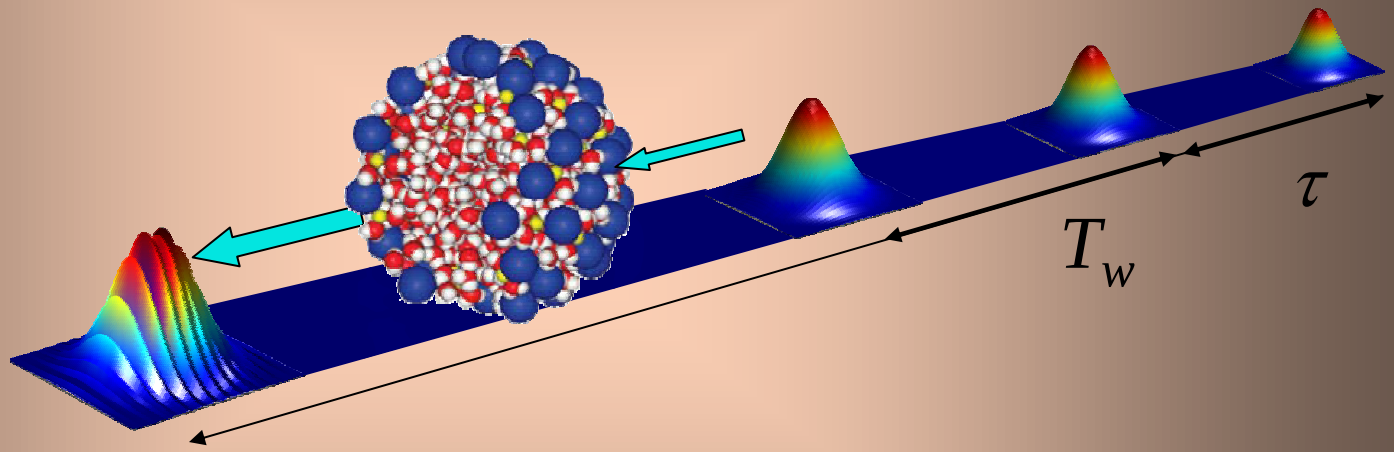
Nanoscopic Water and Proton Transfer



Ultrafast Infrared and Visible Spectroscopy

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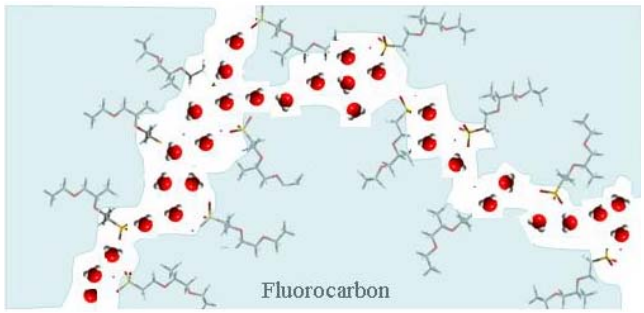
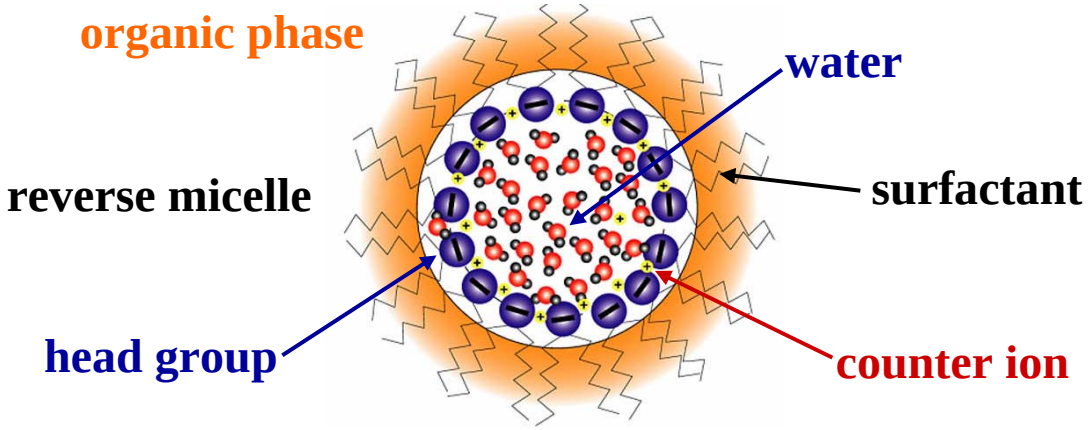
Sanford University
6/26/2006

Nanoscopic Water → **Chemistry, Biology**

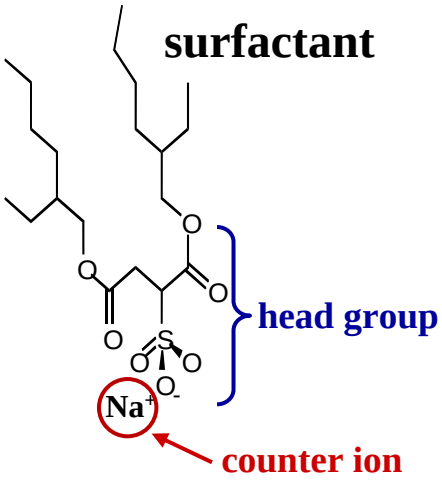
water confined on nm length scale → **Geology, Materials**



Nafion fuel cell membrane



Aerosol OT (AOT) reverse micelles



Same head group as Nafion

w_0 characterizes size

$$w_0 = \frac{[H_2O]}{[\text{surfactant}]}$$

w_0 is directly related to the micelle radius

Nanopool diameter can range from < 1 nm to ~30 nm.

- $w_0 = 2 \rightarrow$ 1.7 nm (~40 H_2O)
- $w_0 = 5 \rightarrow$ 2.4 nm (~300 H_2O)
- $w_0 = 10 \rightarrow$ 4.0 nm (~1000 H_2O)
- $w_0 = 20 \rightarrow$ 7.0 nm (~5400 H_2O)
- $w_0 = 40 \rightarrow$ 17 nm (~77,000 H_2O)
- $w_0 = 60 \rightarrow$ 28 nm (~350,000 H_2O)

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Sanford University
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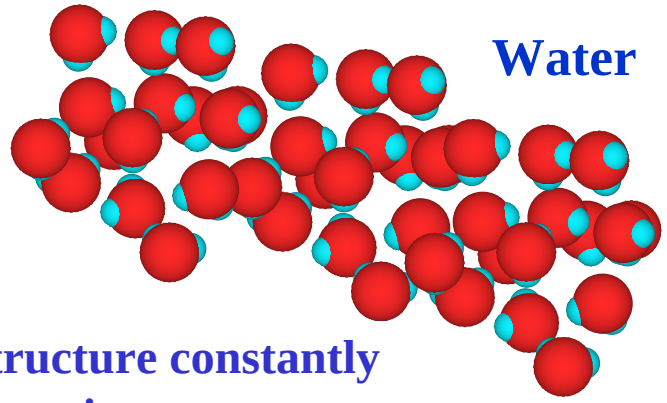
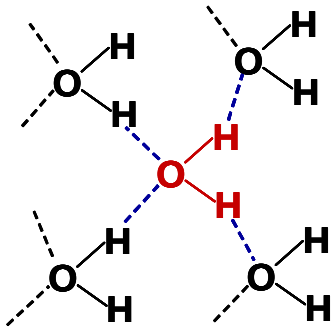
Properties of Water - Hydrogen Bond Network and Its Evolution



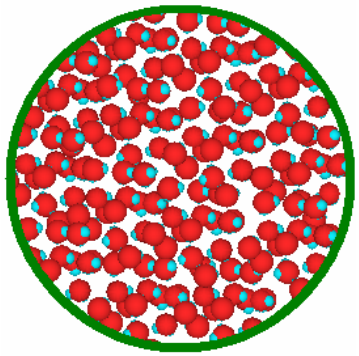
Water

Structure constantly changing.



Water can make up to 4 hydrogen bonds.

Strong bonds become weak.
Weak bonds become strong.
Bonds form.
Bonds break.



How Does Nanoscopic Confinement Change the Properties of Water?

Over what distances are the properties of water changed by confinement?

