reflects
orientational diffusion and energy transfer

Depolarization of HDO:D_2O and H_2O



Low concentration OH: orientational diffusion (τ_{or}= 2.6 ps)

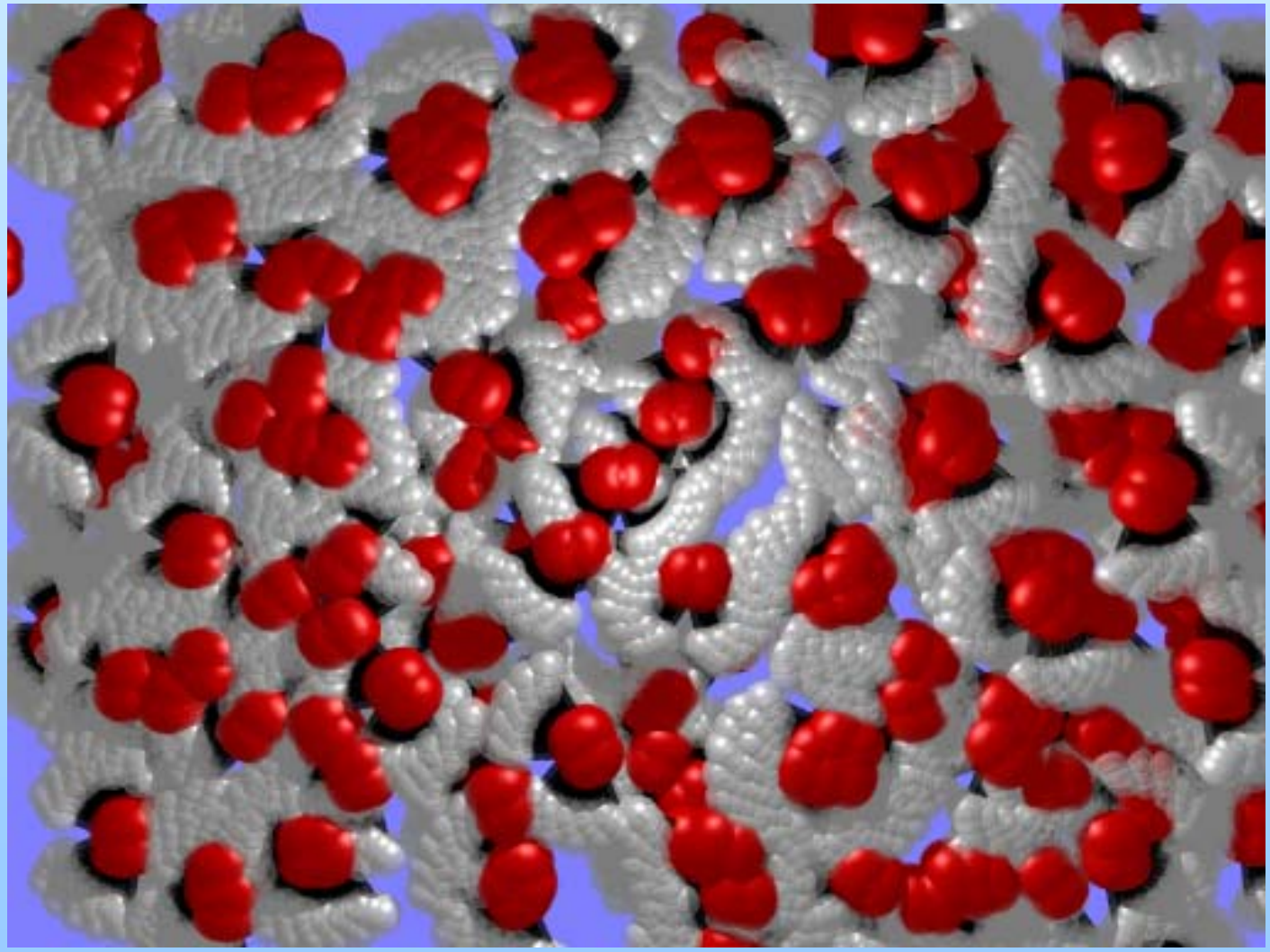
High concentration OH: orientational diffusion + energy transfer

For pure H_2O: depolarization faster than 50 fs!

Dynamics of bulk liquid water

Pictures with shutter time τ

τ

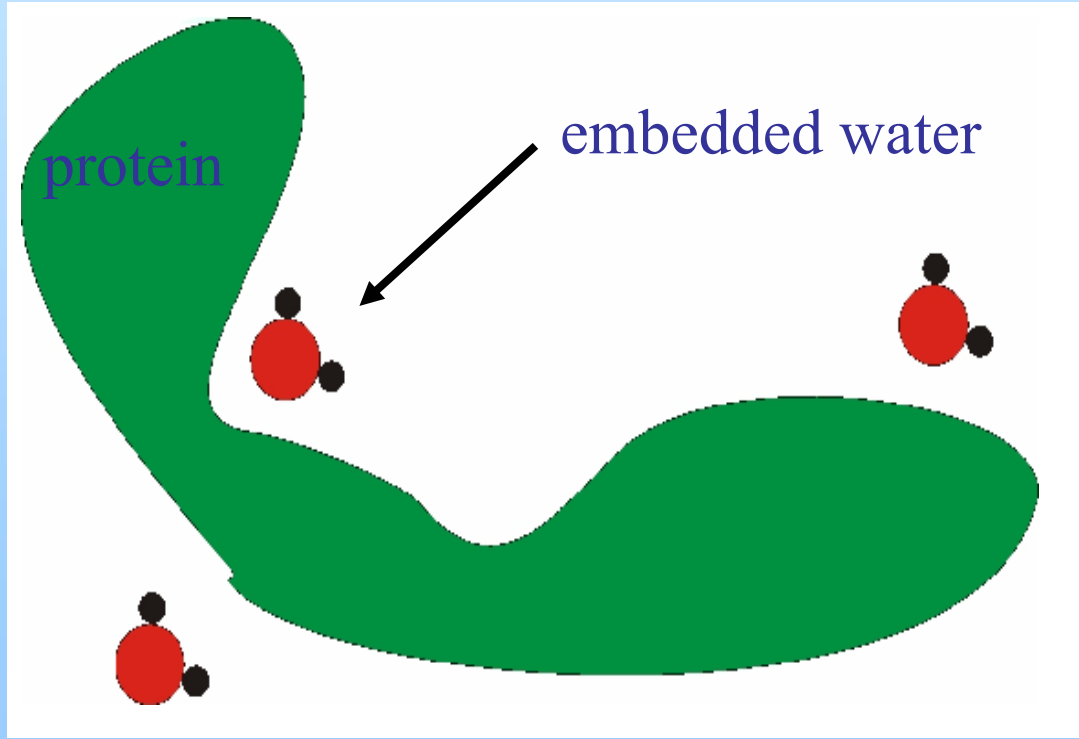


τ_c= 100/700 fs

τ s

IV Vibrational dynamics of embedded H_2O molecules

- Water is important in biochemical reactions:
  (1) determines structure and energetics by solvation interactions
  (2) as a reactant (proton donor/acceptor)
- Role of water is often played by a small number of embedded molecules
- Behavior of isolated (embedded) water molecules may differ from bulk



S.K. Pal, L. Zhao and A.H. Zewail, PNAS **100**, 8113 (2003)

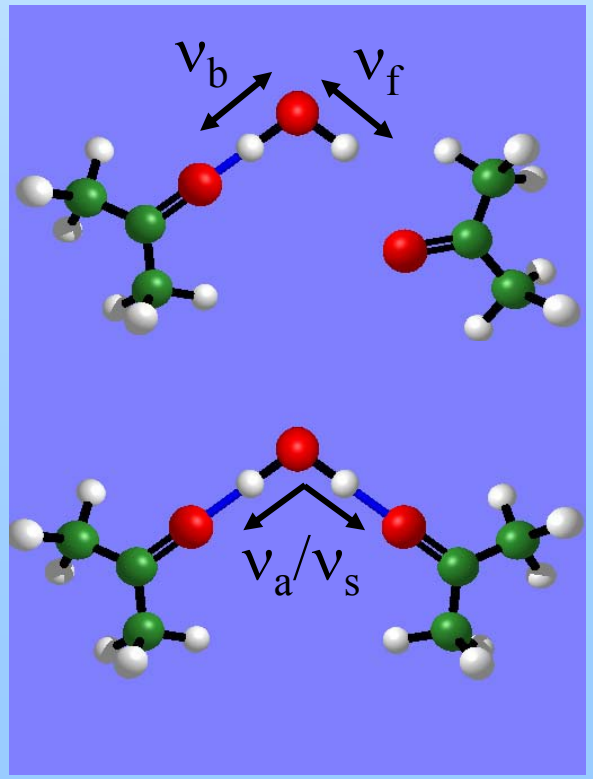
Study of single H_2O molecules embedded by acetone

