Liquid/Semiconductor Interfaces through Vibrational Spectroscopy

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Outline

I. **Justification:** why vibrational spectrocopy?

II. **Background:** making vibrational spectroscopy interface specific: vibrational sum frequency spectroscopy

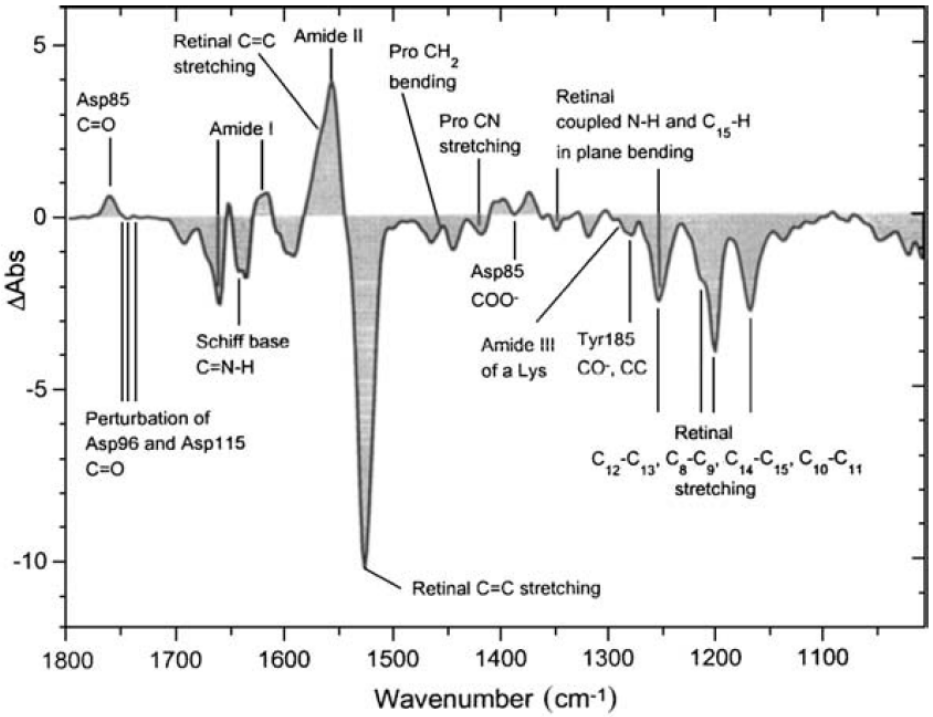
III. **Interfacial Solvent (Water):** structure and dynamics

IV. **Semiconductor Interface:** optical detection of surface phonons

Why vibrational spectroscopy?

Vibrations report, label free, on inter/intramolecular forces (and structure)

Macromolecules (proteins)



Barth and Zscherp (2002) Quarterly Reviews of Biophysics, **35**, 4
from
Zscherp and Heberle (1997) Journal of Physical Chemistry B, **101**, 10542

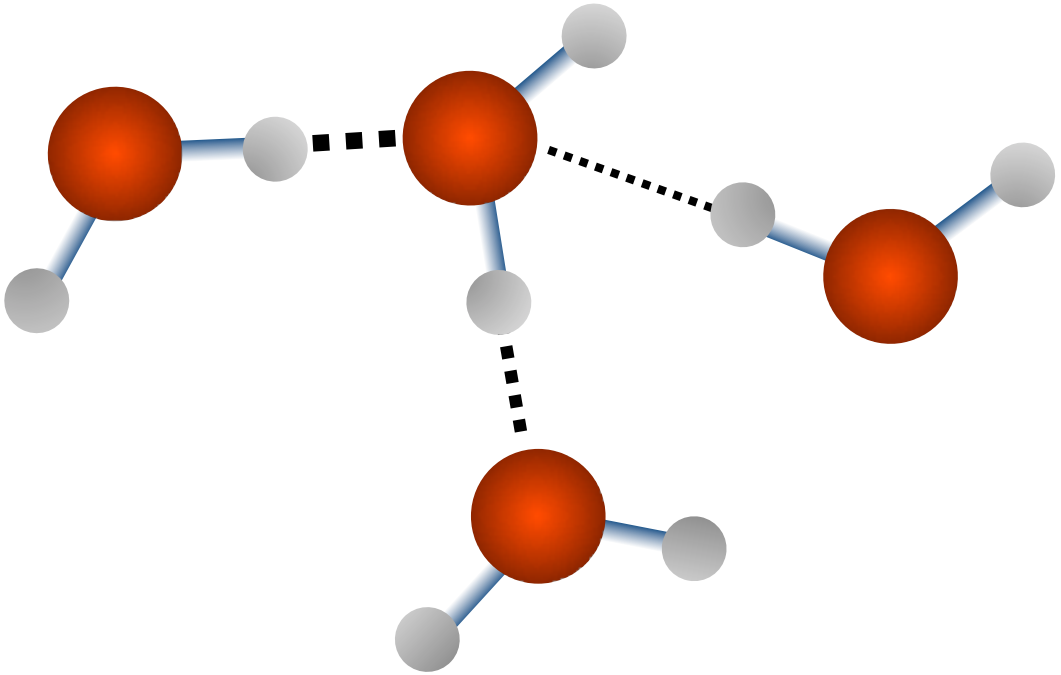
Spectrum of local oscillators modified by environment,

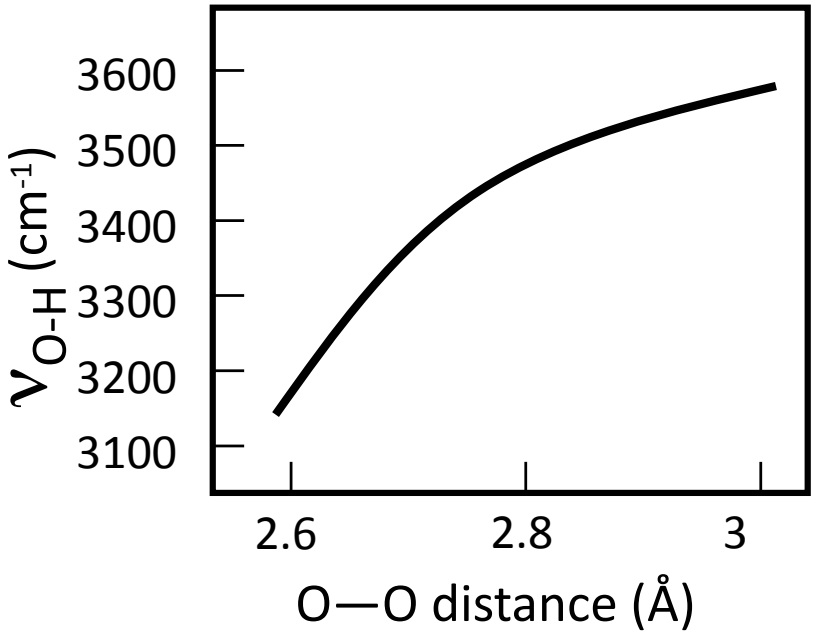
1. *Through-bond coupling*
2. *Hydrogen bonding*
3. *Transition dipole coupling*

Why vibrational spectroscopy?

Vibrations report, label free, on interatomic/molecular forces (and structure)

Liquids (water)

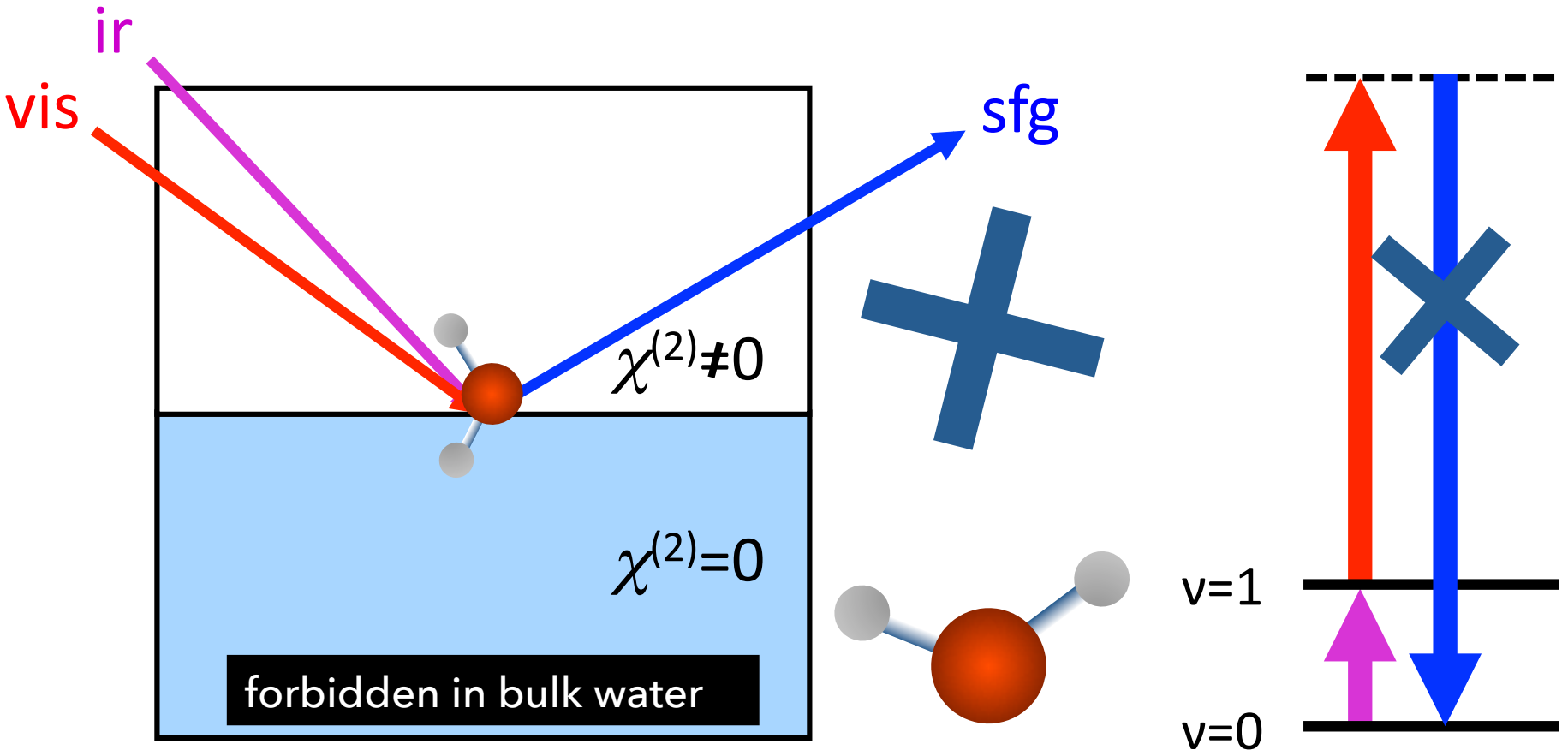




OH stretch modulated by anharmonic coupling to low frequency modes.

Interface specific vibrational spectroscopy

Vibrational Sum Frequency Spectroscopy



What is detected?