M.D. Fayer
Sanford University
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IR Spectroscopy of Water Hydroxyl Stretch – Direct Probe of Hydrogen Bond Network and Its Dynamics

Four Experimental Observables

1. **Absorption spectra – FT-IR measurements**
2. **Vibration population relaxation – Ultra fast IR pump-probe measurements**
3. **Orientational relaxation – Ultrafast IR pump-probe polarization measurements**
4 **Spectral diffusion – Ultrafast IR vibrational echo measurements**

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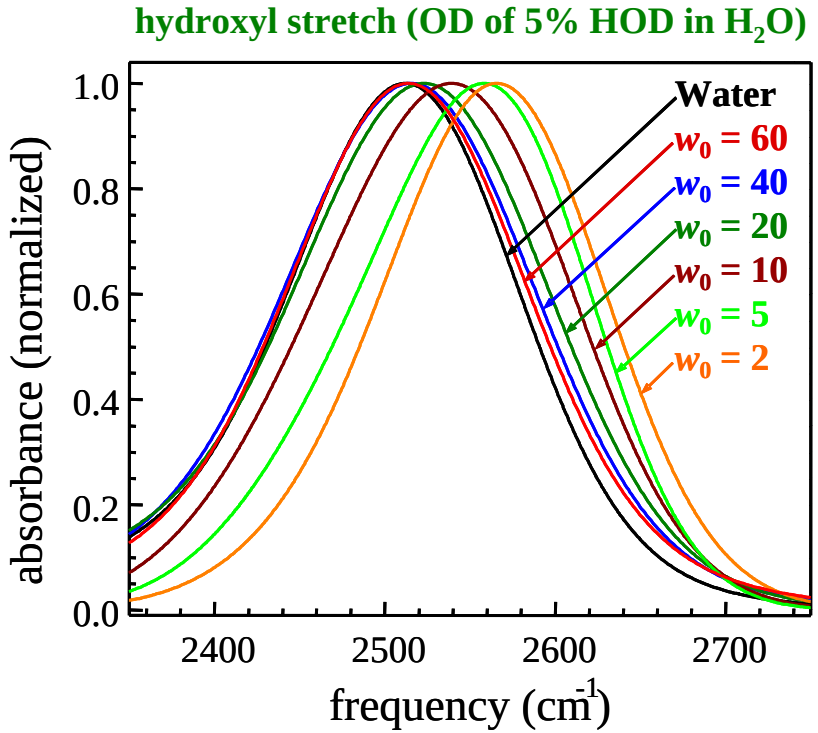
Linear absorption spectra blue shift as water nanopool gets smaller



	d (nm)	# H_2O
water	-	-
$w_0 = 60$	28	350,000
$w_0 = 40$	17	77,000
$w_0 = 20$	7.0	5400
$w_0 = 10$	4.0	1000
$w_0 = 5$	2.4	300
$w_0 = 2$	1.7	40

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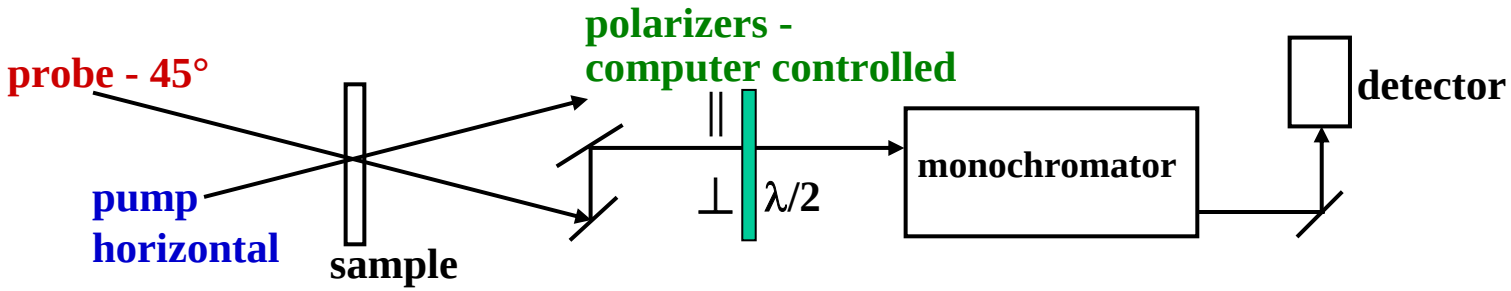
Ultrafast IR Wavelength Selected Polarized IR Pump-Probe Experiments
Population Relaxation and Orientational Relaxation



$$S_{\parallel}(t) = Ae^{-t/\tau}(1 + 0.8C_2(t)) \qquad S_{\perp}(t) = Ae^{-t/\tau}(1 - 0.4C_2(t))$$

C_2(t) is the orientational correlation function for a dipole transition (second order Legendre polynomial).

population relaxation $\quad P(t) = S_{\parallel}(t) + 2S_{\perp}(t)$

orientational anisotropy $\quad r(t) = \dfrac{S_{\parallel}(t) - S_{\perp}(t)}{S_{\parallel}(t) + 2S_{\perp}(t)} = 0.4C_2(t)$

$C_2(0) = 1$; therefore $r(0) = 0.4$

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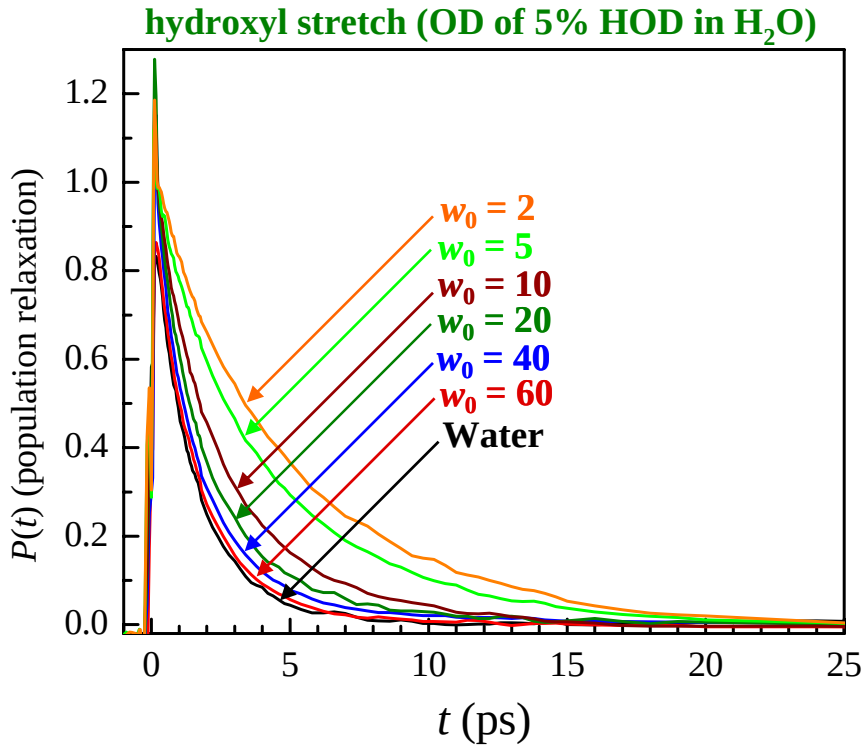
Vibrational Population Relaxation Slows as Water Nanopool Gets Smaller.