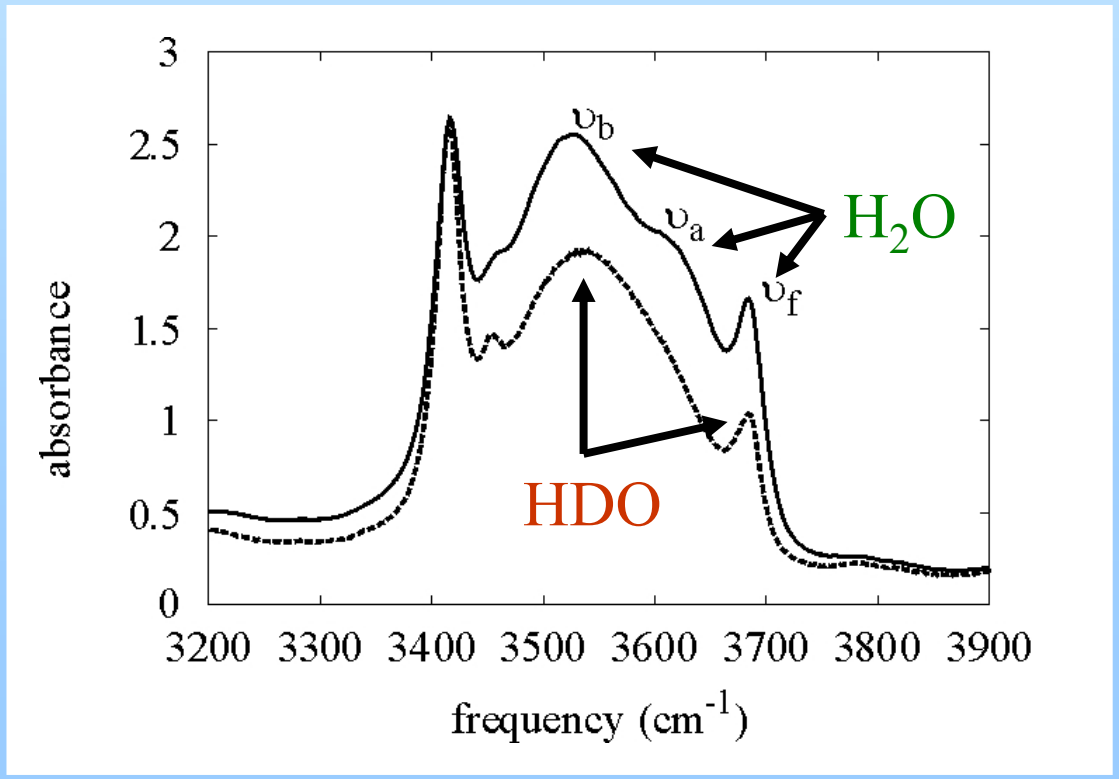
H_2O in C_3H_6O and CCl_4

Two conformations
1. Singly bonded
2. Doubly bonded

- bonded: $\nu_b = 3530\ cm^{-1}$
- free: $\nu_f = 3690\ cm^{-1}$

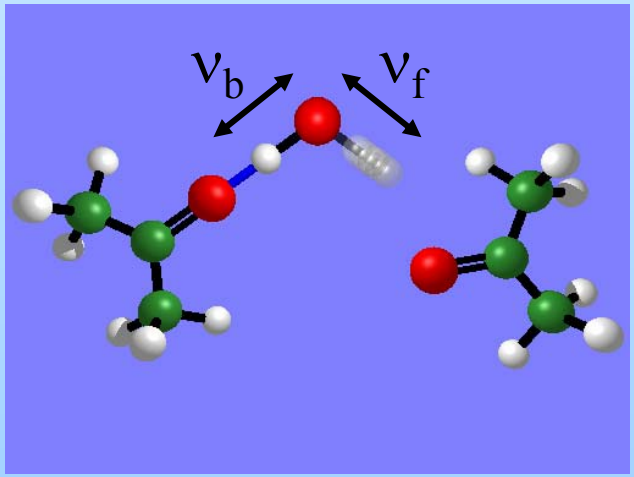
- anti-symmetric: $\nu_a = 3625\ cm^{-1}$
- symmetric: $\nu_s = \pm 3500\ cm^{-1}$