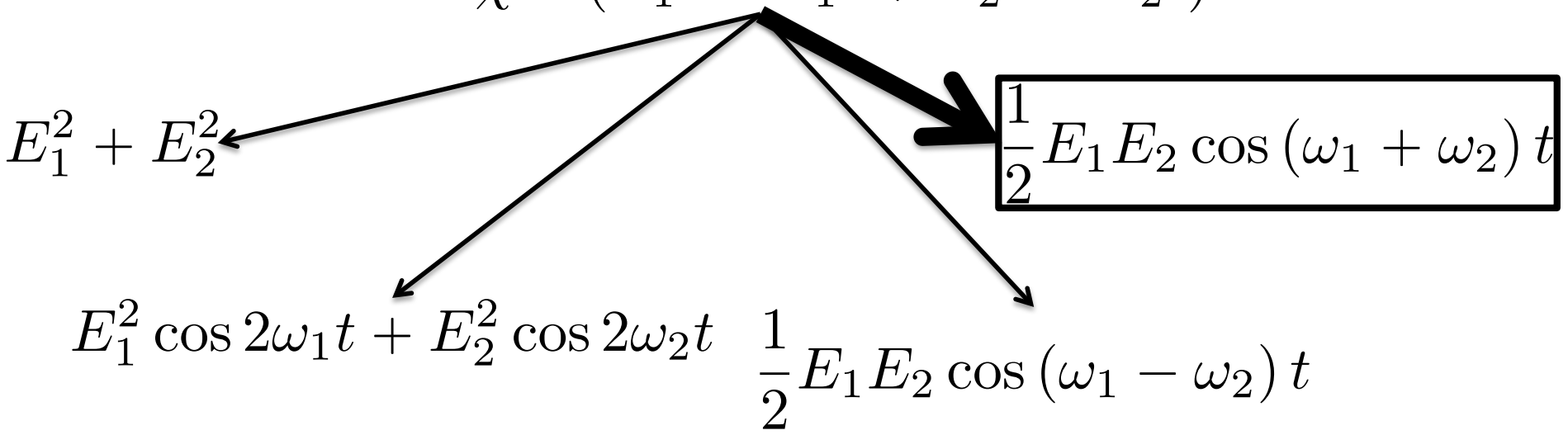
The field radiated by the second order induced polarization

Induced polarization can be expanded in a Taylor series

$$P \propto \chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \dots$$

Assuming two incident plane waves and just considering the second order term,

$$P^{(2)} \propto \chi^{(2)} \left(E_1 \cos \omega_1 t + E_2 \cos \omega_2 t\right)^2$$



Origin of Interfacial Specificity

Even order nonlinear susceptibilities

Second order nonlinear susceptibilities are third rank tensors

…

Changing the sign of all indices is equivalent to inverting the axes: the material response must change sign…

$$\chi^{(2)}_{ijk} = -\chi^{(2)}_{-i-j-k}$$

But, with inversion symmetry, all directions are equivalent so…

$$\chi^{(2)}_{ijk} = \chi^{(2)}_{-i-j-k}$$

For materials with inversion symmetry ($\chi^{(2)}=0$), *inversion symmetry is always broken at interfaces.*

Origin of Chemical Specificity

Raman scattering off an excited, coherent, vibration

$$\chi^{(2)}_{ijk} = N \sum_{i'j'k'} \langle R_{ii'} R_{jj'} R_{kk'} \rangle \beta^{(2)}_{i'j'k'}$$

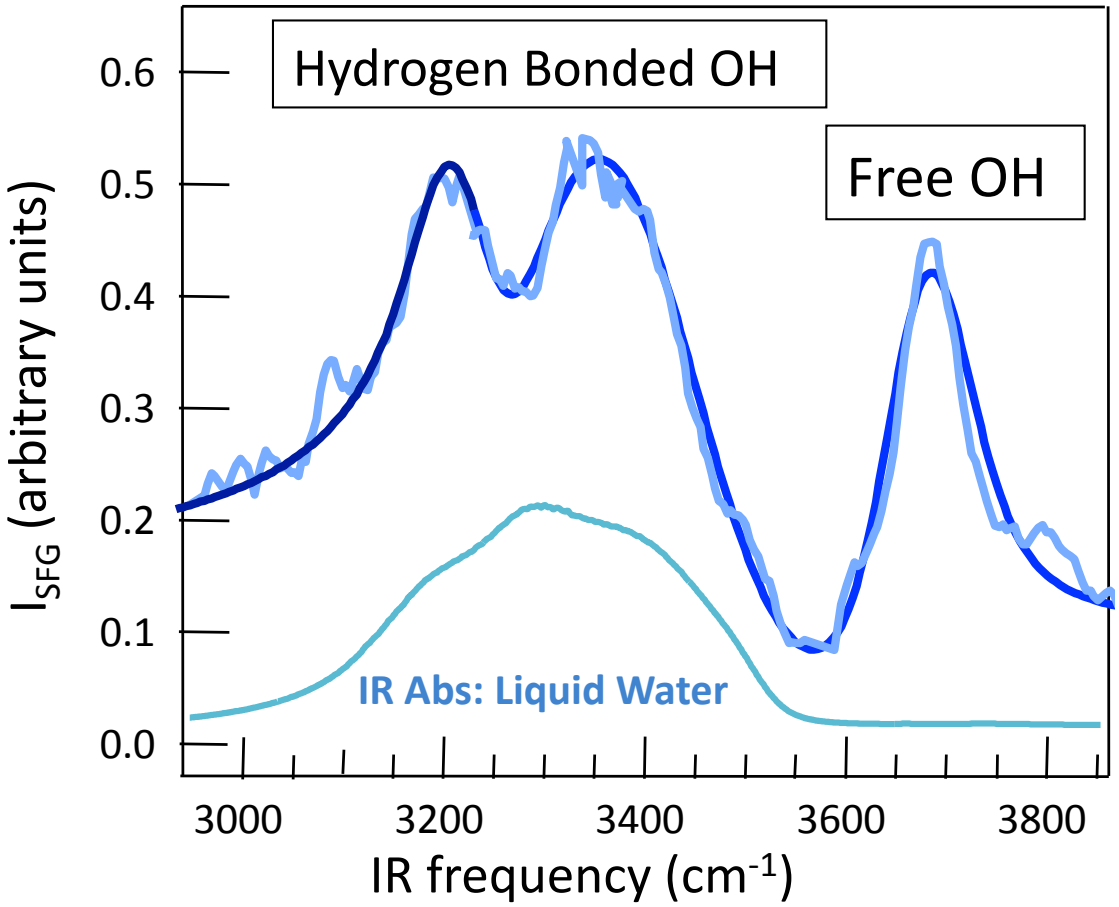
$$\beta^{(2)}_{i'j'k'} = \sum_{q} \frac{M_{i'j'} A_{k'}}{\omega_q - \omega_{ir} - i\Gamma}$$

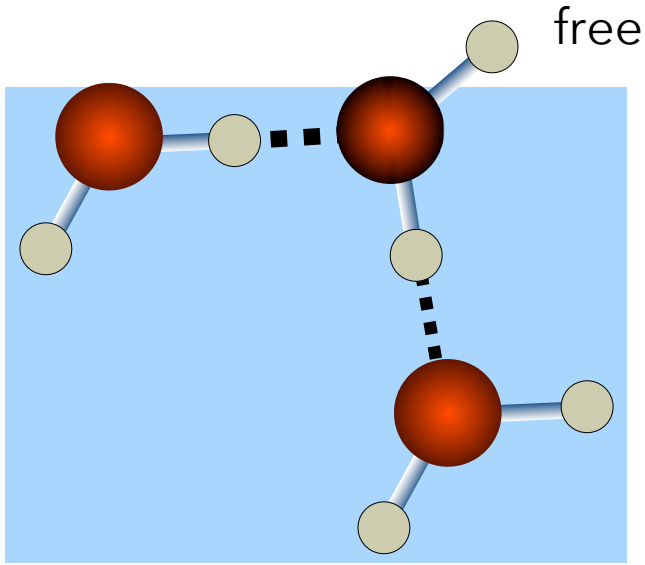
VSF active modes must be Raman and IR active.

III. Approaching the Interface from the Solvent Side: Interfacial Water Structure

The OH stretch at the air/water interface

Two (or three) qualitative populations



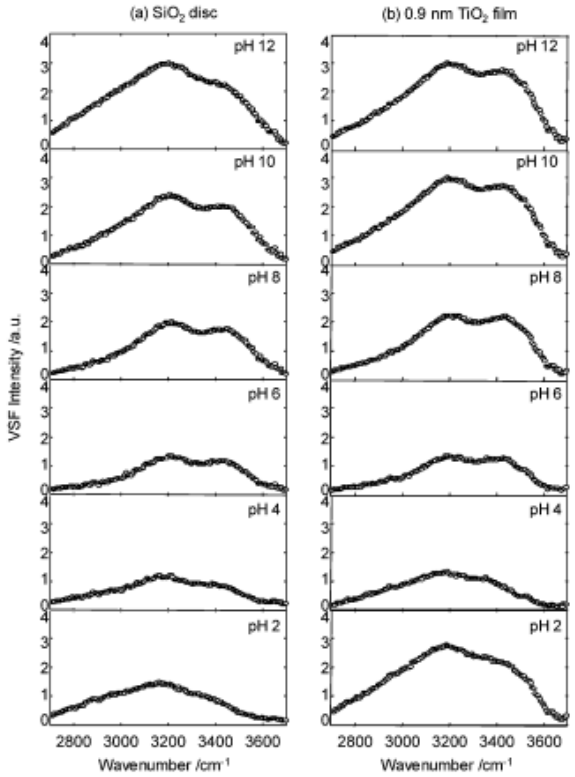


VSF spectral features are apparent that are absent in bulk IR.

Is the double peaked feature general?

Yes!

Double peaked feature appears at all interfaces



Kataoka,…, Cremer (2004) Langmuir, 20(5), 1662

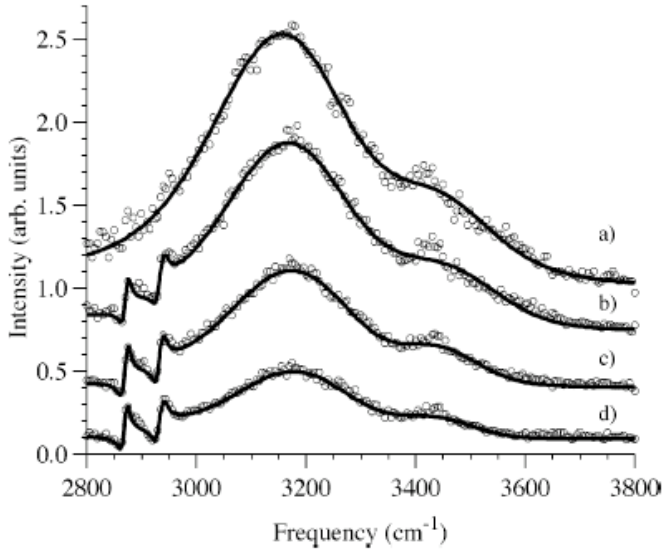


Figure 7. VSFS spectra (symbols) and curve fits (solid line) of the CaF_2/H_2O/stearate interface at (a) neat CaF_2/H_2O and (b) 5.6, (c) 11.0, and (d) 18.0 μM stearate. Spectra are offset for clarity.

Becraft and Richmond (2005) Journal of Physical Chemistry B, 109(11), 5108

Is the free OH feature general?