	$P(t)$
w_0 = 2	5.2 ps
w_0 = 5	4.4 ps
w_0 = 10	2.7 ps
w_0 = 20	2.1 ps
w_0 = 40	1.7 ps
w_0 = 60	1.8 ps
water	1.7 ps

	d (nm)	# H_2O
water	-	-
w_0 = 60	28	350,000
w_0 = 40	17	77,000
w_0 = 20	7.0	5400
w_0 = 10	4.0	1000
w_0 = 5	2.4	300
w_0 = 2	1.7	40

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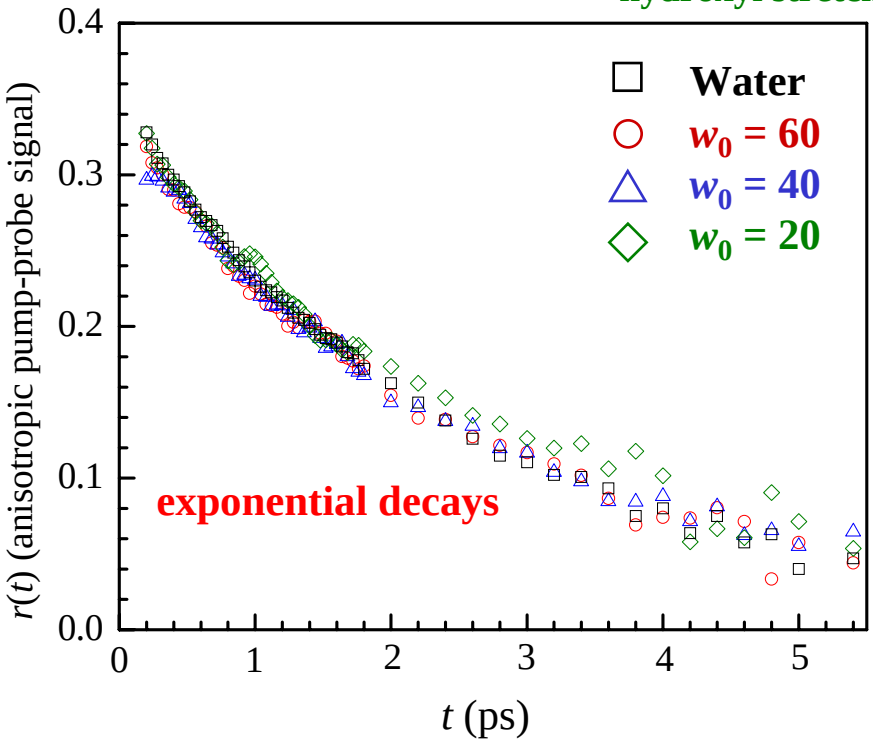
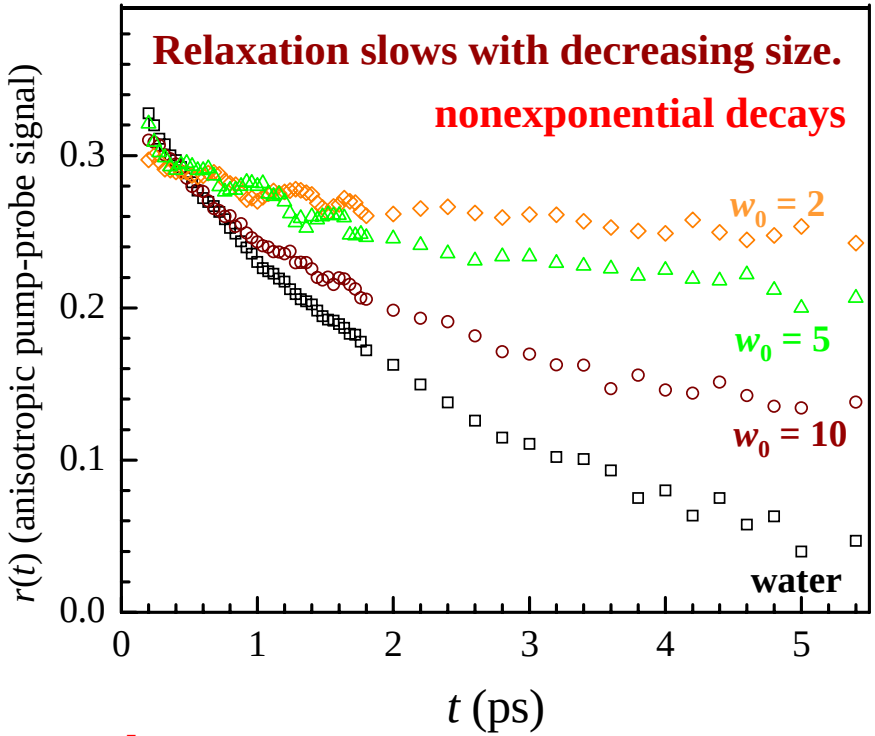
Orientational Anisotropy Relaxation

hydroxyl stretch (OD of 5% HOD in H_2O)





	d (nm)	# H_2O	slowest component
water	-	-	2.7 ps
w_0 = 60	28	350,000	2.7 ps
w_0 = 40	17	77,000	2.8 ps
w_0 = 20	7.0	5400	3.0 ps
w_0 = 10	4.0	1000	18 ps
w_0 = 5	2.4	300	30 ps
w_0 = 2	1.7	40	50 ps

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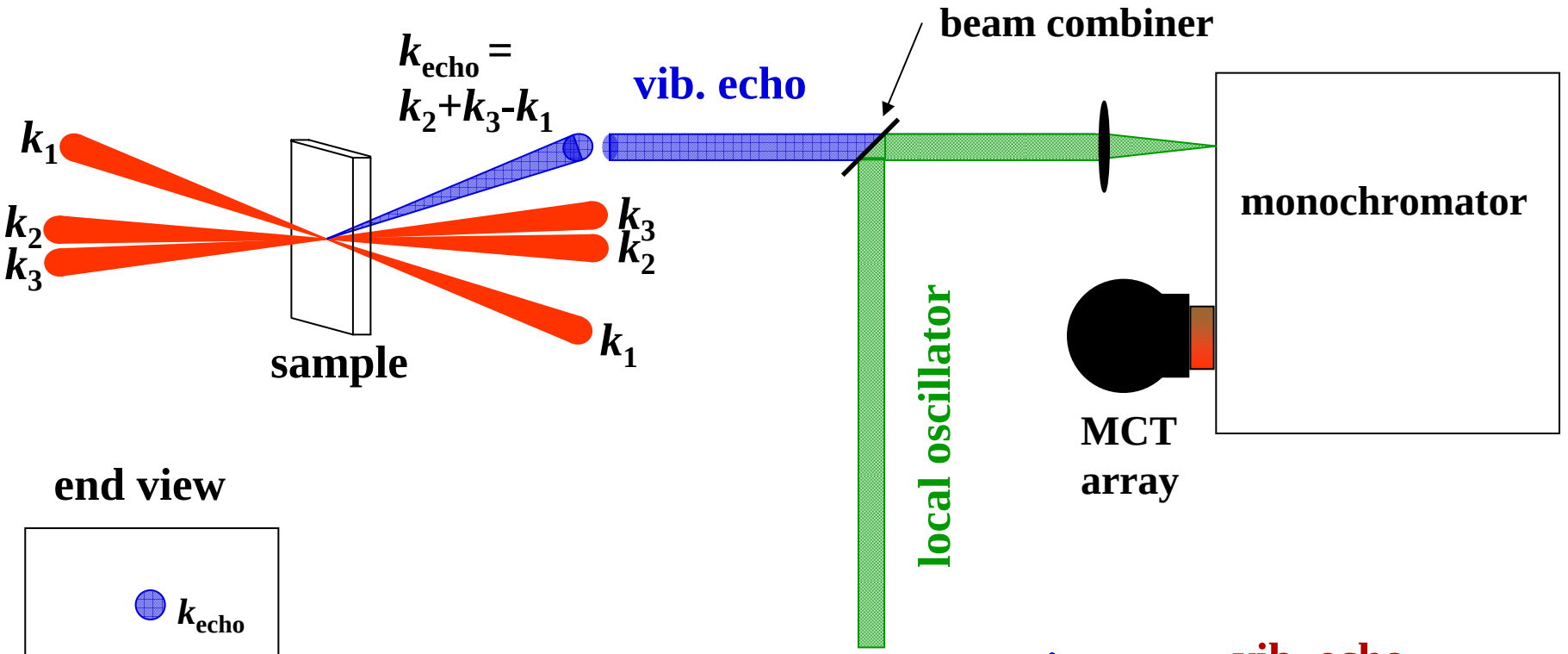
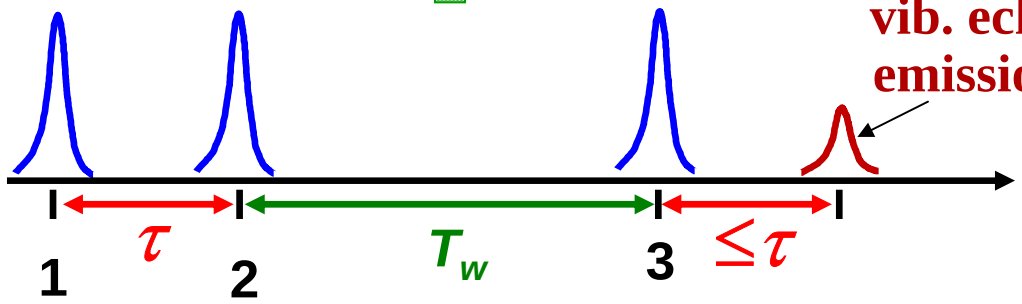
Ultrafast 2D Infrared Vibrational Echo Spectroscopy