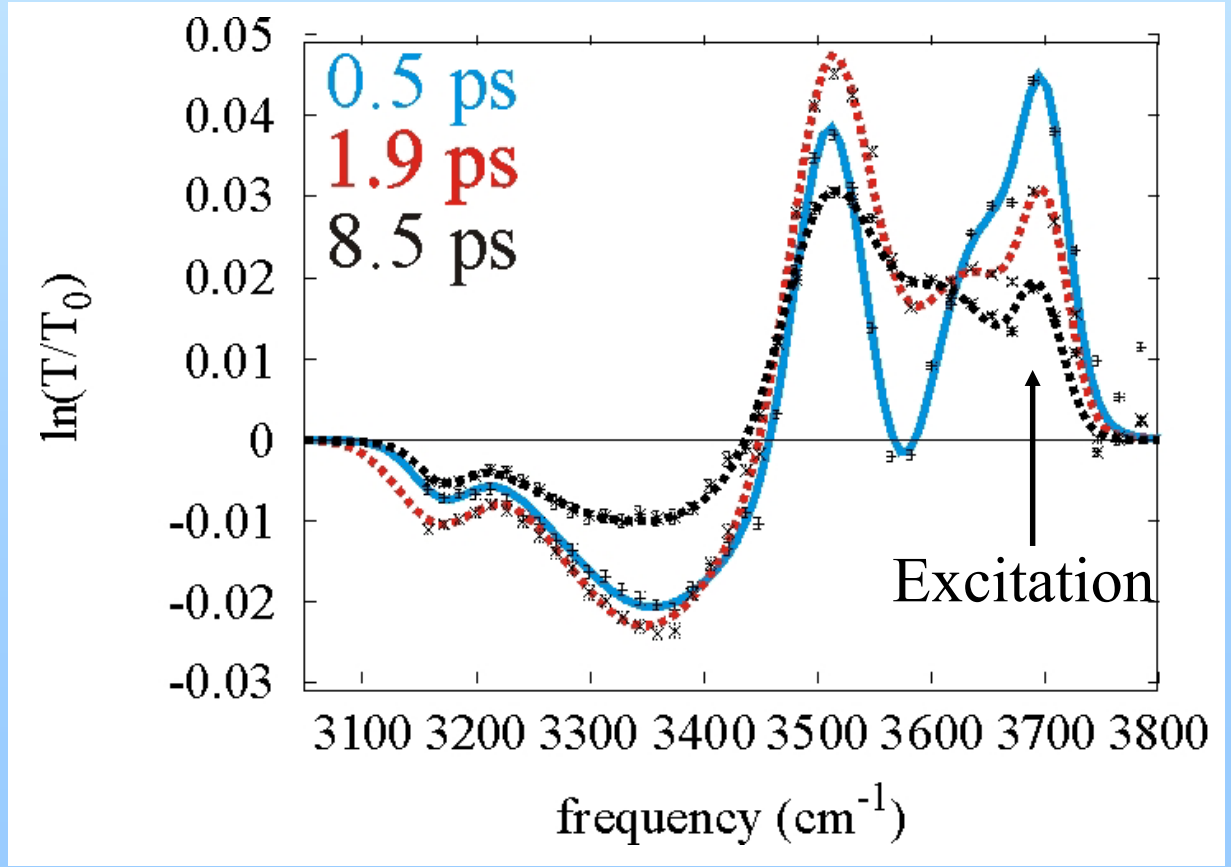




Transient spectra after pumping of ν_f

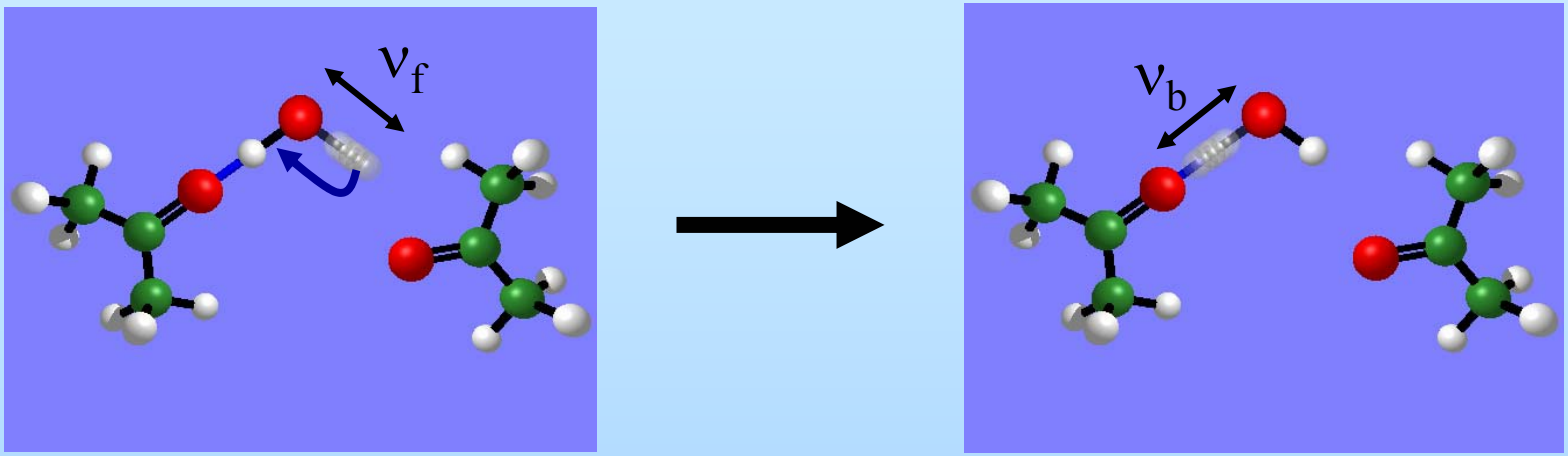
Transfer $\nu_f \Rightarrow \nu_b$



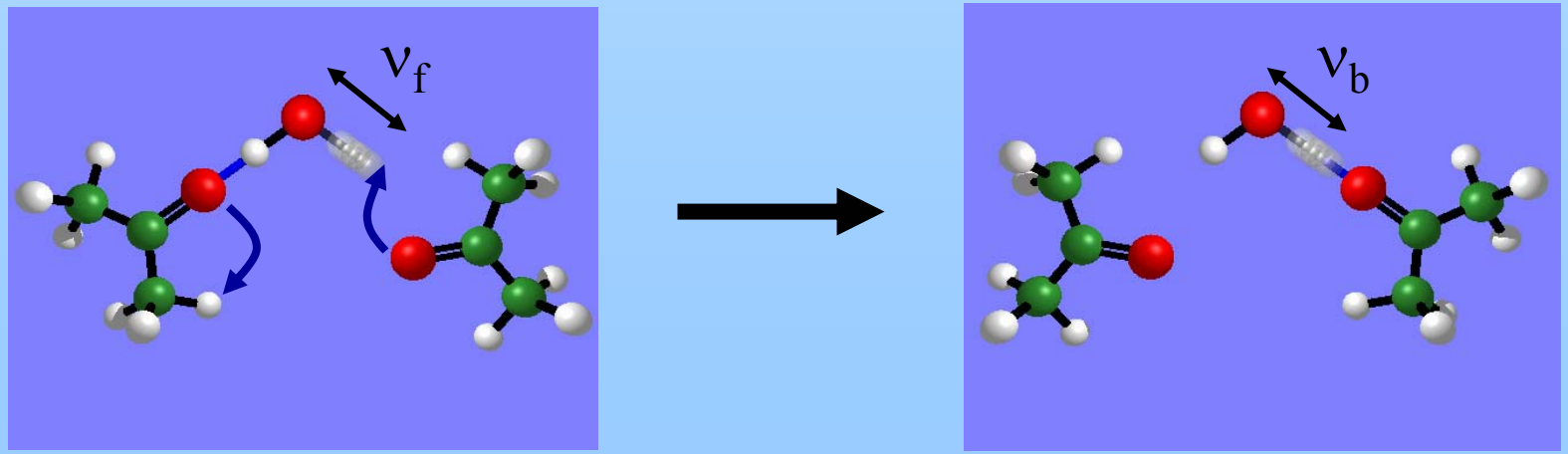


Two possible mechanisms for transfer $\nu_f \Rightarrow \nu_b$

1) Intramolecular energy transfer



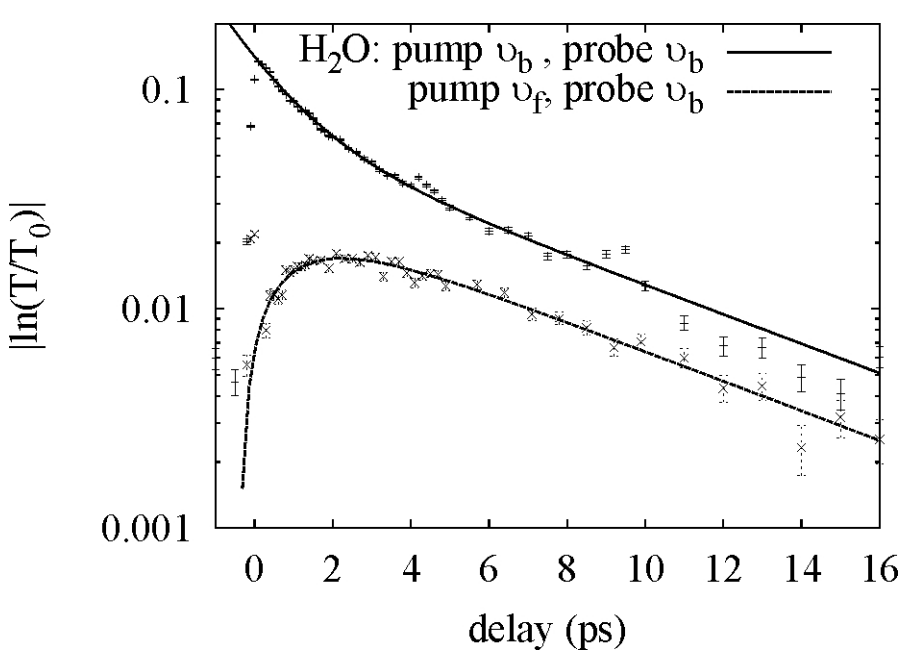
2) Hydrogen-bond dynamics

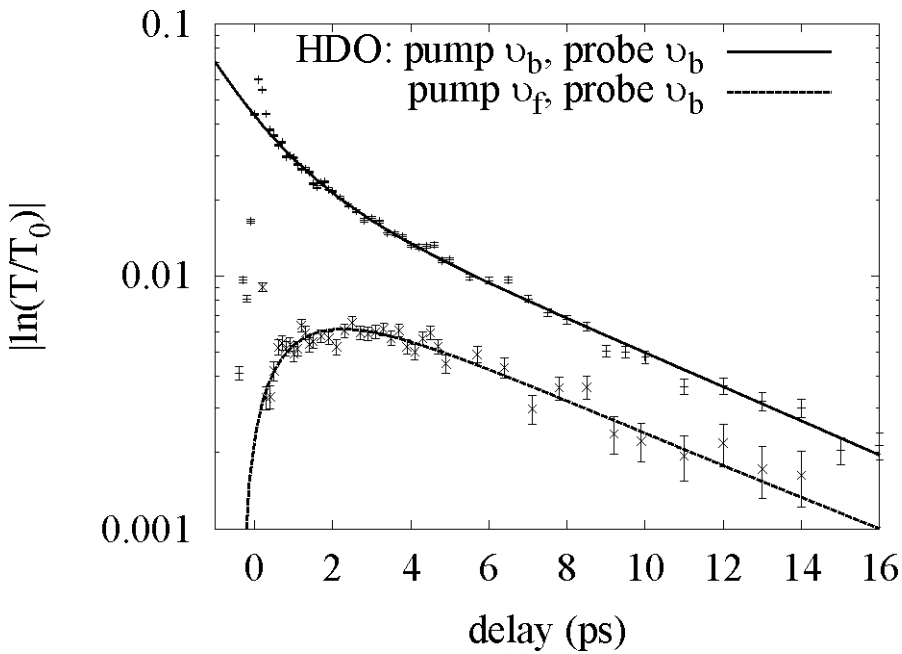


Comparison of the dynamics of H_2O with HDO

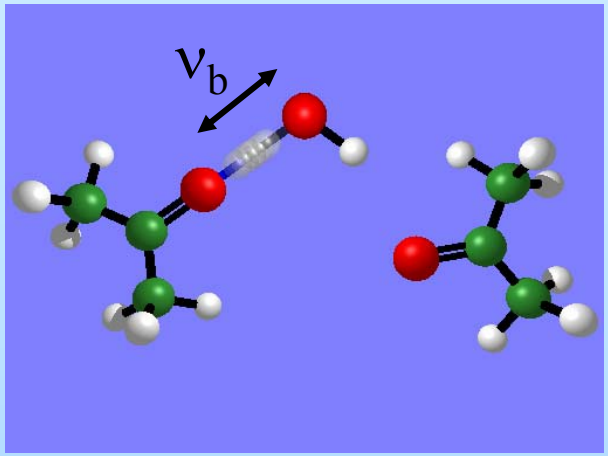
The 4 delay scans have the same time scales
of 6.3 (±0.5) ps and 1.3 (±0.3) ps