It appears at all hydrophobic interfaces

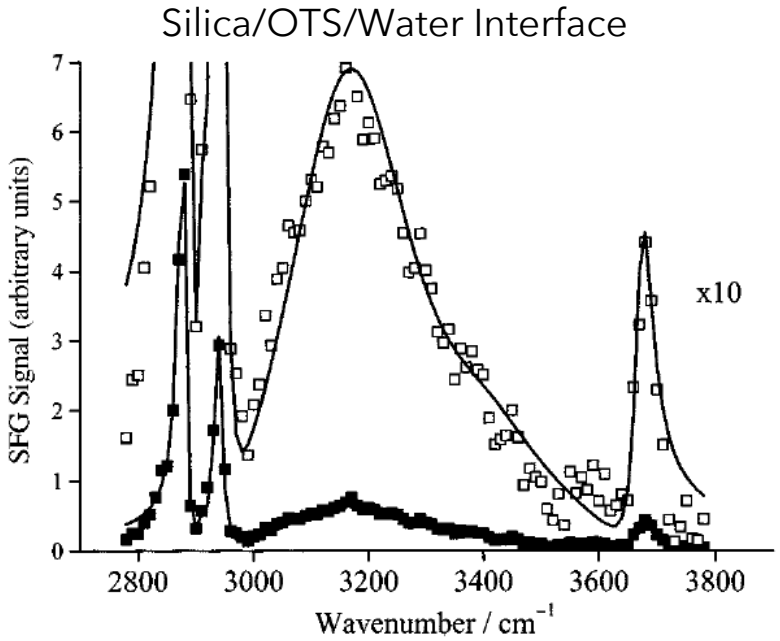
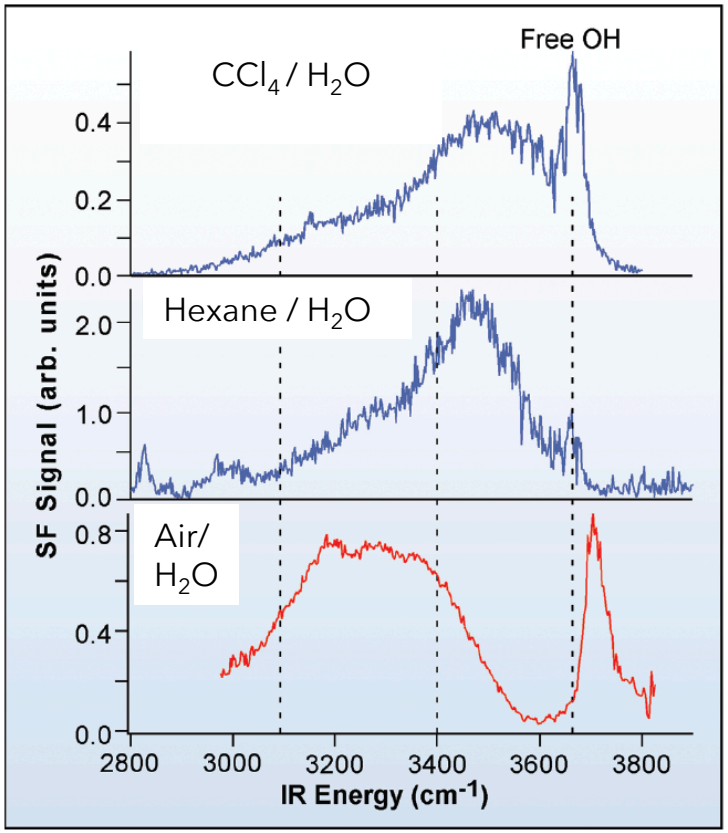


Fig. 4 SFG spectrum of a fused quartz surface modified by an OTS monolayer with full coverage in a neutral phosphate buffered solution of pH 7, in the region of 2800 to 3800 cm^{-1}. Also shown is the same spectrum at an enlarged scale (10 times) in the OH region.

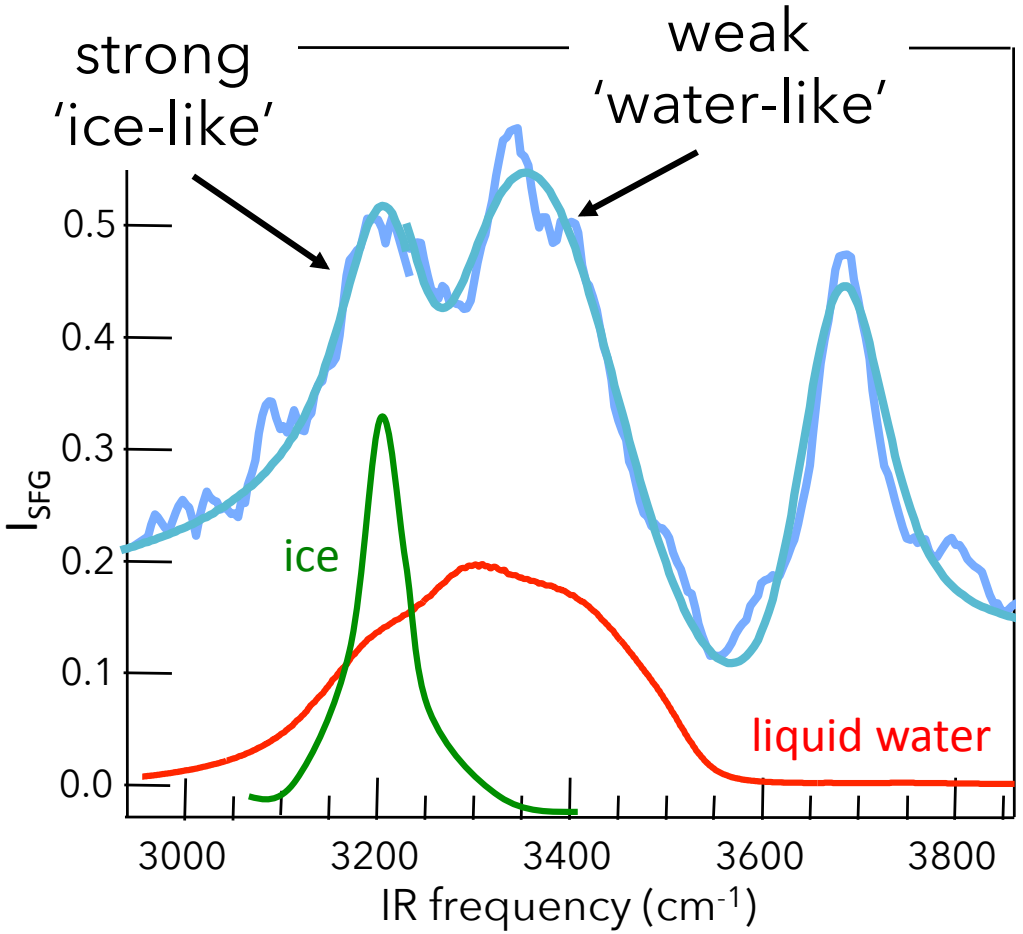
Ye, Nihonyanagi, Uosaki (2001) PCCP, 3(16), 3463



Scatena, Brown, Richmond (2001) Science, 292, 908

What causes the double peaked feature ?

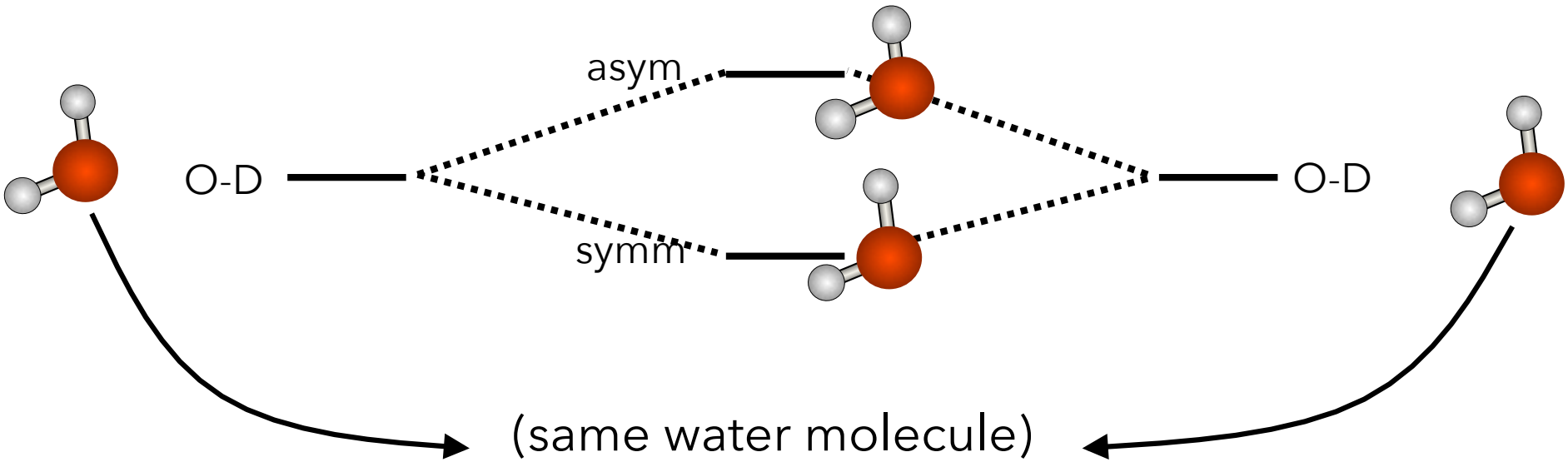
One idea: interfacial structural heterogeneity



Du,…, Shen(1993) Physical Review Letters, 70(15), 2313

What causes the double peaked feature ?

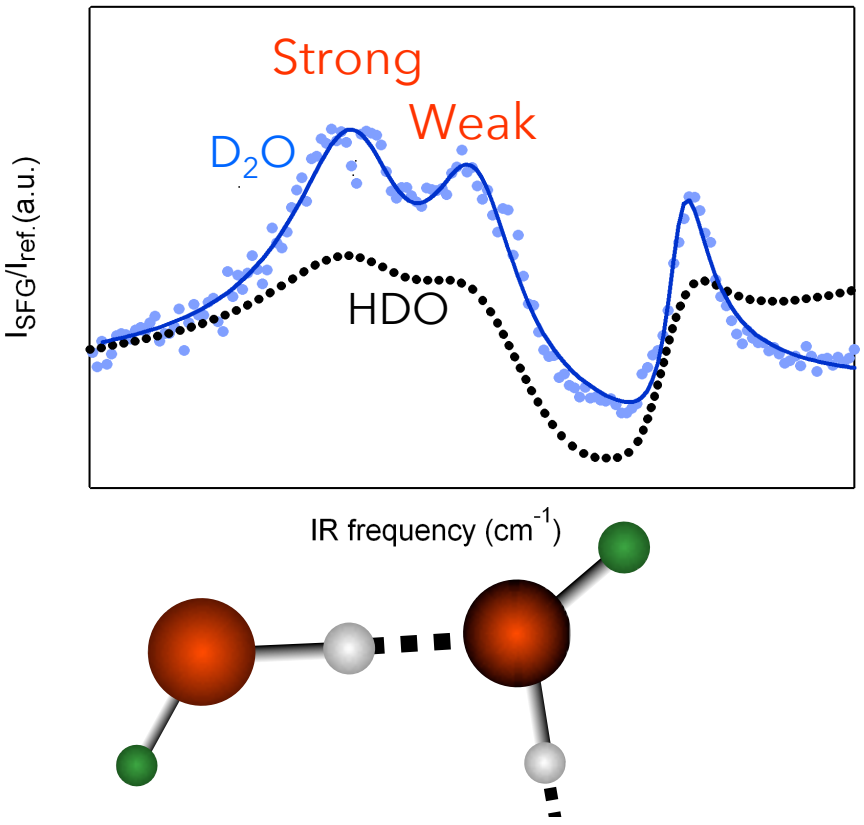
A second idea: symmetric/asymmetric stretch



How can we distinguish these scenarios experimentally

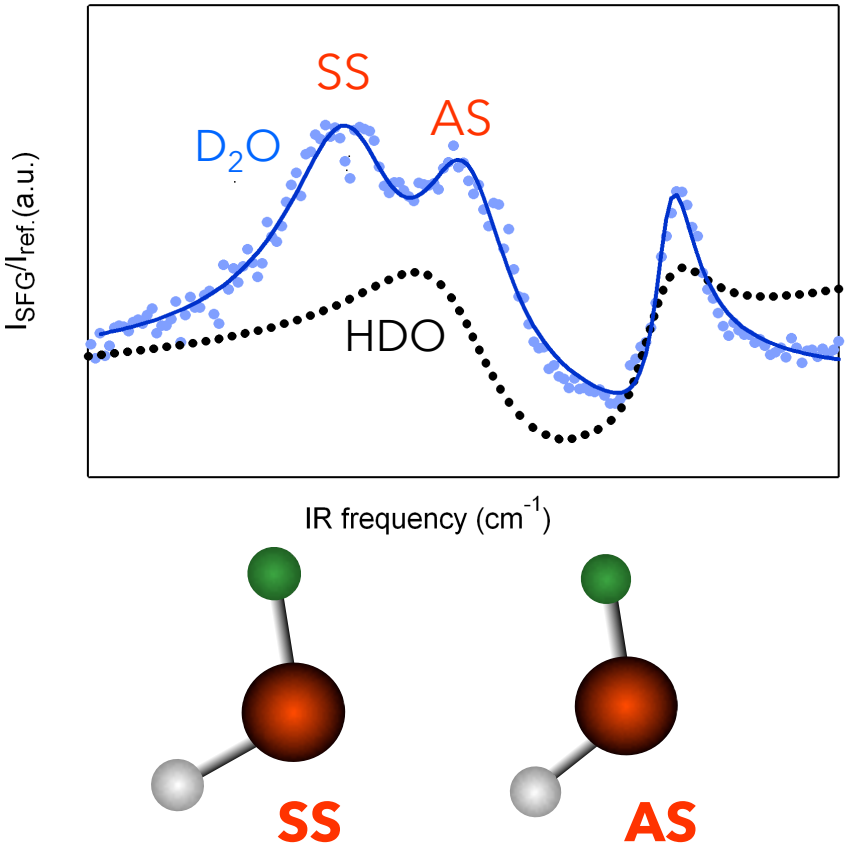
Isotopic dilution

'Ice/Liquid-like' hypothesis



The amplitude of the whole spectrum should change.