τ – coherence periods

T_w – populations period

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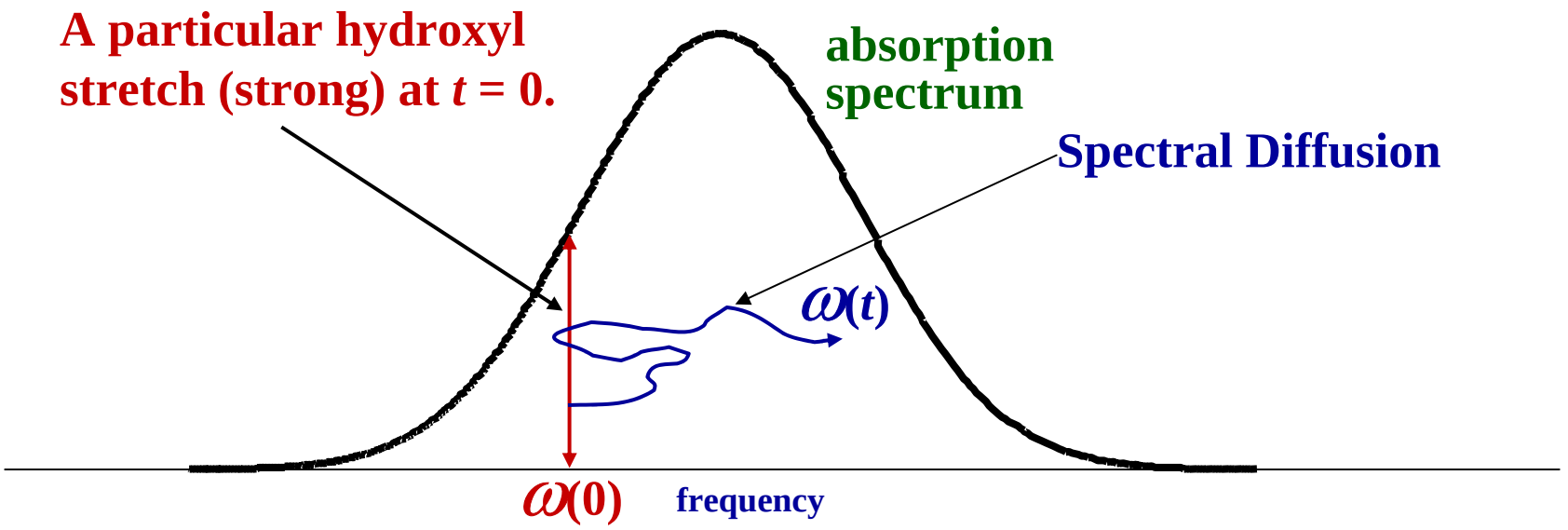
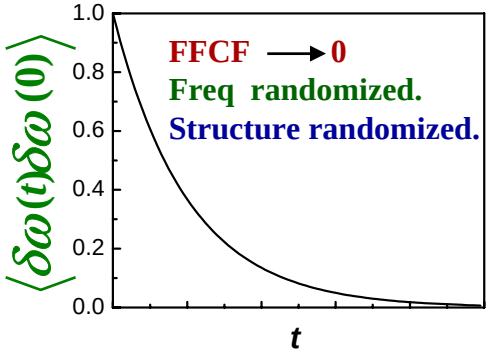


Measure spectral diffusion → **hydrogen bond network evolution**

frequency at $t = 0$ → $\omega(0)$

frequency at t → $\omega(t)$



Frequency-Frequency Correlation Function → **FFCF**

Probability that $\omega(t)$ *is same as* $\omega(0)$ averaged over all starting frequencies.

→ $\langle \delta\omega(t)\,\delta\omega(0) \rangle$

The FFCF is the connection between microscopic water models and experimental observables.

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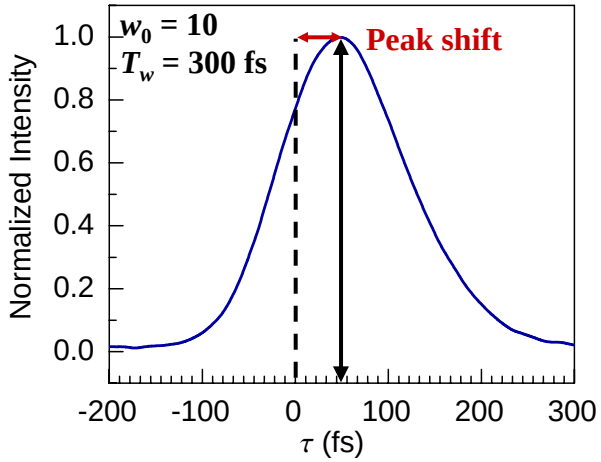
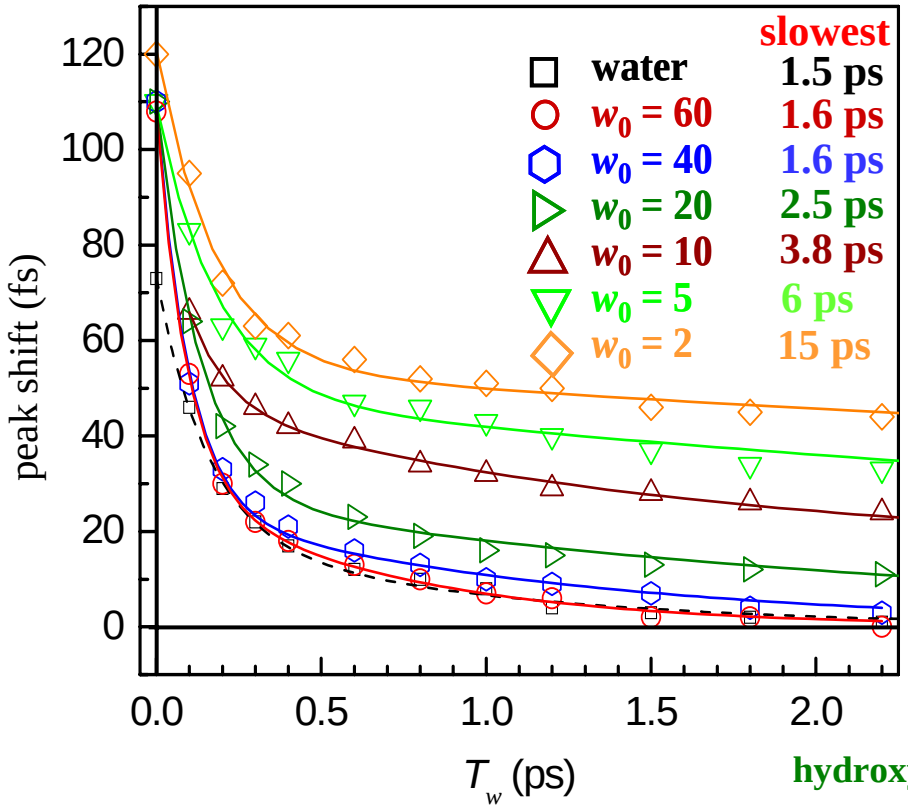
Spectrally Resolved Vibrational Echoes



The vibrational echo peak shift is determined by the frequency-frequency correlation function.
As T_w increases,
there is more spectral diffusion that
makes the vibrational echo decay faster, and
reduces the peak shift.