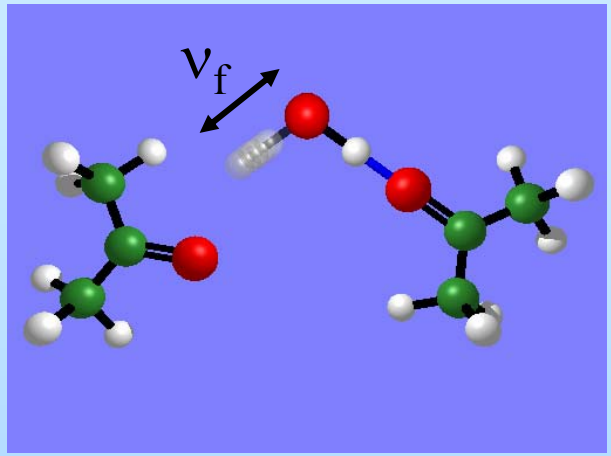
Resemblance between H_2O and HDO indicates
that transfer $\nu_f \Rightarrow \nu_b$ is governed by **hydrogen-bond dynamics**

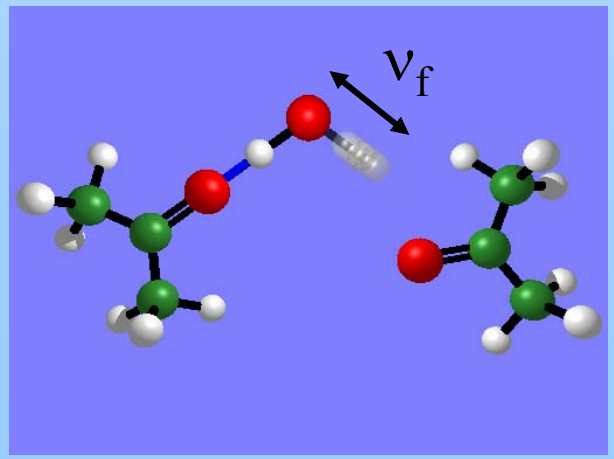


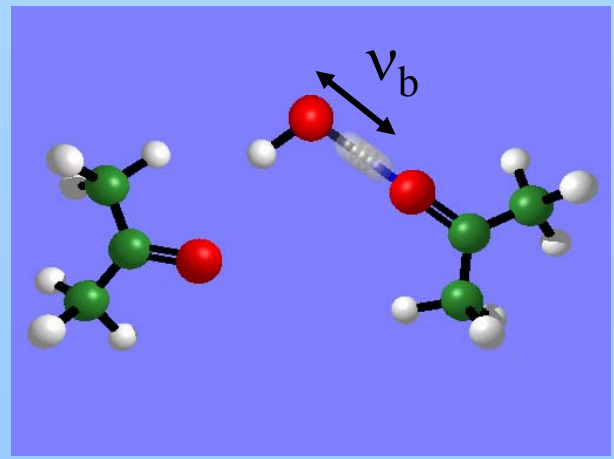


Model (1)