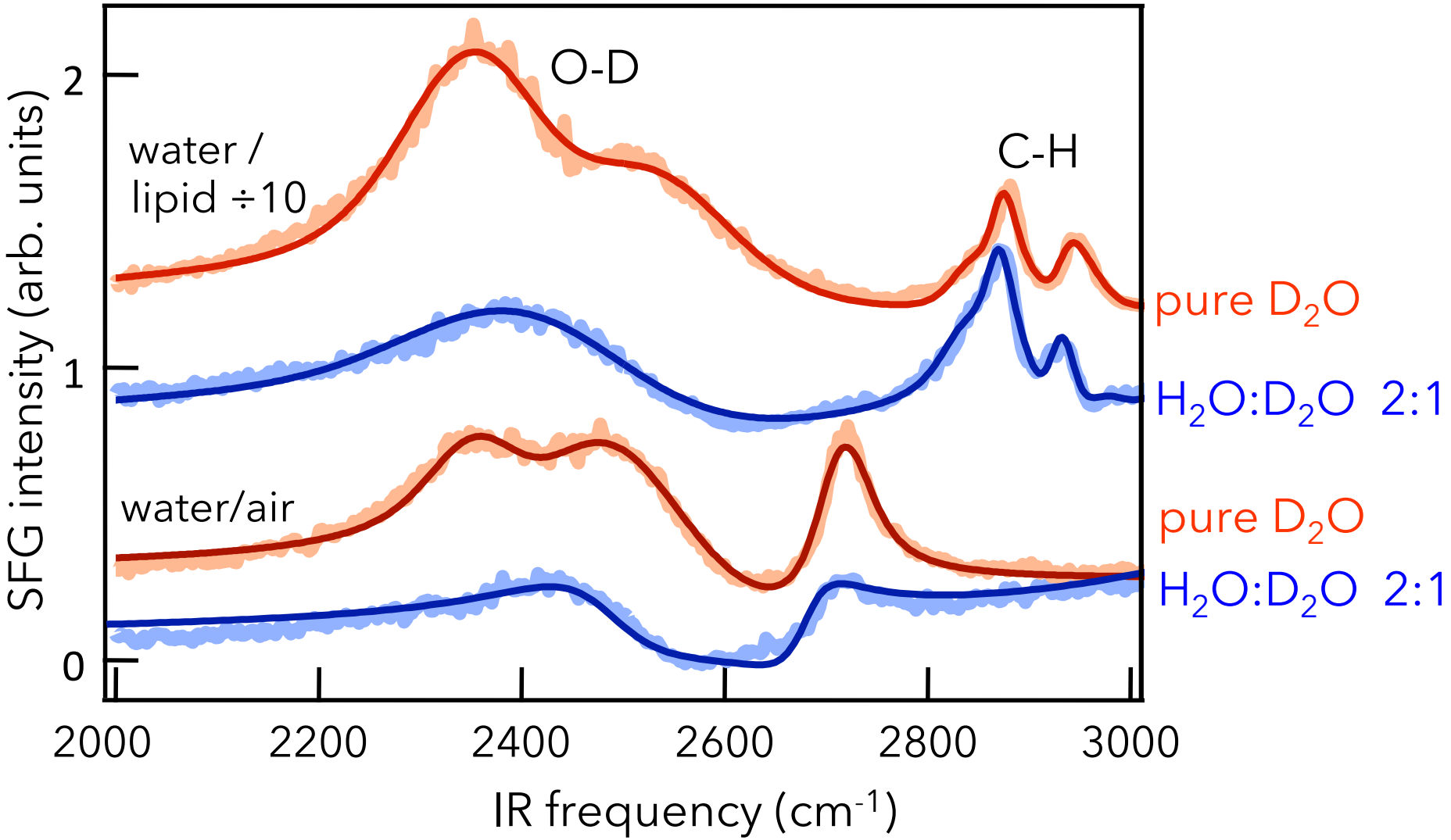
Sym/Asym hypothesis



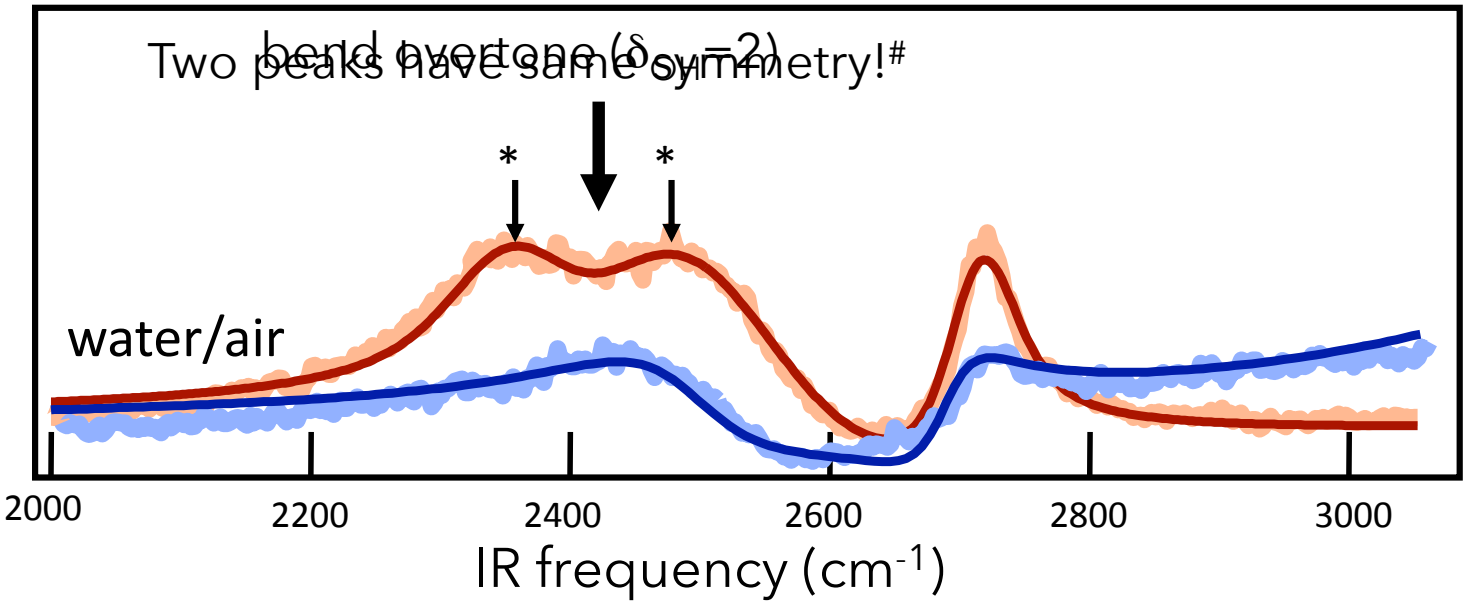
Two peaks should collapse to one

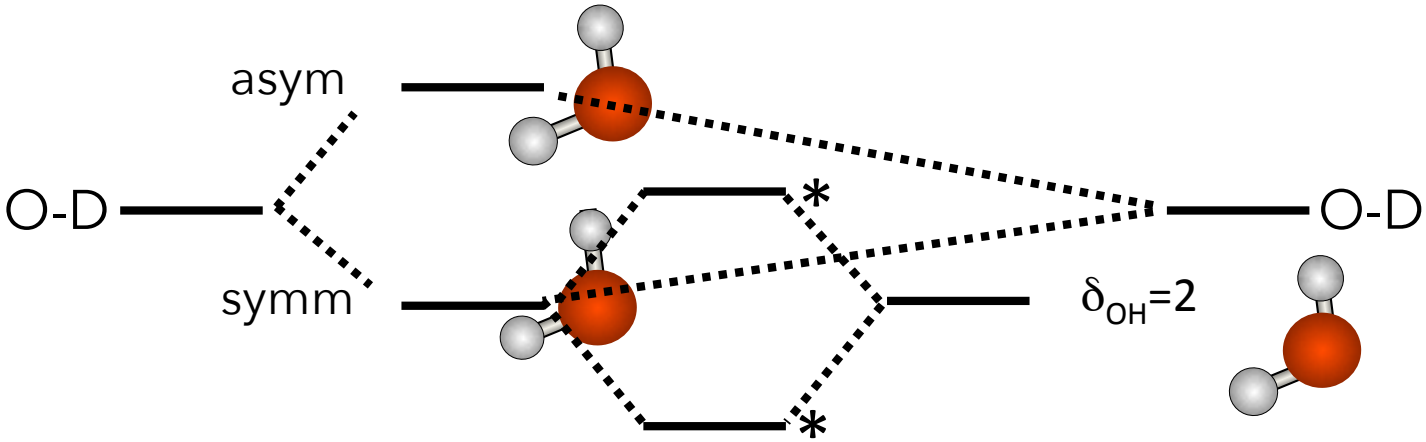
Two peaks collapse to one

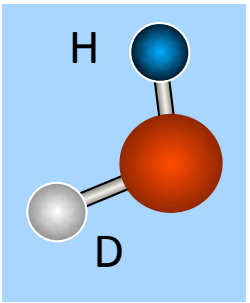
double peaked spectral feature ≠ water structure



Are the two peaks sym/asym?