Detailed fitting of FFCF to full set of decay curves and linear spectrum for each size shows:

fastest components, very local motions, change somewhat,

major change in slowest component, global hydrogen bond network rearrangement slows dramatically as water nanopool becomes smaller.

hydroxyl stretch (OD of 5% HOD in H_2O)

M.D. Fayer
Sanford University
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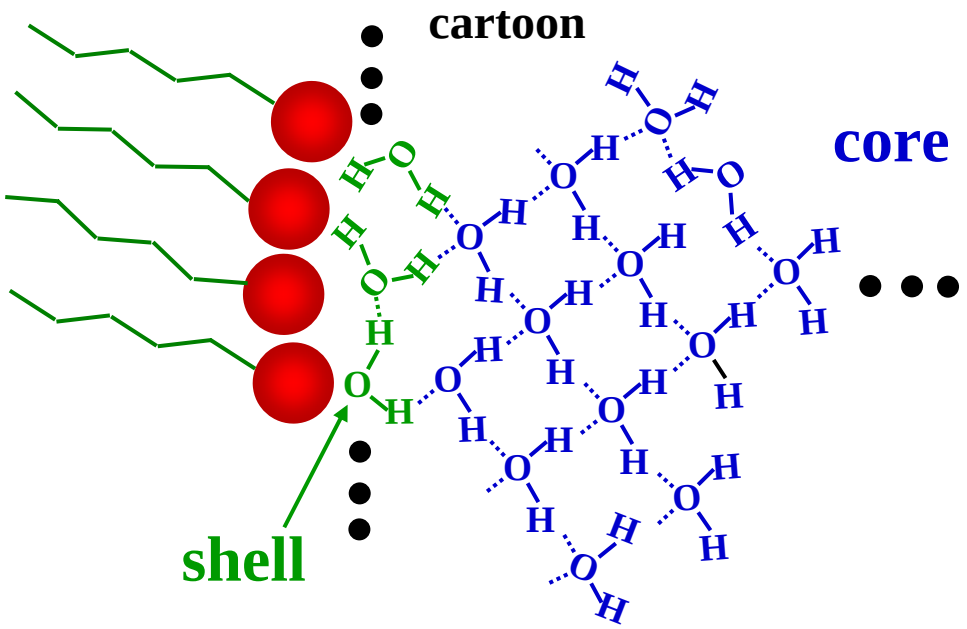
Orientational relaxation and spectral diffusion are intimately related to

H-bond network evolution.

Core and shell H-bond networks are continuous.

Dynamics in the core and shell are coupled through the H-bond network.



Core-shell exchange time very slow.

Complete orientational relaxation and complete spectral diffusion require randomization of the H-bond network.

Core-shell dynamics coupled.

J. Phys. Chem. A 110, 4585-4599 (2006).

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Sanford University
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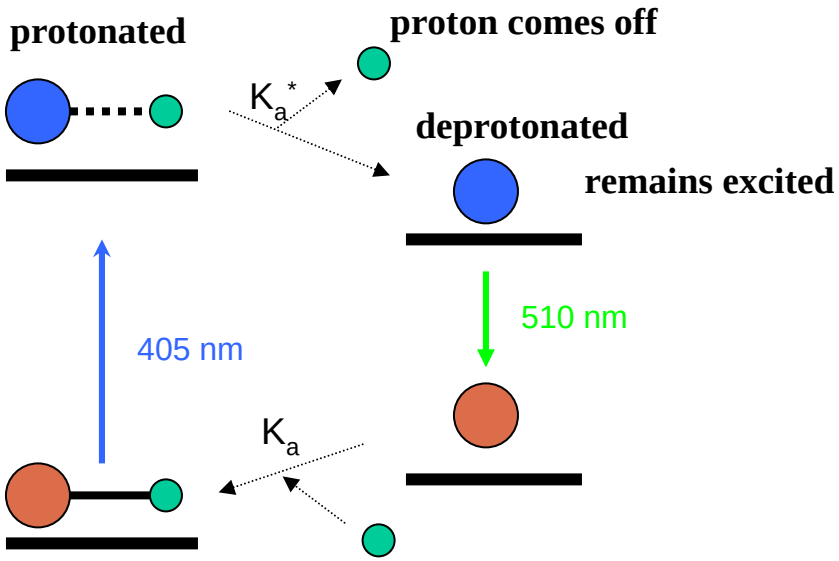
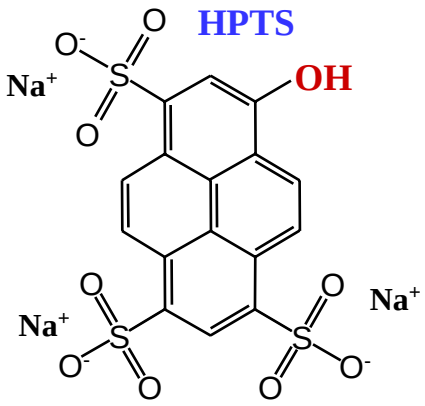
Proton Transfer in Nanoscopic Water – Photoacid Dynamics

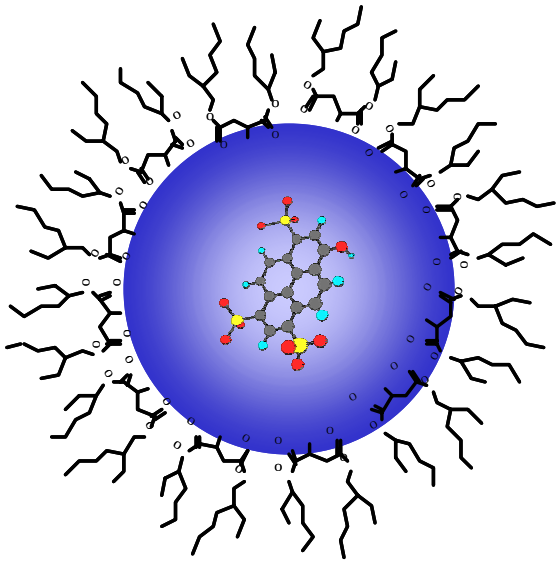
Photoexcitation - K_a increases 10^7





How does nanoscopic water dynamics influence proton transfer?

HPTS in reverse micelle



Sulfonates and Na^+ counter ions same as head groups and counter ions of AOT.

A variety of experiments (anisotropy decays, spectra) demonstrate that HPTS in water nanopool, not associated with AOT head groups or buried in surfactant.

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Sanford University
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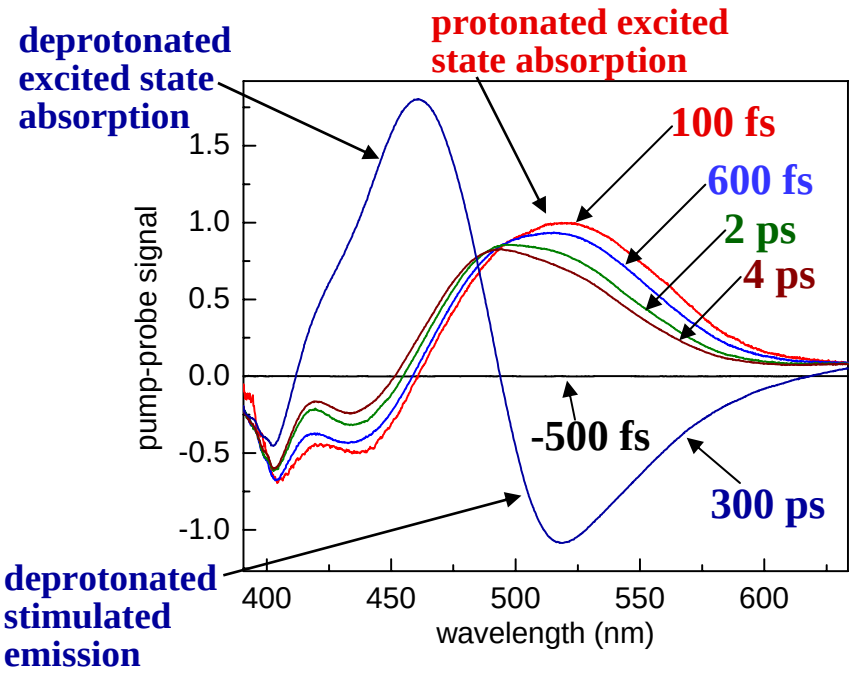
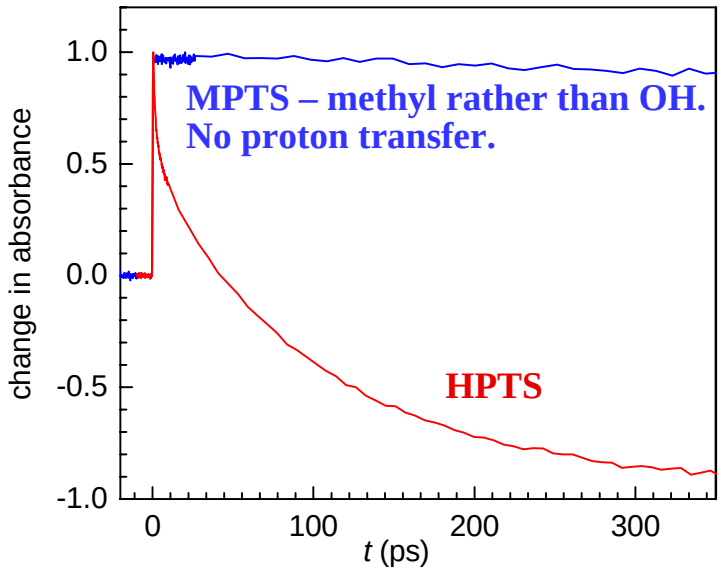
First, what happens in bulk water.