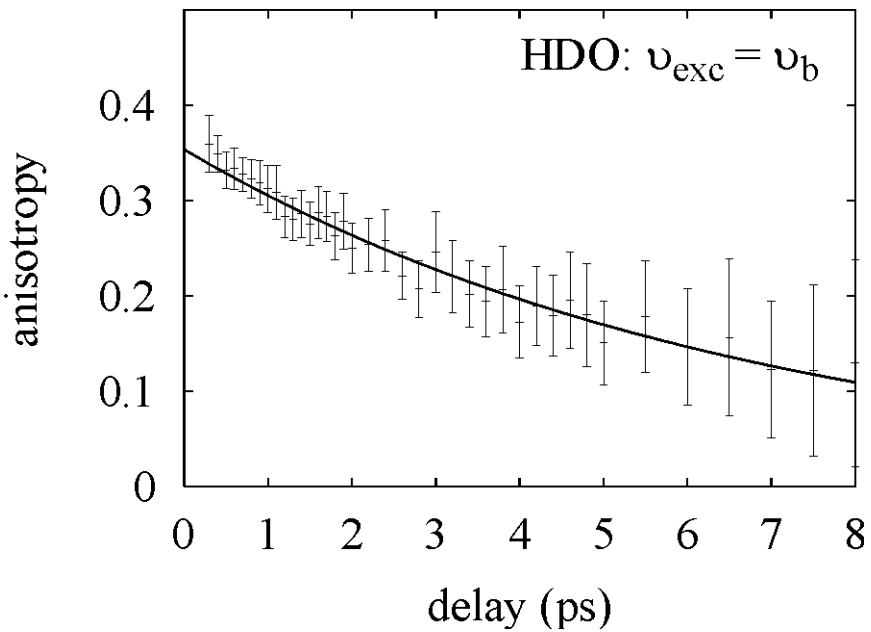
Comparison of anisotropy dynamics

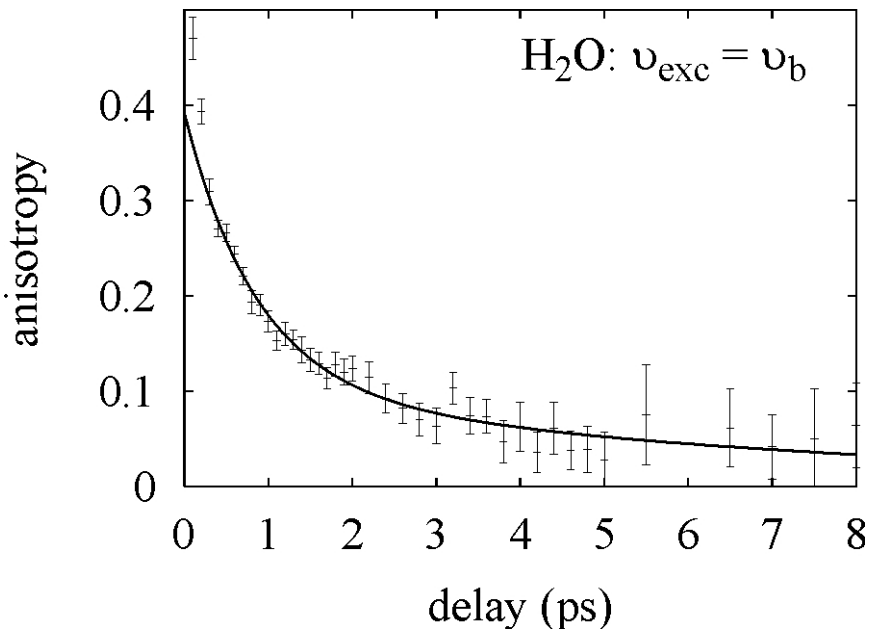
HDO

Mono-exponential decay
- molecular reorientation 6 (±1) ps

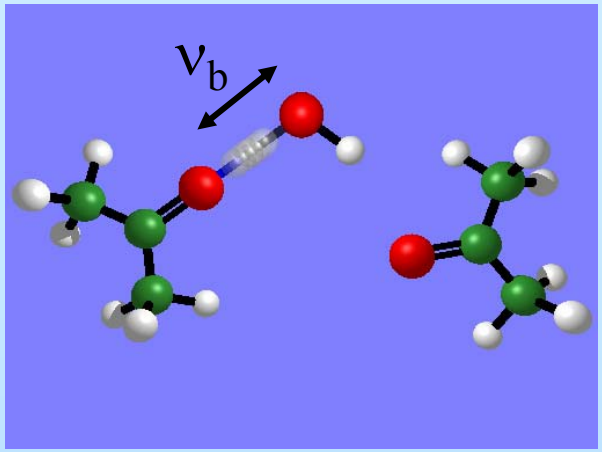
H_2O

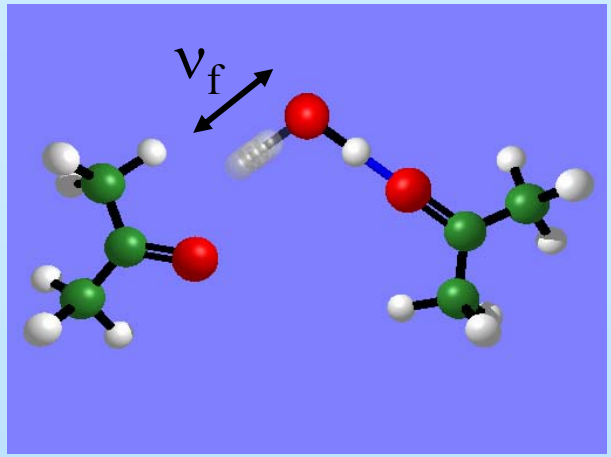
Bi-exponential decay
- energy transfer: 1.3 (±0.3) ps
- molecular reorientation: 6 (±1) ps

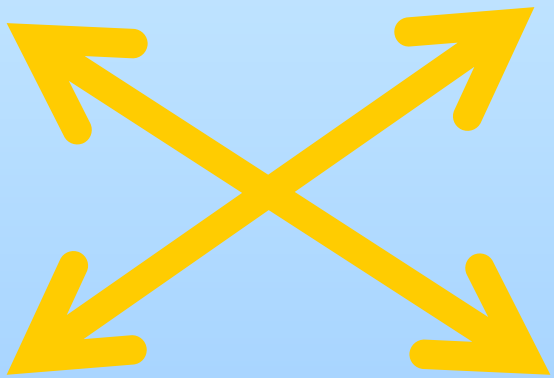


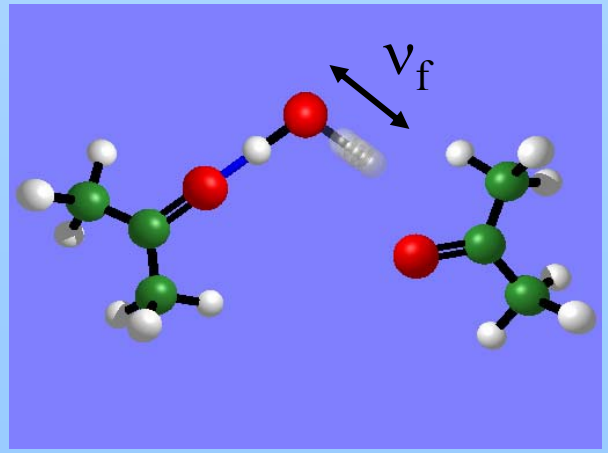


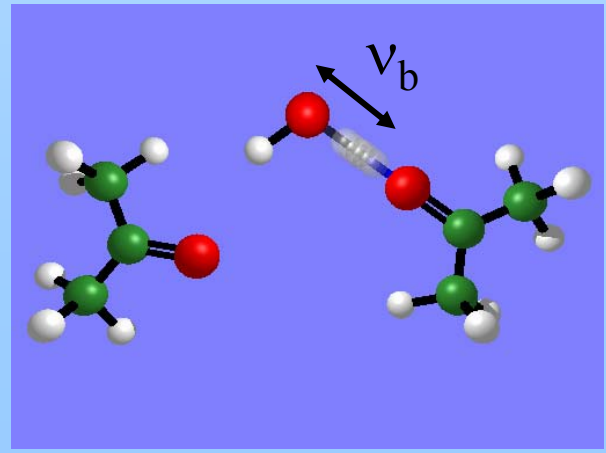
Model (2)