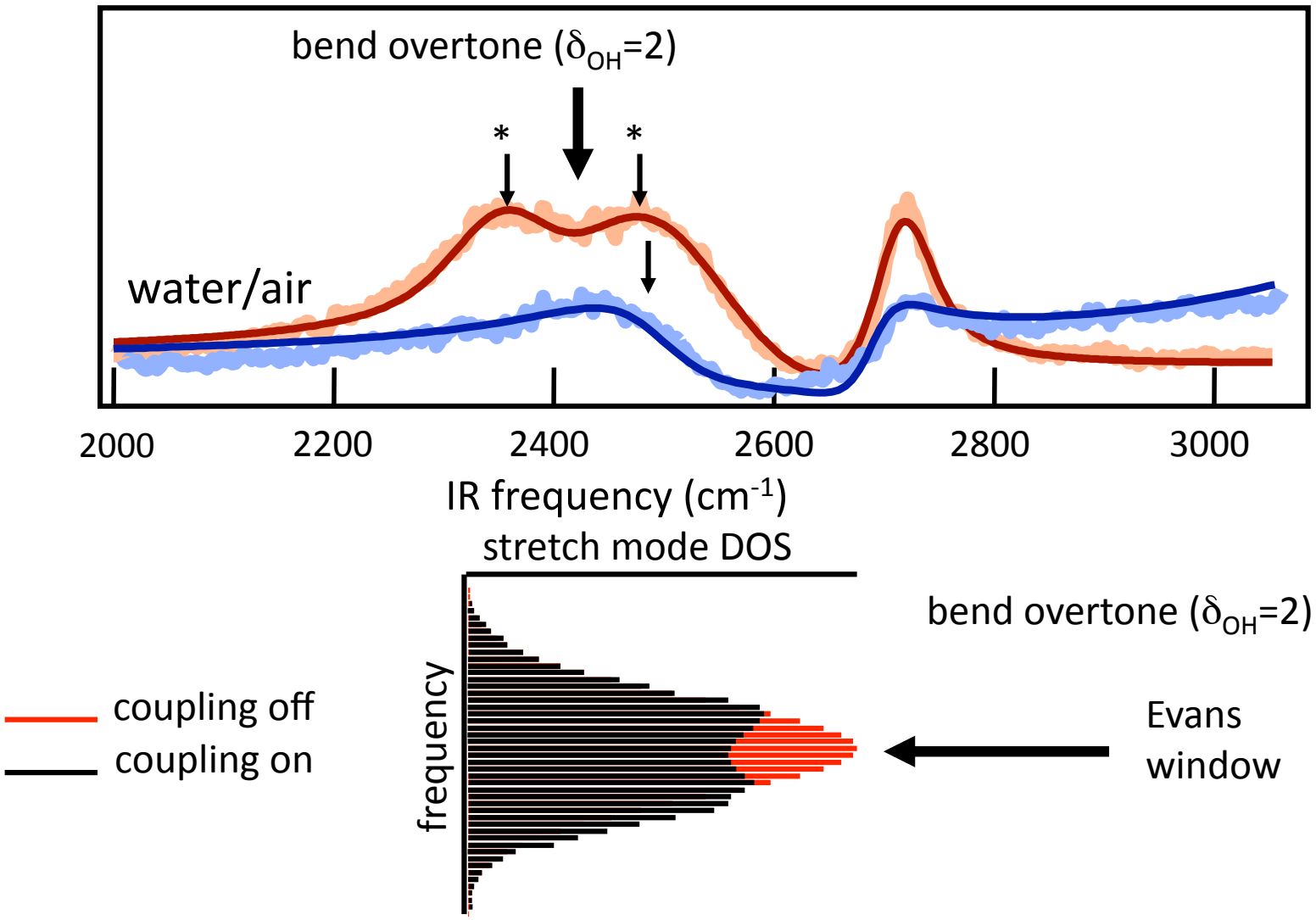




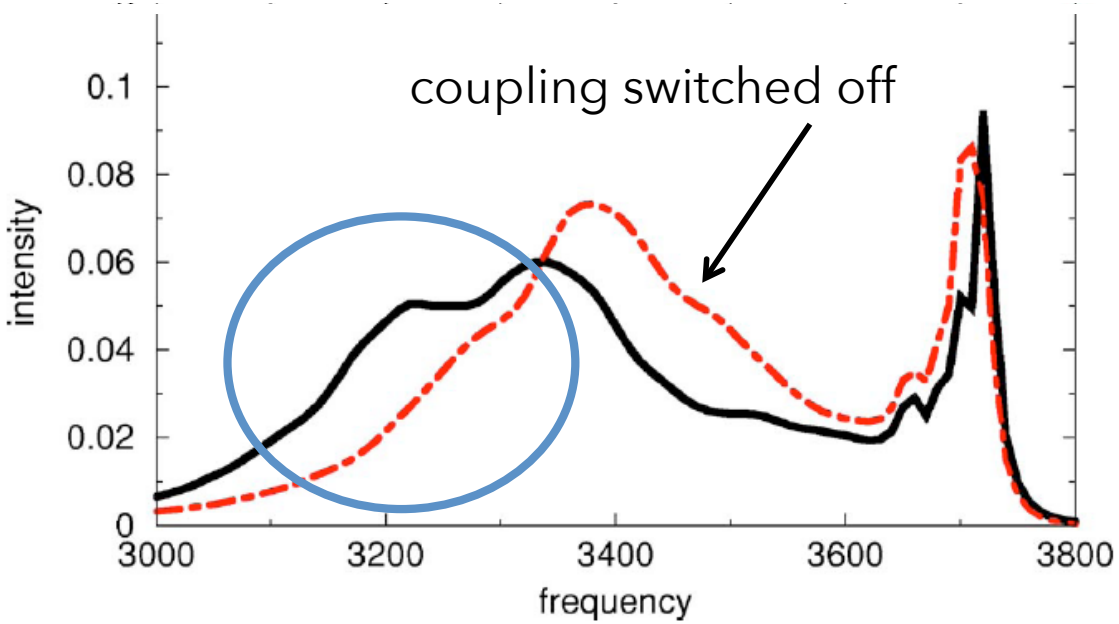
D_2O → HOD switches off coupling

[#] Gan,…, Wang (2006) Journal of Chemical Physics, 124, 114705.

Hypothesis one: two peaks are from a Fermi Resonance with the Bend Overtone



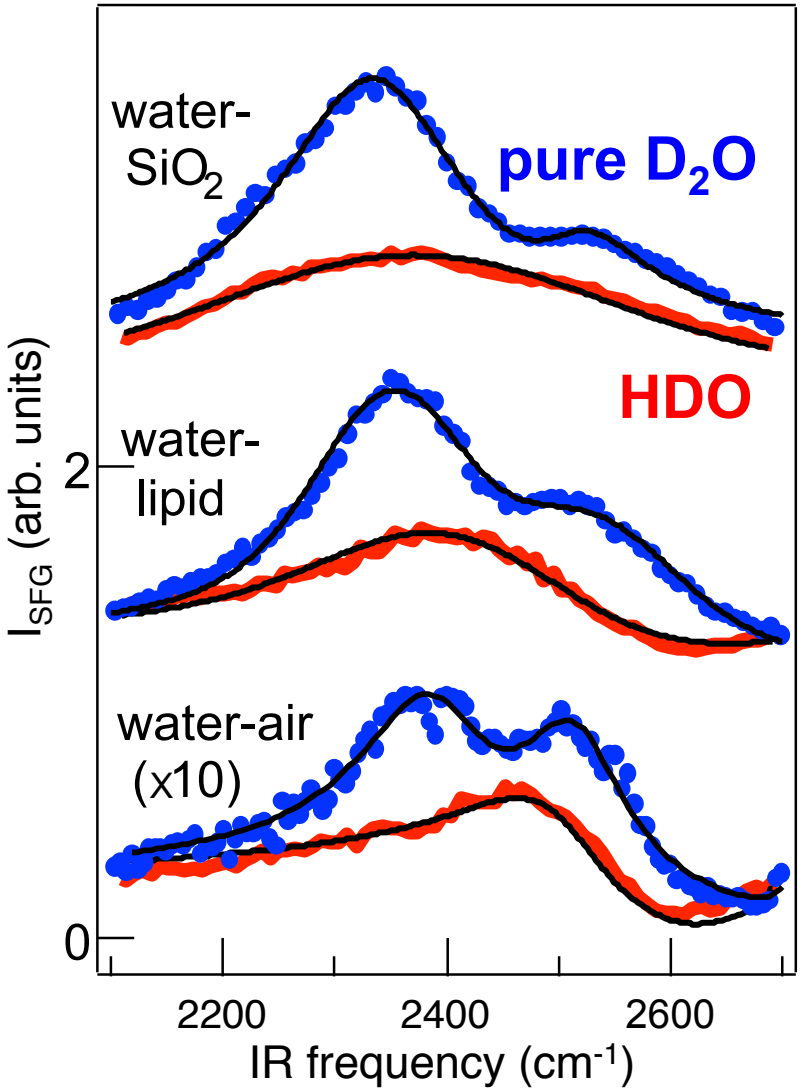
Hypothesis two: low frequency peak from collective effects (intermolecular coupling)



Buch et al. (2007) Journal of Chemical Physics, 127(20), 204710

Computation suggests the low frequency peak is a the result of intermolecular coupling (vibrational delocalization).

In either case using HDO allows more straightforward access to structure



Fitting the HDO data

	$\nu_{HDO}(cm^{-1})$	$\Gamma_{HDO}(cm^{-1})$
water-air	2510	150
water-lipid	2470	240
water- SiO_2	2420	270

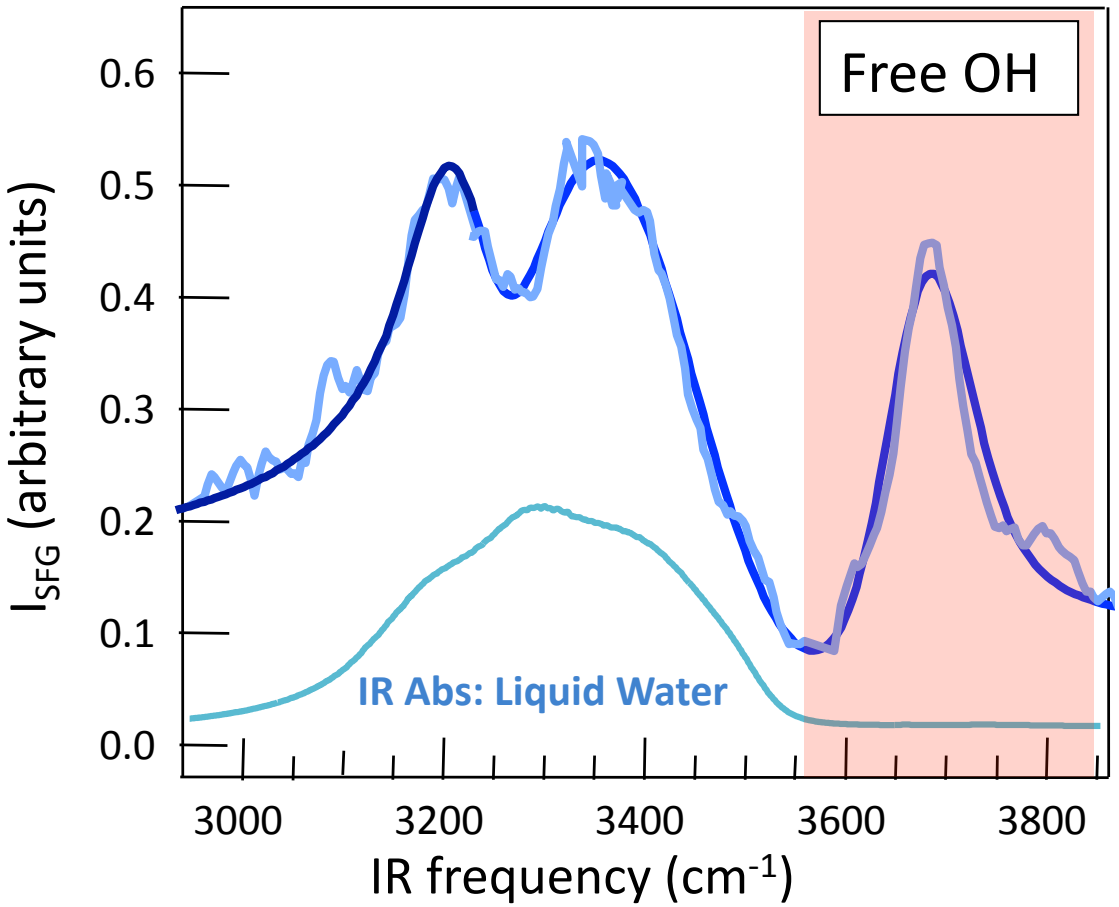
Similar to bulk

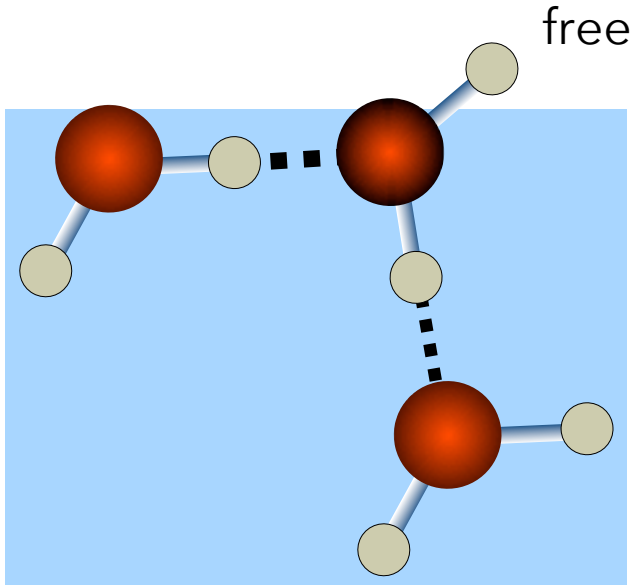
Solid/Charged Interfaces:

1.) Stronger H-bonding

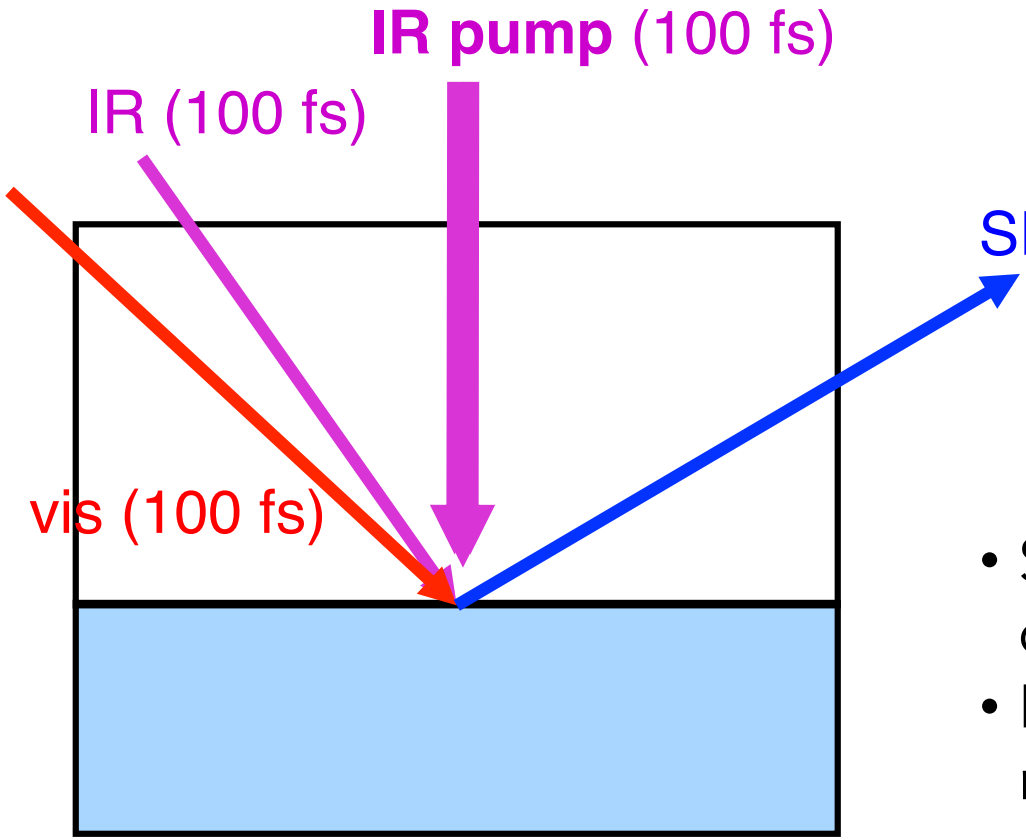
2.) More heterogeneity

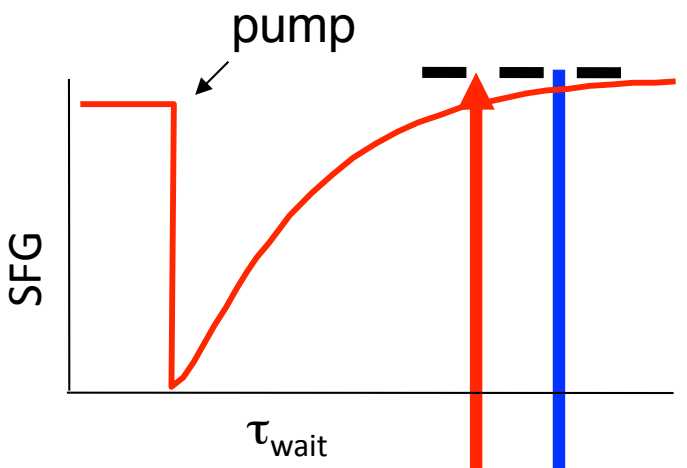
III. Solvent to Interface: Dynamics



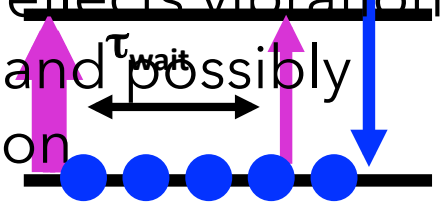


Probing dynamics: IR pump – VSF Probe

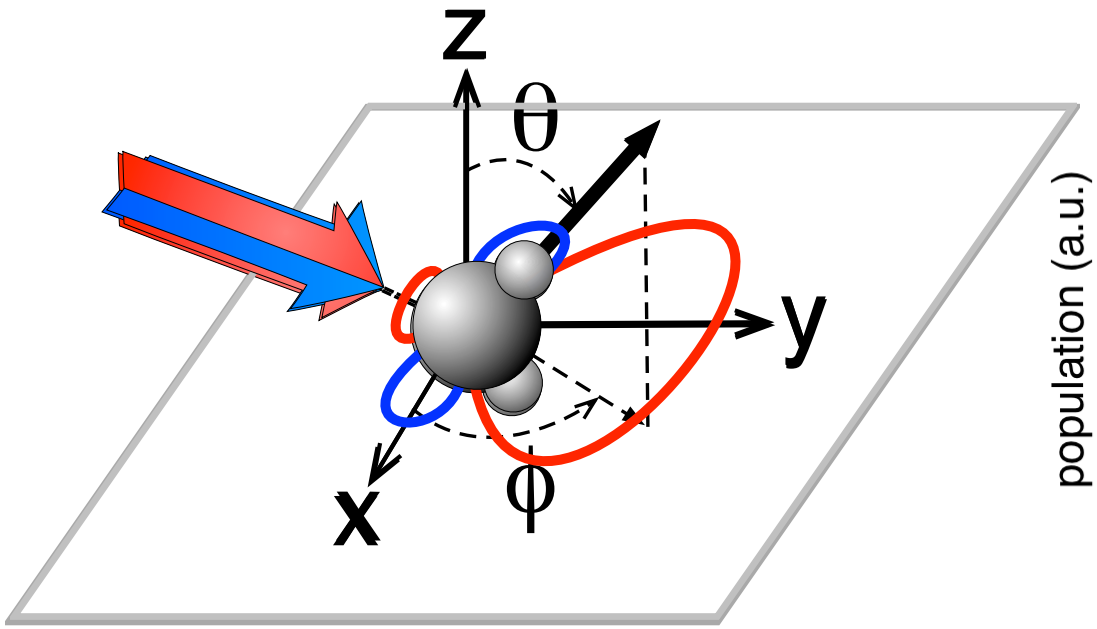


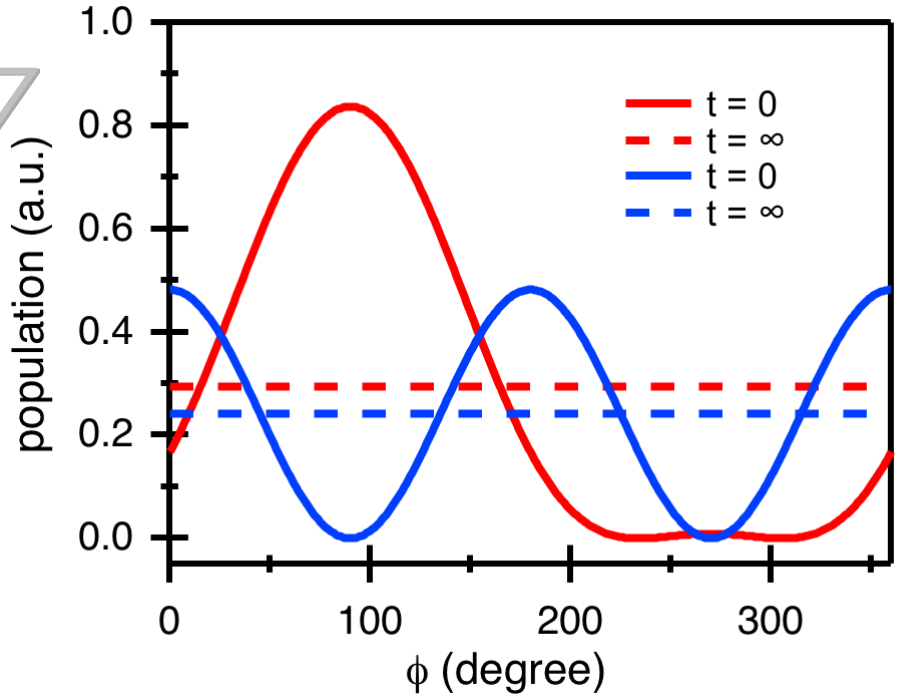


- SFG signal decreases due to depletion of ground state.
- Recovery reflects vibrational relaxation and possibly reorientation