HPTS – pump 405 nm; continuum probe



Pump – 405 nm; probe 540 nm



Time Line

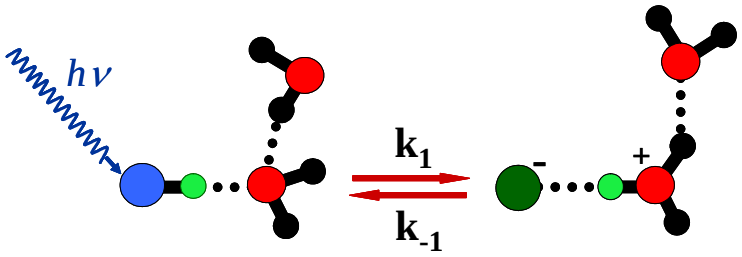
Stoke's Shift ~1 ps → | **Initial Proton Transfer – Local** ~5 ps → | **Proton Transfer – Non-Local – Migration** ~100 ps →

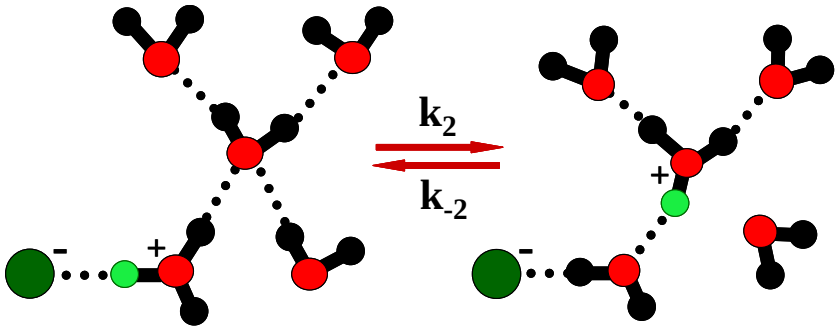
Detailed MCD and polarization studies show that none of the dynamics involves shifting of the electronic excited states of the protonated form following optical excitation.

M.D. Fayer
Sanford University
6/26/2006

Model and Fitting

P. Leiderman, L. Genosar, and D. Huppert, J. Phys. Chem. A., 109, 5965 (2005).



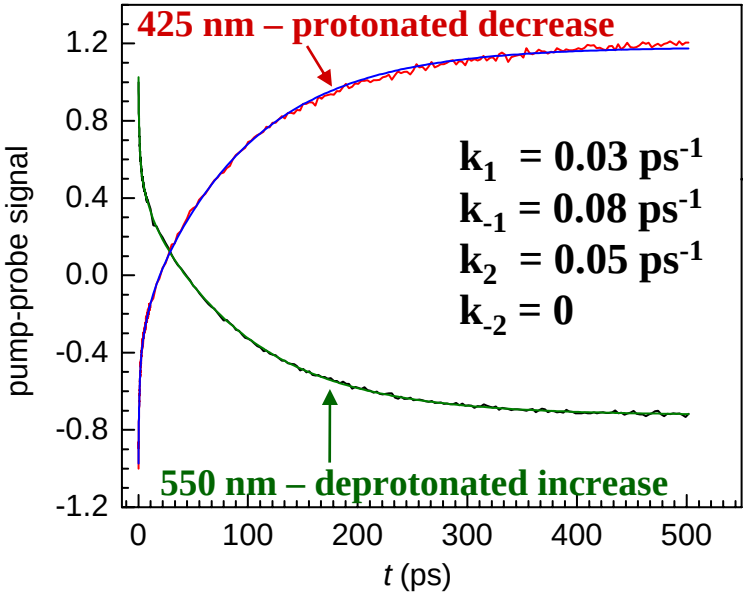


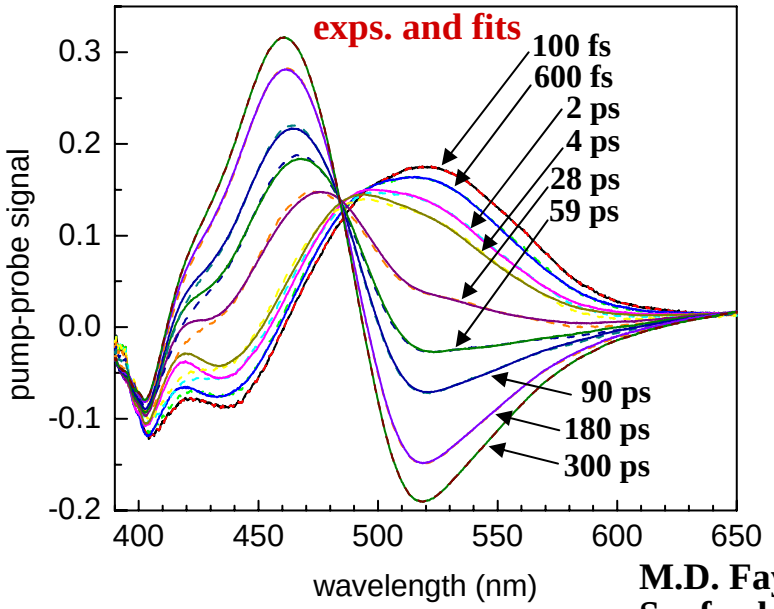
Formation of charge-transfer complex.
Four coordinate hydrogen bond complex becomes three coordinate hydronium ion.
Establish equilibrium.

Charge separation.
A more global rearrangement of hydrogen bond network is required to separate the anion and hydronium.

Solve differential equations for above model. Fit data.

Fits include: Stoke's shift, formation of charge-transfer complex, charge separation.





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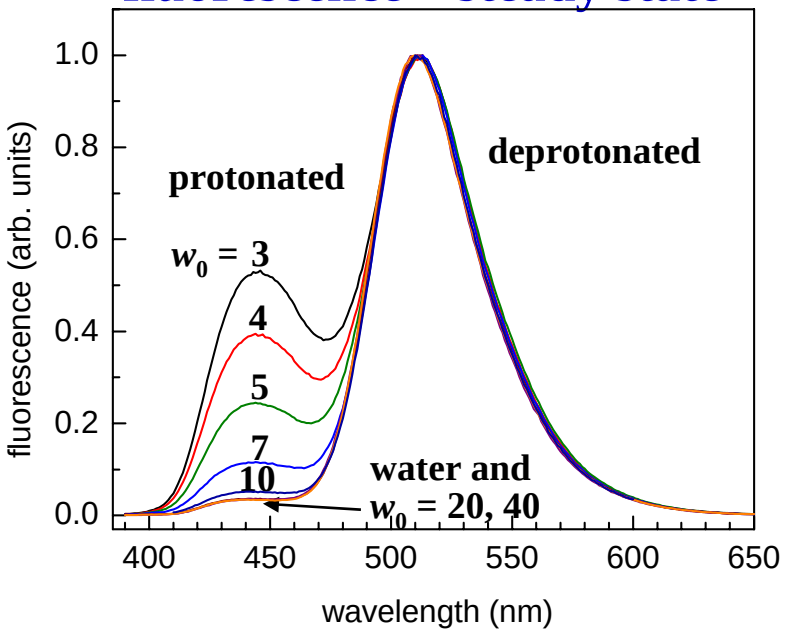
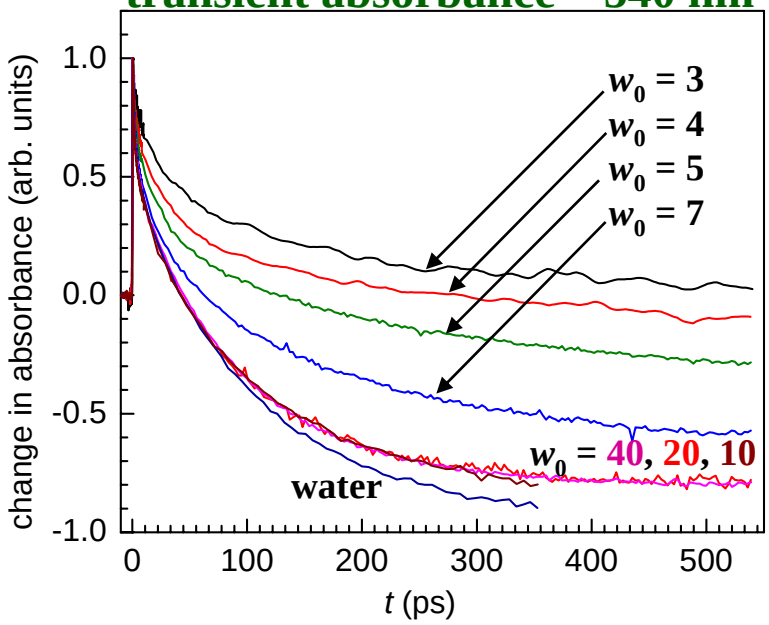
On to Nanoscopic Water – AOT Reverse Micelles