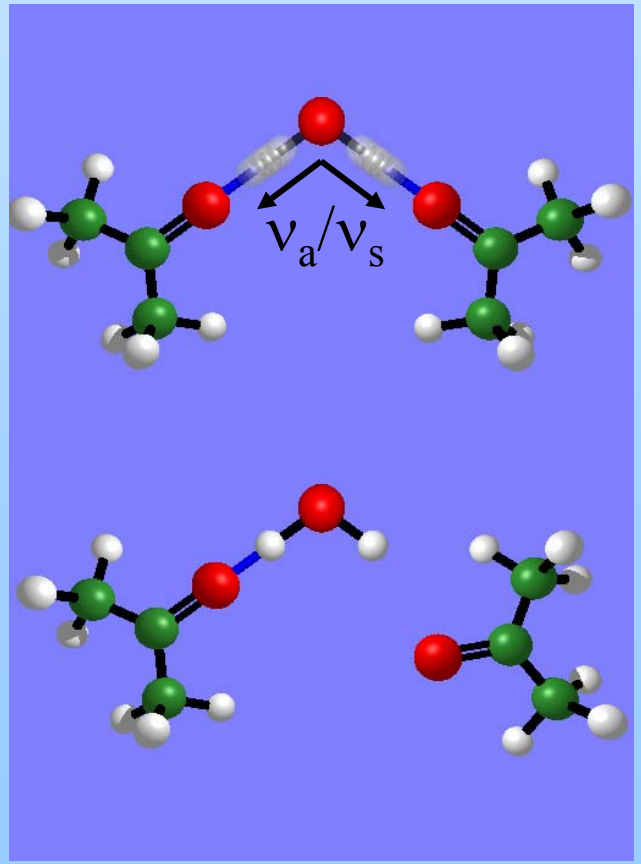


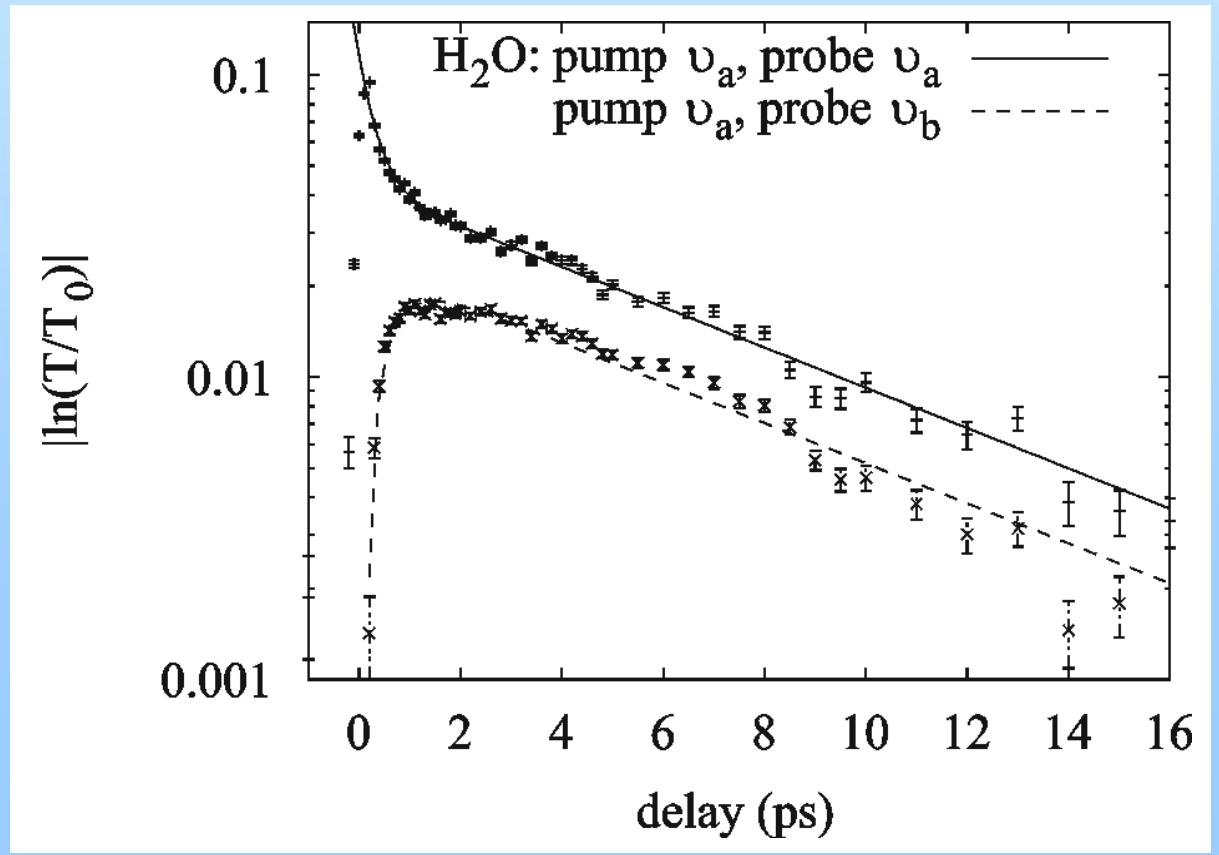




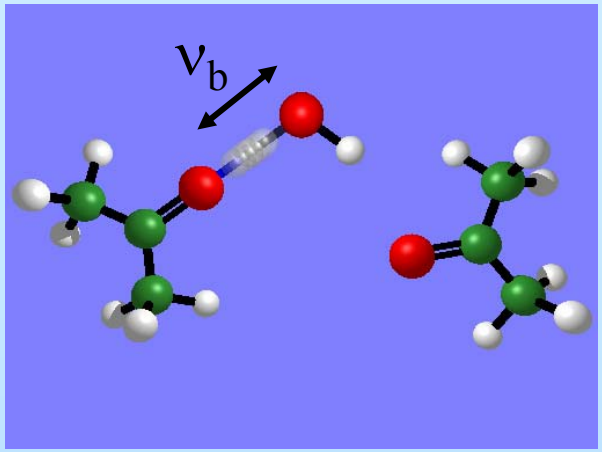
Pumping of the ν_a mode (specific for H_2O)

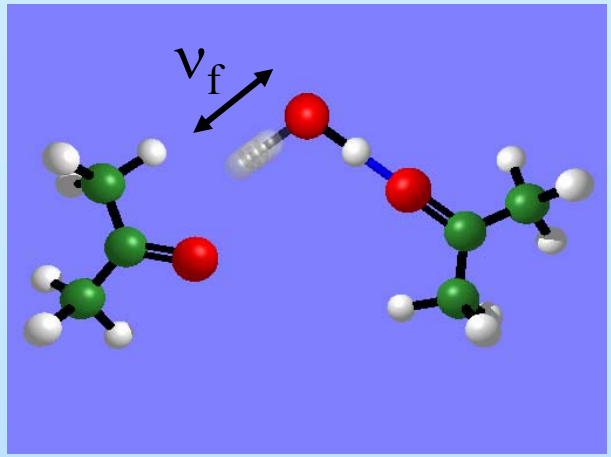
Energy Transfer $\nu_a \Rightarrow \nu_b$ in 500 fs

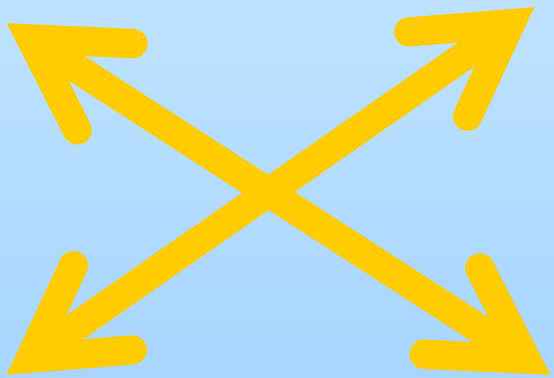


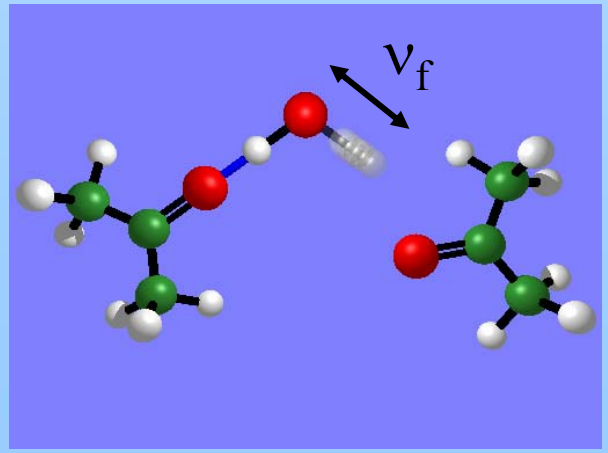


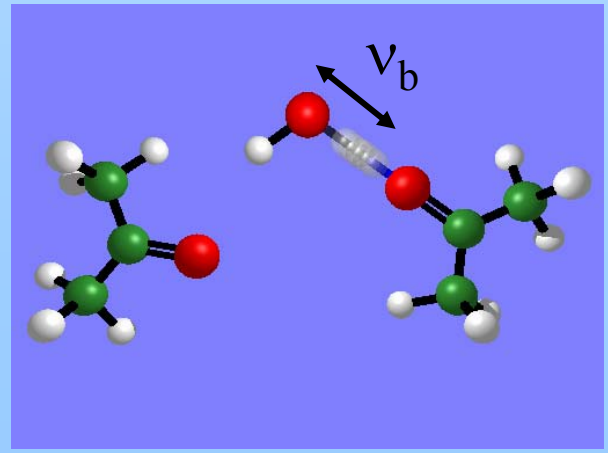
Model (3)?