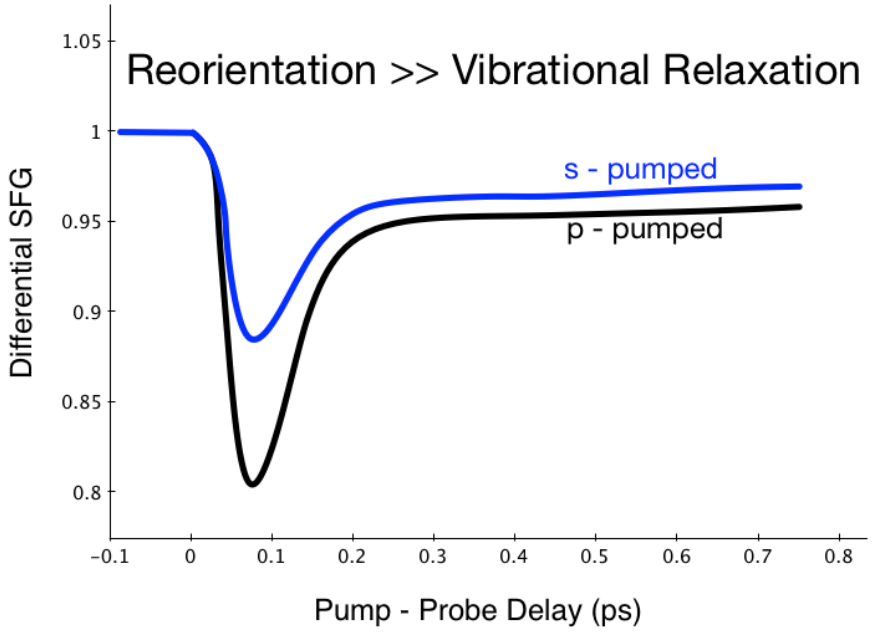


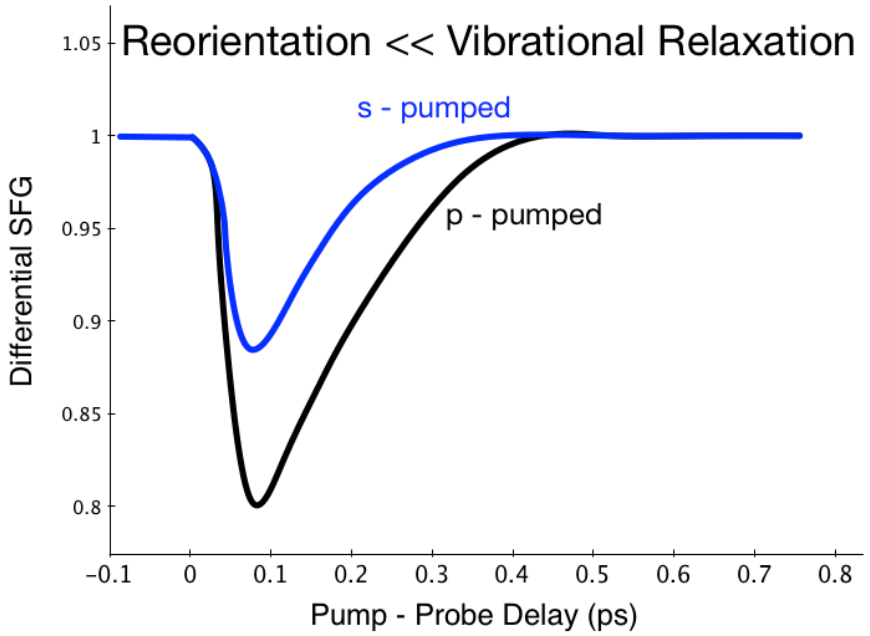
Probing reorientation of the free OH





Developing intuition for the signal





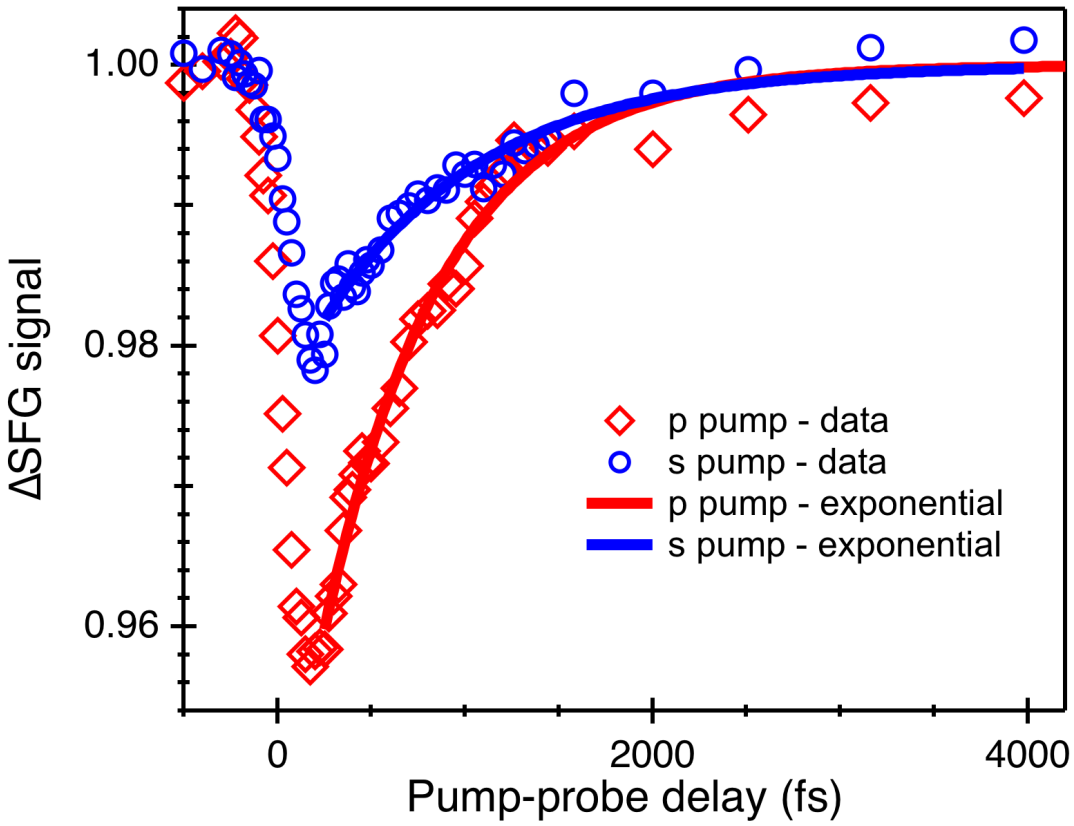
Signals relax at…

different rates *the same rate*

At long times…

signals do not converge *signals converge*

Free OH relaxation is intermediate

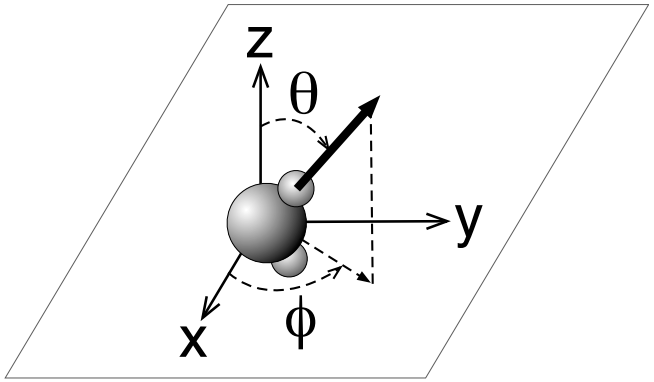


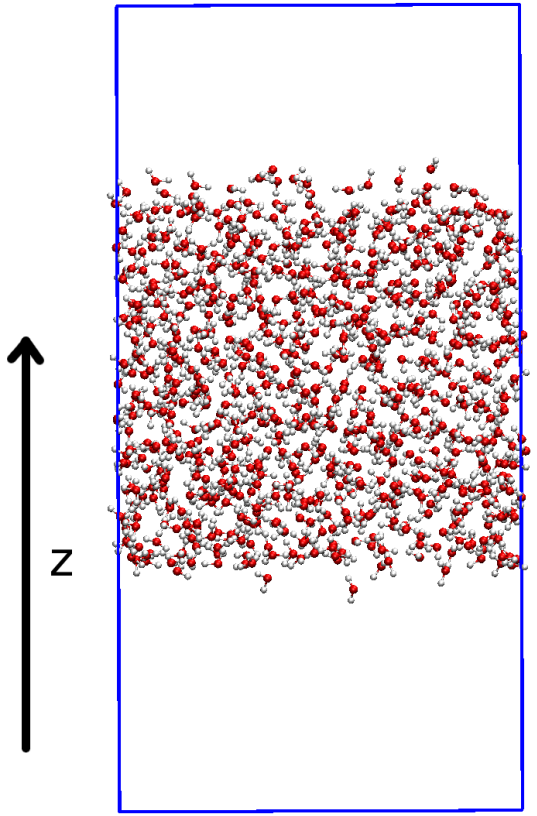
$\tau_{p,\ pump} = 640 \pm 20$ fs

$\tau_{s.\ pump} = 870 \pm 50$ fs

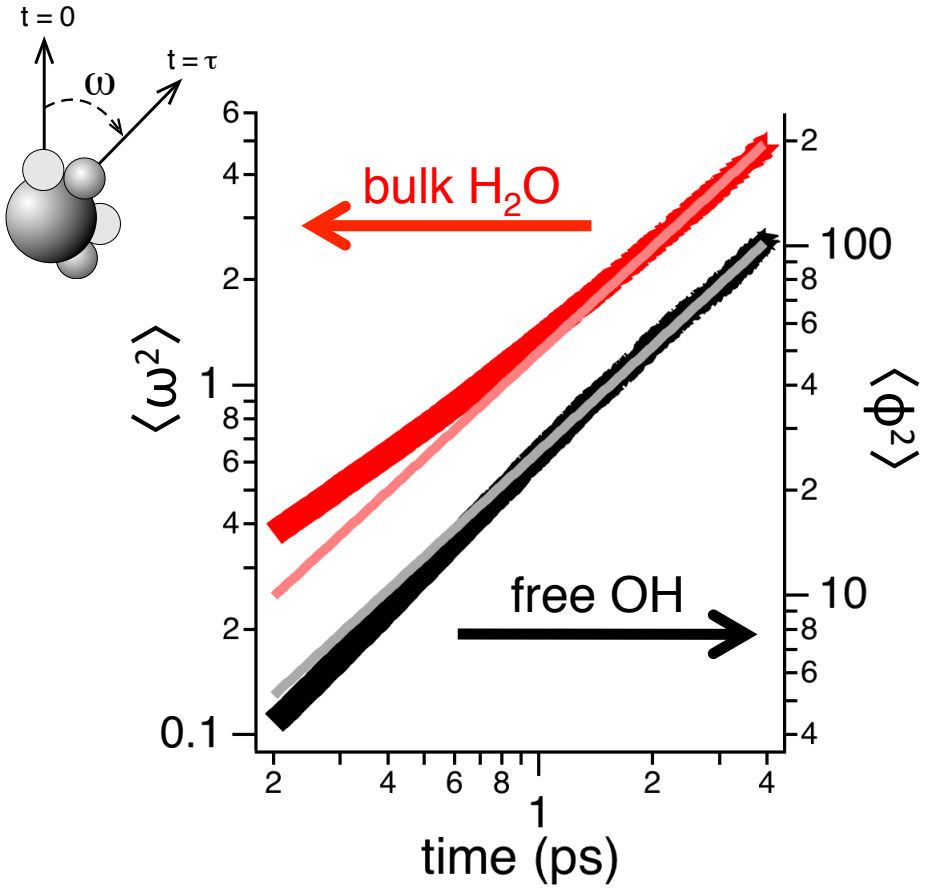
A brief simulation interlude

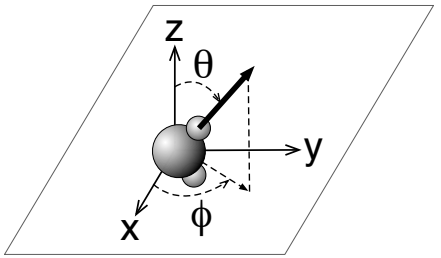
- Simulation box is 30*30*60 Å.
- Periodic boundary conditions.
- NVE at T = 300 K.
- Simulation run for 2 ns (step = 1 fs).
- SPC/E potential.

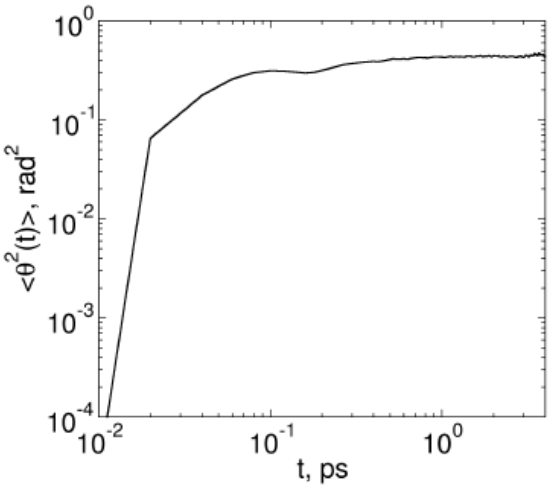




Free OH reorientation is diffusive (in MD)





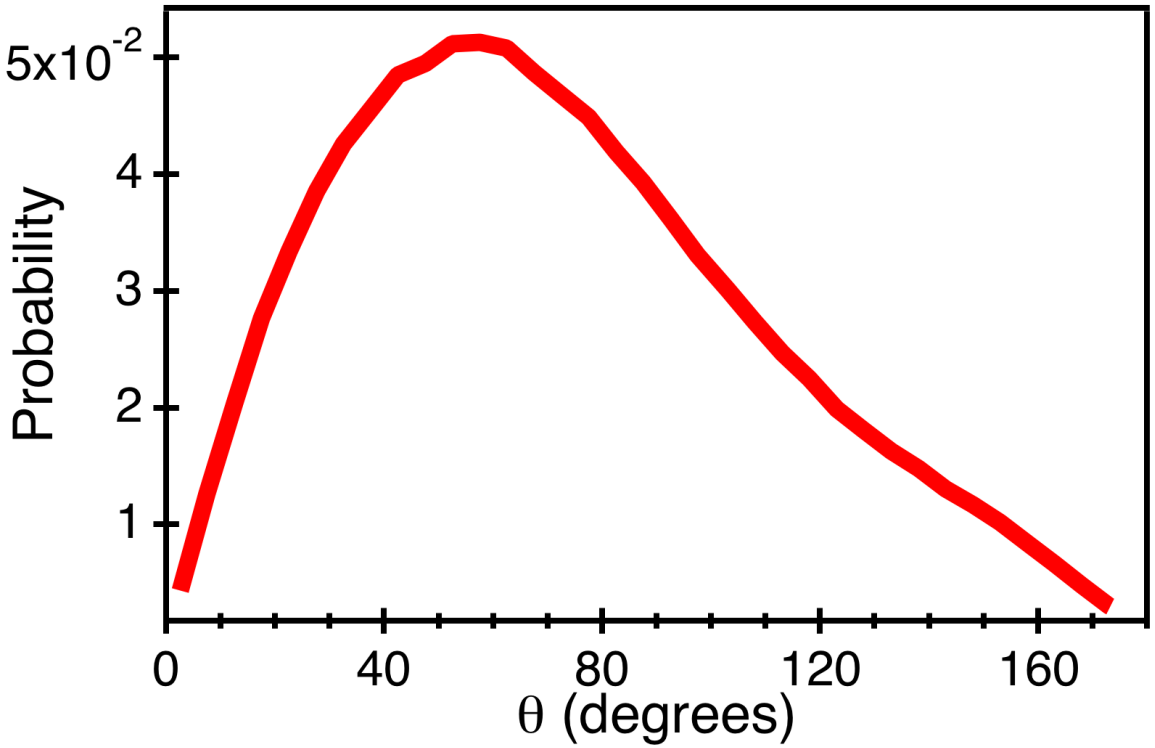


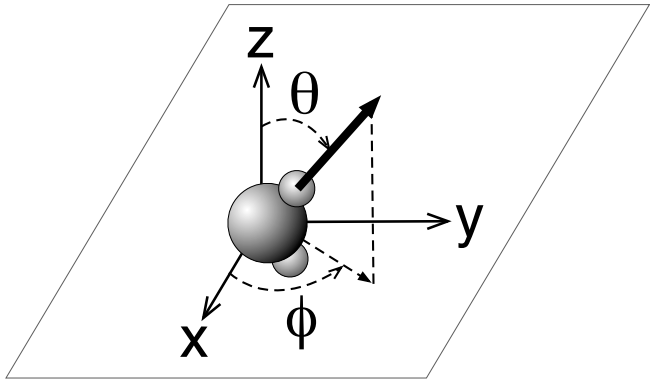
ϕ = yes

θ = maybe (diffusion within a potential)