fluorescence – steady state



transient absorbance – 540 nm



Because the excited state lifetimes are so long, the steady state fluorescence spectra reflect the end points of the photoinduced proton transfer but prior to recombination on the ground state surface.

The proton transfer dynamics have a well defined size dependence similar to the dynamics of nanoscopic water in AOT. Nanoscopic water dynamics first deviates from bulk at w_0 = 10 rather than 7. The largest sizes (d = 17 nm, 7 nm, and 4 nm) show no size dependence and are almost the same as bulk water. The difference is the long time asymptotic value.

M.D. Fayer
Sanford University
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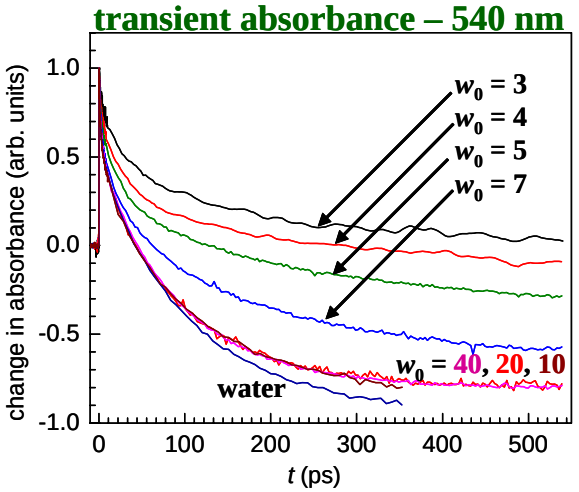
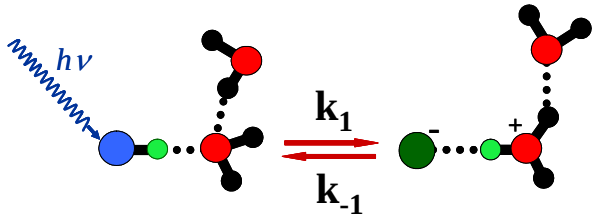
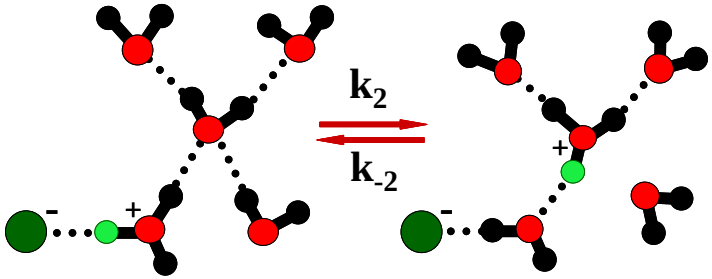


sample	k_1	k_{-1}	k_2	k_{-2}	K_{eq}
water	0.033	0.079	0.048	0	∞
w_0 = 40, 20, 10	0.024	0.041	0.039	0.0004	57
w_0 = 7	0.020	0.031	0.015	0.002	5.2
w_0 = 5	0.017	0.029	0.009	0.003	1.6
w_0 = 4	0.021	0.046	0.009	0.005	0.8
w_0 = 3	0.013	0.039	0.011	0.007	0.5

The proton transfer dynamics in nanoscopic water are fit with the same model used for bulk water. The same quality of fits are obtained over all times and wavelengths.





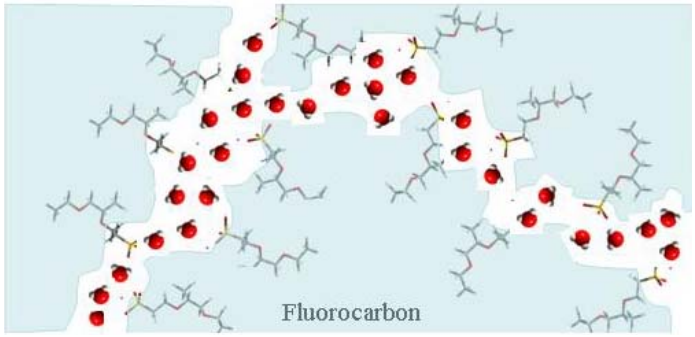
k_1 – initial forward proton transfer kinetics slow as water nanopool becomes smaller

$K_{eq} = \frac{k_1 k_2}{k_{-1} k_{-2}}$ – becomes smaller as nanopool gets smaller. Less generation of "free" protons. Long time off-set increases.

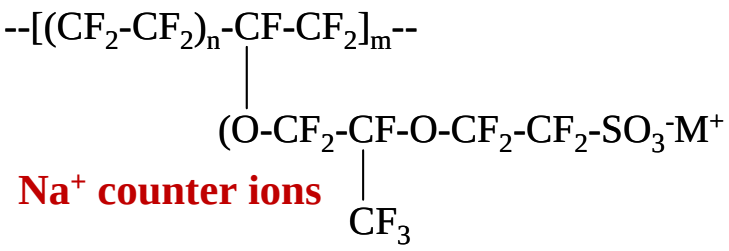
Smallest reverse micelles, w_0 = 4 and 3, d < 2 nm, don't fall all trends. Head group water shell, 0.4 nm thick. HPTS contacting interface?

M.D. Fayer
Sanford University
6/26/2006

Nafion fuel cell membrane

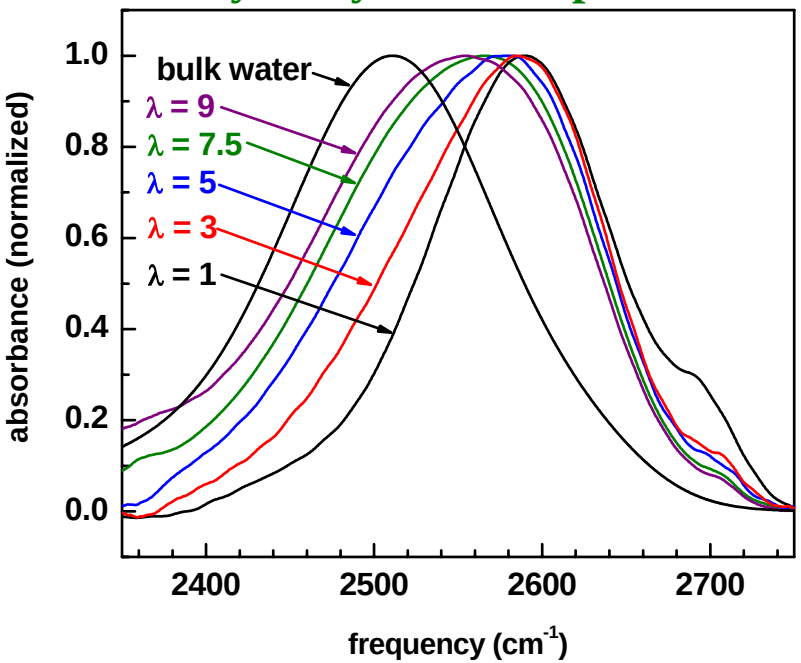


Teflon with side chains, sulfonate head groups.