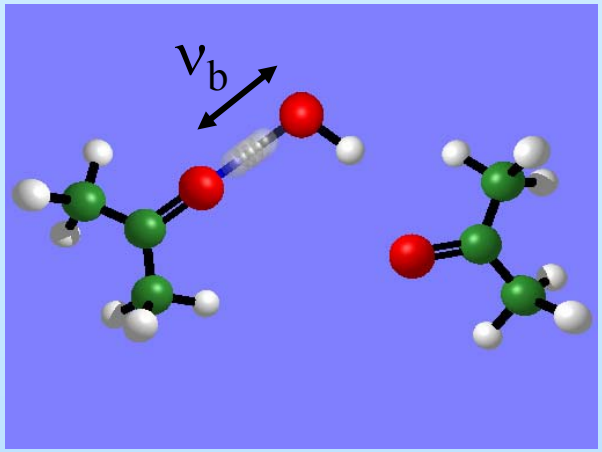


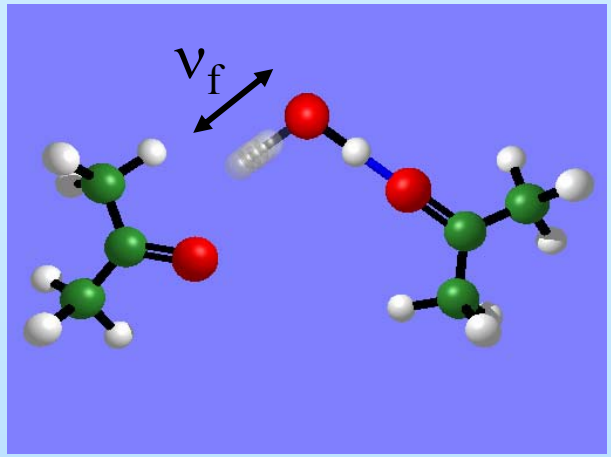


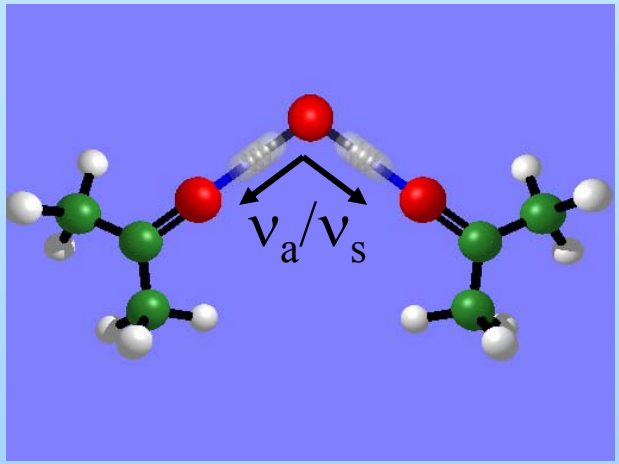


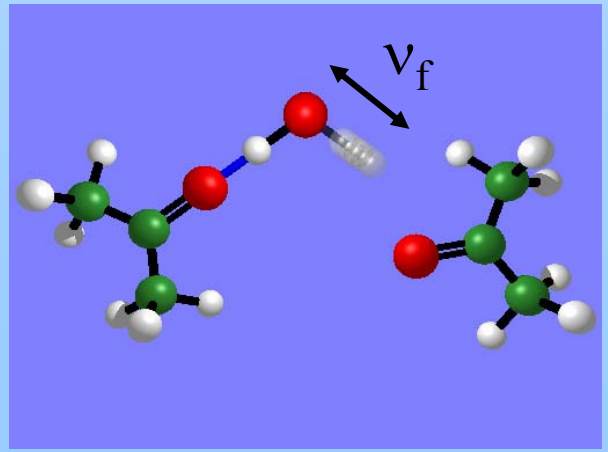


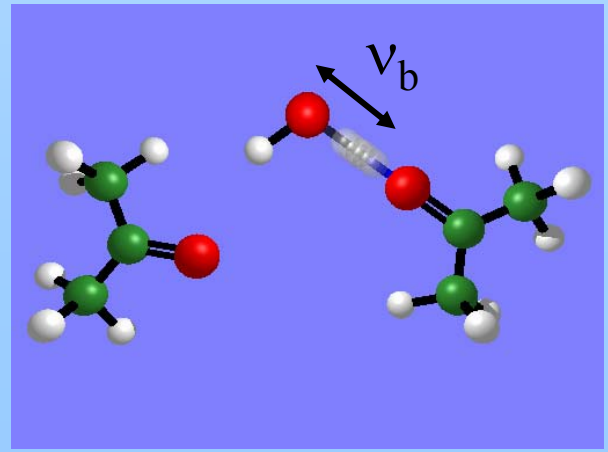
Model (3)!



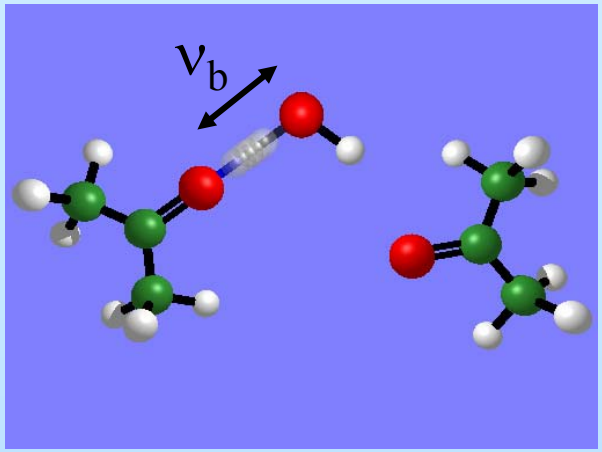


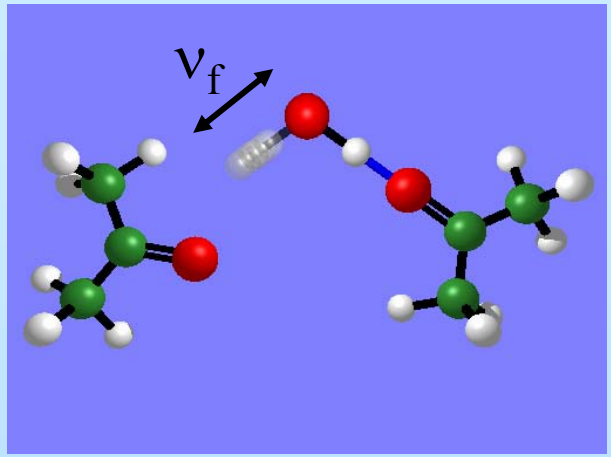






Model (3)



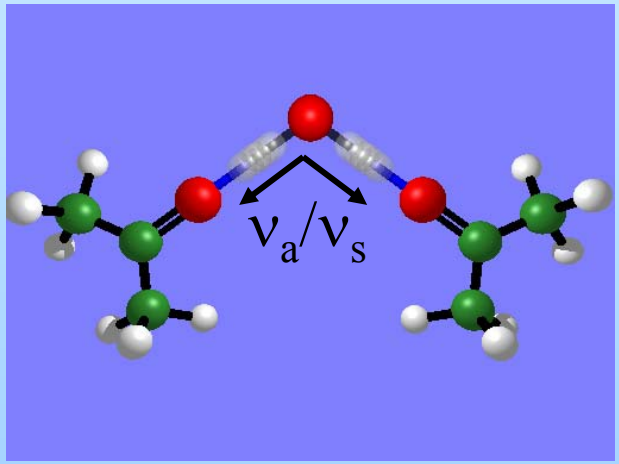


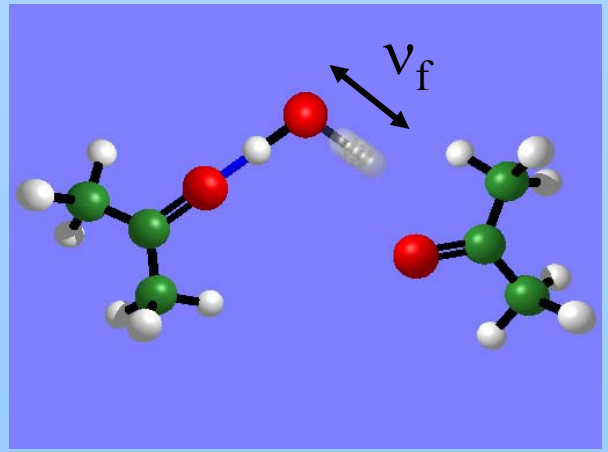
1.0 ps

1.1 ps

1.0 ps

0.7 ps



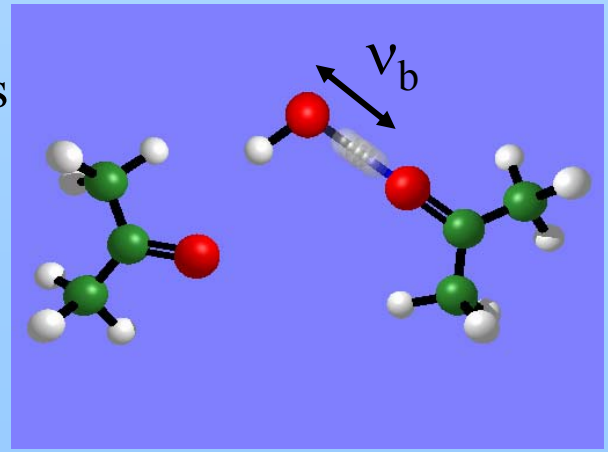


0.7 ps

1.0 ps

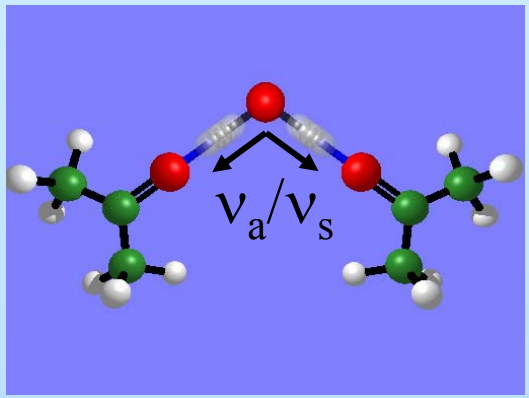
1.0 ps

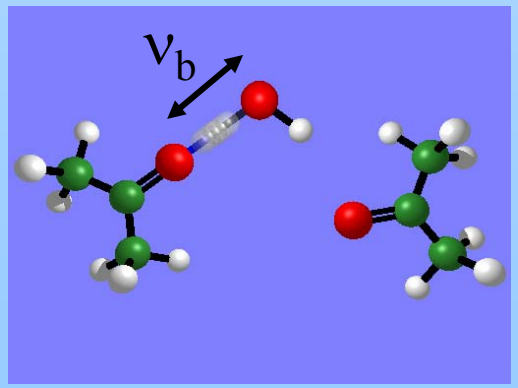
1.1 ps

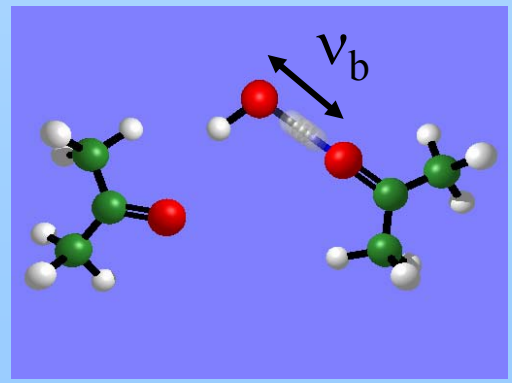


PNAS **102**, 3202 (2005)

Energy landscape



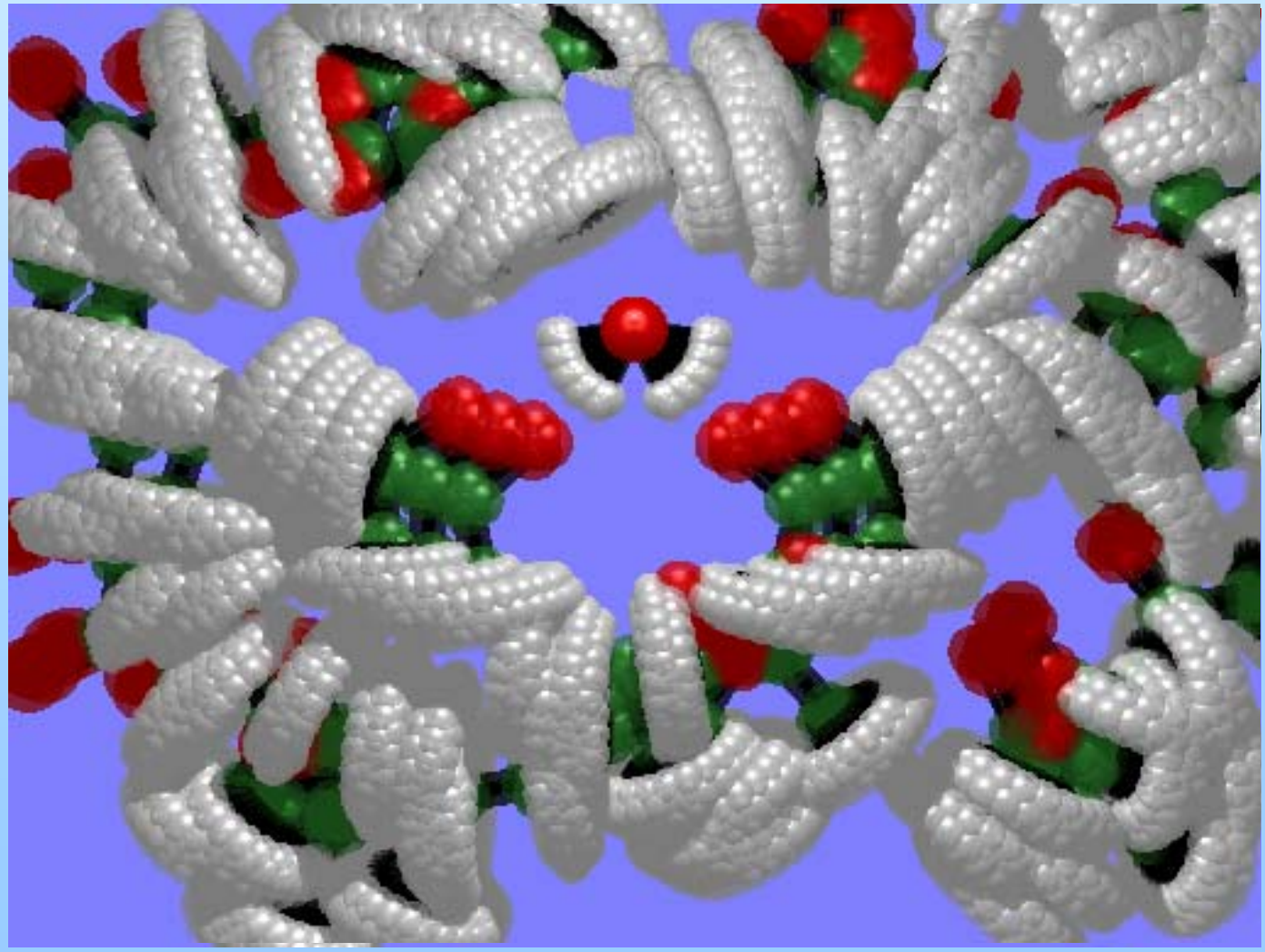




Dynamics of a single water molecule in acetone

Pictures after delay τ with shutter time τ

τ



$\tau_{or} = 6$ ps

$T_1 = 6.3$ ps

V Conclusions

• The dynamics of embedded H_2O strongly differ from bulk H_2O:

	H_2O (bulk)	H_2O:C_3H_6O
τ_{ET}	<50 fs	1.3 ps
τ_c	100/700 fs	~1 ps
τ_{or}	2.6 ps	6 ps
T_1	200 fs	6.3 ps

$\Rightarrow$ For embedded water the energy transfer and energy relaxation are 20 times slower than for bulk water.

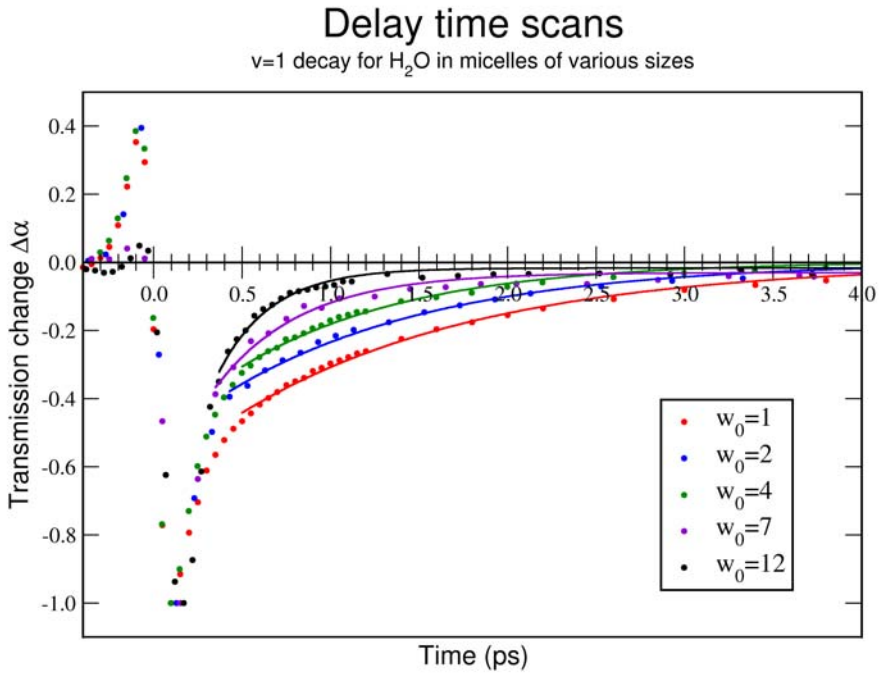
$\Rightarrow$ For embedded water the H-bond and orientational dynamics are 3 times slower, although the hydrogen bonds are weaker than in the bulk liquid!

•The energy transfer of embedded water molecules is completely mediated by hydrogen bond breaking and formation dynamics.

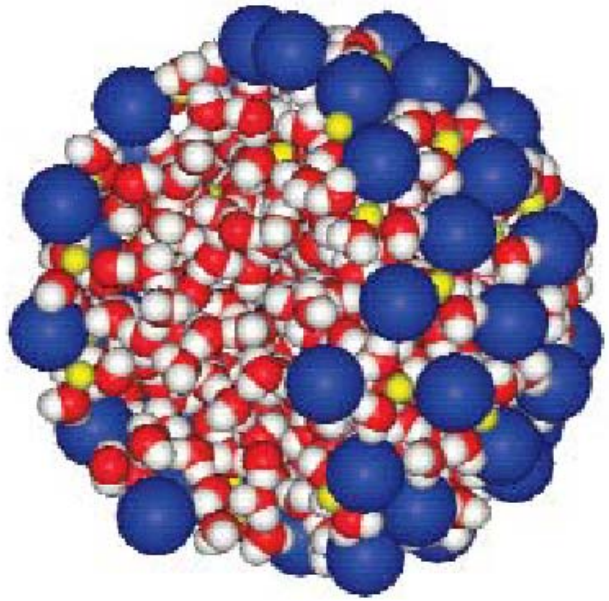
VI Outlook

Study of water intermediate between bulk and single water molecules:

Reverse micelles (water + AOT in octane)



W_0 ([H_2O]/[AOT])	1	2	4	7	12
N_{H_2O}	5	20	80	400	2000
T_1 (ps)	0.9	0.7	0.5	0.4	0.3



Model confinement. Modeled reverse micelle (w_0 = 7.5), showing the surfactant head groups and a slice of the interior. The micelle contains 70 AOT surfactant molecules, 70 Na^+ counterions, and 525 water molecules.