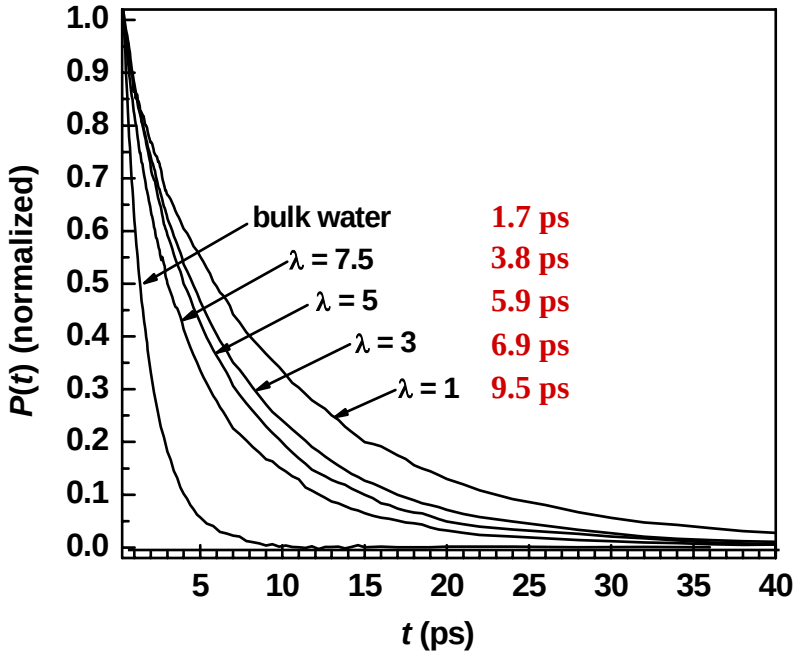


Nanoscopic water channels, proton transport.

hydroxyl stretch spectra



vibrational lifetimes



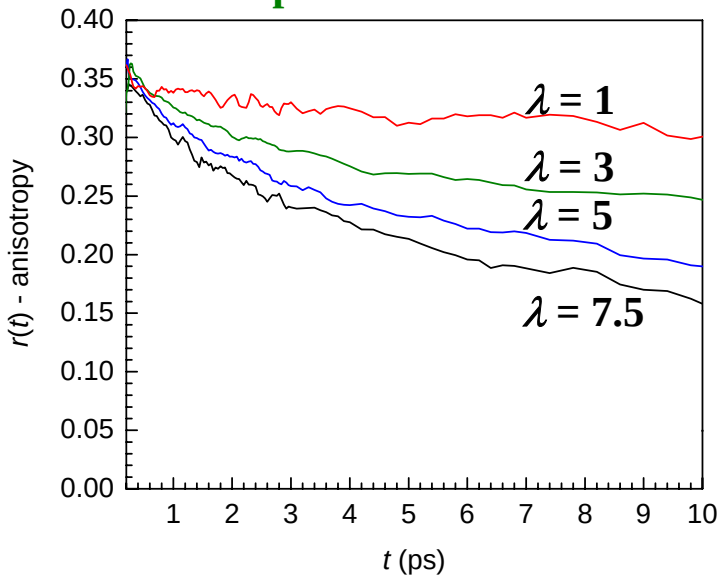
λ – number of water molecules per sulfonate head group

hydroxyl stretch (OD of 5% HOD in H_2O)

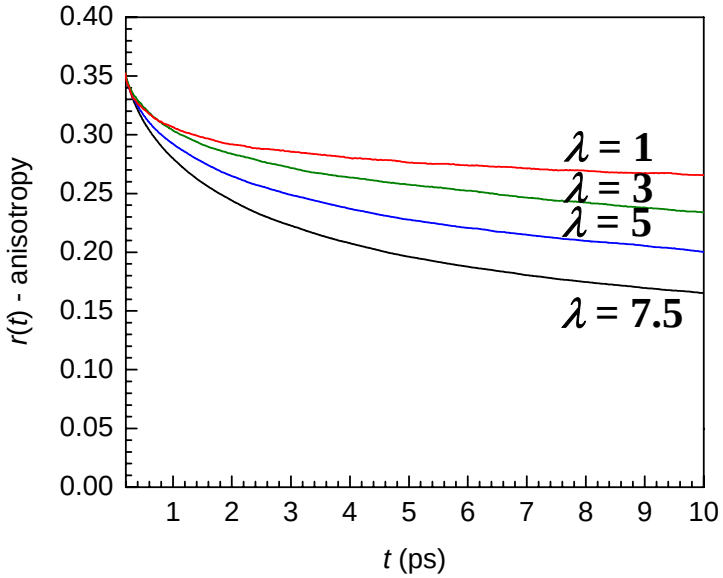
M.D. Fayer
Sanford University
6/26/2006

Orientational Anisotropy Decays and Simulations of Water in Nafion Nanochannels

Experimental Data



Simulations – Voth and Co-workers



Decays are non-exponential – comparison of slowest components that leads to complete randomization.

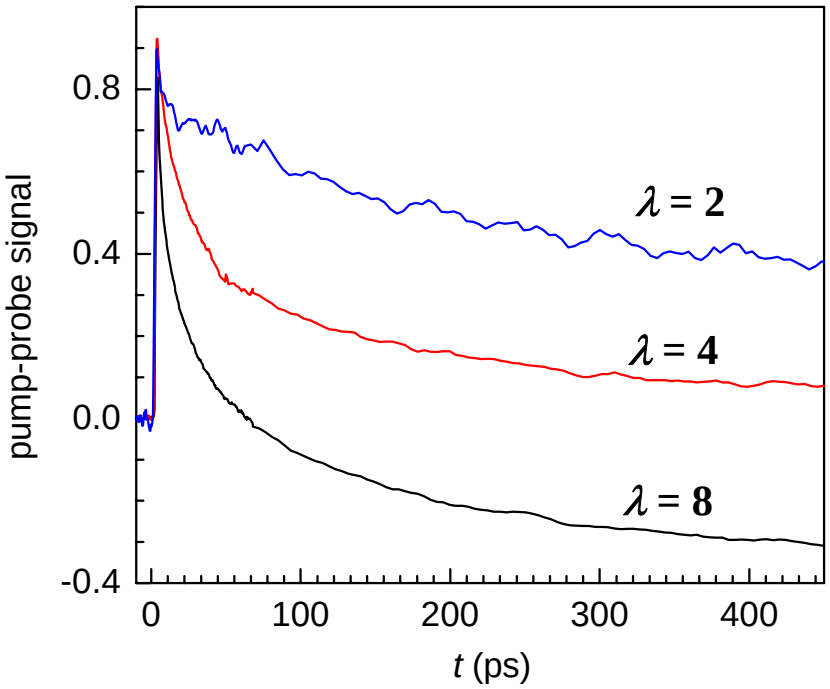
slowest component

sample	experiment	simulation
$\lambda = 1$	81 ps	73 ps
$\lambda = 3$	47 ps	33 ps
$\lambda = 5$	21 ps	24 ps
$\lambda = 7.5$	18 ps	13 Ps
water	2.6 ps	–

hydroxyl stretch (OD of 5% HOD in H_2O)

M.D. Fayer
Sanford University
6/26/2006

Proton Transfer in Nanoscopic Water Channels – HPTS in Nafion



Like the HPTS experiments in AOT reverse micelles, as the water channels contain less water, proton transfer dynamics slow.

Nafion becomes a proton transport membrane for $\lambda > 5$.

M.D. Fayer
Sanford University
6/26/2006

Key Points

Water dynamics slow dramatically in reverse micelles with small water nanopools, particularly H-bond network global structural rearrangement.

Photoacid HPTS experiments in bulk water occur on three time scales, Stoke's shift, local charge transfer complex formation, and proton migration. Excellent agreement between data and model calculations.

Photoacid HPTS proton transfer dynamics unaffected in large reverse micelles, but slow dramatically in small water nanopools. Equilibrium constant shift, less dissociation

Water dynamics slow substantially in water nanochannels of Nafion membranes in a manner akin to reverse micelles. Simulations do a good job of reproducing orientational relaxation.

HPTS photoacid experiments in Nafion water channels show the influence of channel size (amount of water per head group) on proton transfer dynamics. Proton transfer dynamics slow significantly as water content is reduced.

M.D. Fayer
Sanford University
6/26/2006

Reverse Micelles - Water
Ivan Piletic
David Moilanen
Ben Spry
Prof. Nancy Levinger

Proton transfer
Ben Spry
Ksenija Glusac

Nafion – Water
David Moilanen

Support
DOE

M.D. Fayer
Sanford University
6/26/2006