Free OH has a preferred distribution in θ

Consistent with diffusion in a potential

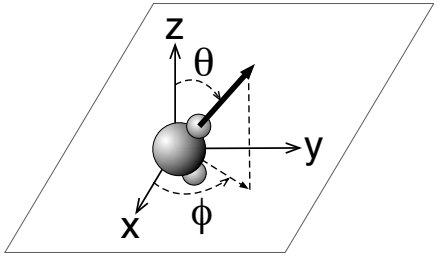




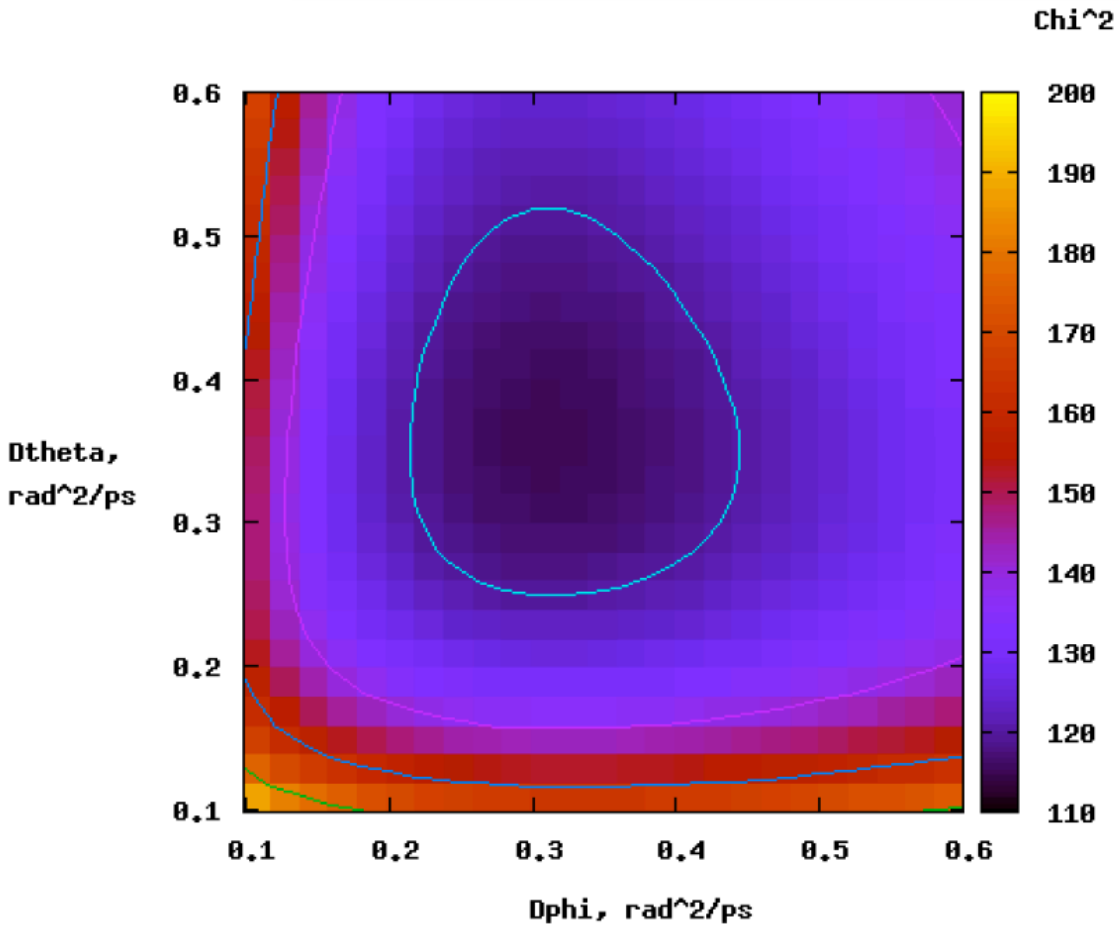
Model reorientation as diffusive in a potential

$$\frac{\partial \rho}{\partial t} = \frac{D_\phi}{\sin^2\theta}\frac{\partial^2 \rho}{\partial \phi^2} + \frac{D_\theta}{\sin\theta}\frac{\partial}{\partial \theta}\sin\theta\frac{\partial \rho}{\partial \theta} + \frac{D_\theta}{k_B T}\frac{\partial \rho}{\partial \theta}\frac{\partial V}{\partial \theta} + \frac{\rho D_\theta}{k_B T \sin\theta}\frac{\partial}{\partial \theta}\sin\theta\frac{\partial V}{\partial \theta}$$

$$V(\theta) = \frac{k_B T}{2\left(\Delta\theta\right)^2}\left(\theta - \theta_0\right)^2$$

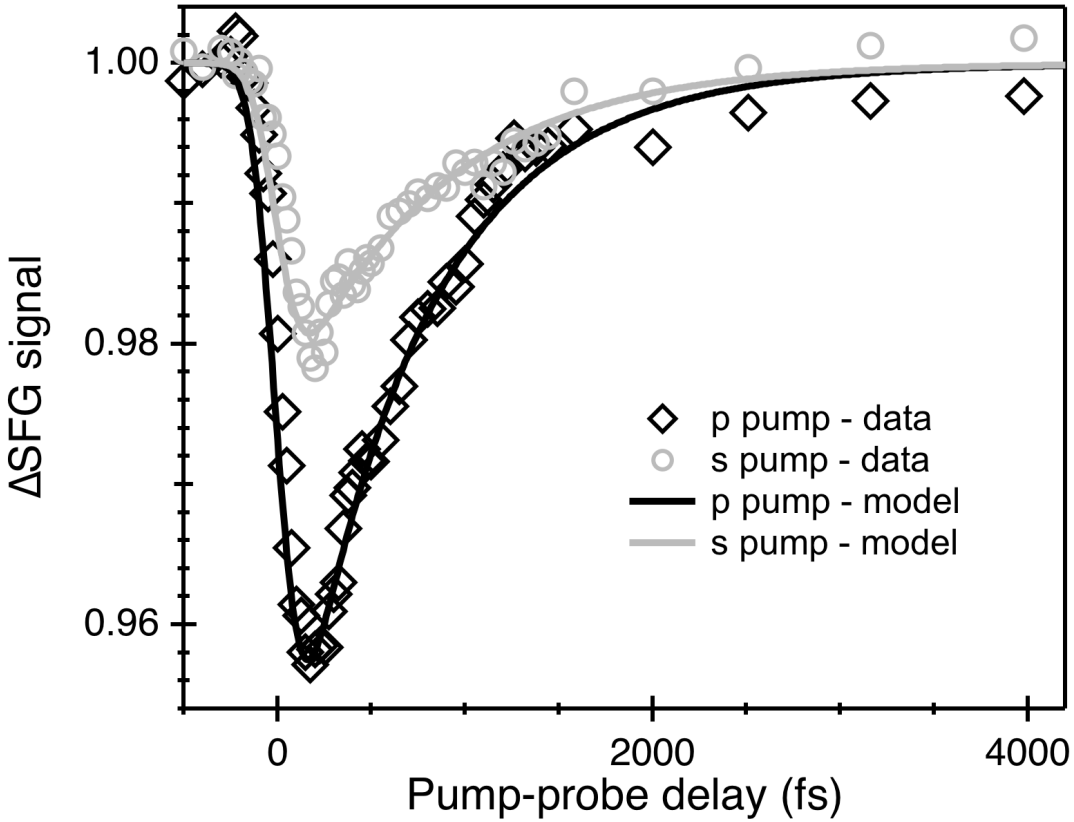


Fitting 2D diffusion model to simulation output



$D_\phi = 0.32$ rad^2/ps, $D_\theta = 0.36$ rad^2/ps

MD results describe data without adjustable parameters



$$D_\theta = 0.36 \frac{rad^2}{ps}$$

$$D_\phi = 0.32 \frac{rad^2}{ps}$$

$$\theta_0 = 59°$$

$$\Delta\theta = 26°$$

$$\tau_v = 800 \text{ fs}$$

Free OH reorientation relative to bulk

Bulk (arb orient)	Free OH
$D_\phi = 0.1\ rad^2/ps$	$D_\phi = 0.32\ rad^2/ps$
$D_\theta = 0.1\ rad^2/ps$	$D_\theta = 0.36\ rad^2/ps$

On average, free OH reorient ≈ 3x faster than bulk

Phonon spectroscopy in bulk α-qtz

TABLE II. Phonon frequencies of α-quartz at 0 K at Γ (cm^{-1}).

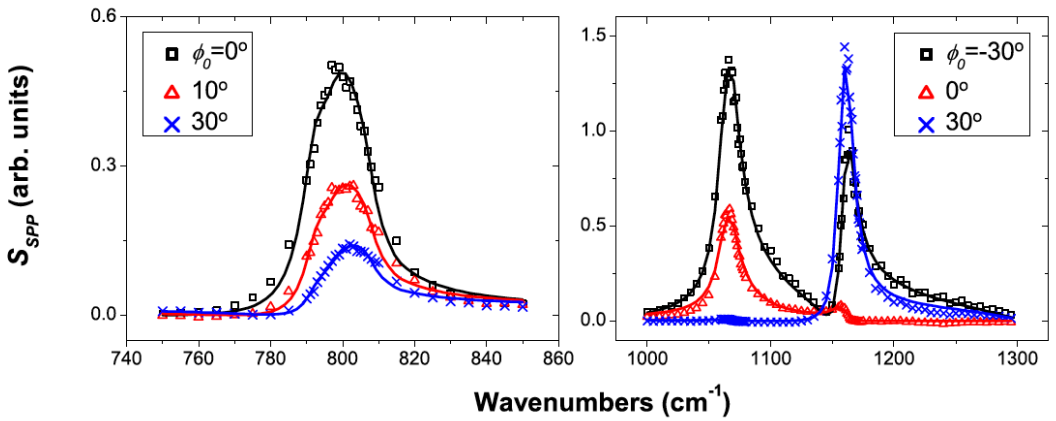
Theory		Experiment[a]	
		A_1 modes	
238.9		219	
339.3		358	
461.7		469	
1061.2		1082	
TO	LO	TO	LO
		A_2 modes	
341.4	365.7	361.3	385
493.4	540.5	499	553
762.4	784.7	778	791
1056.5	1218.3	1072	1230
		E modes	
133.3	133.4	133	133
261.3	263.2	269	269
377.6	389.2	393.5	402
443.8	498.6	452.5	512
690.8	694.5	698	701
791.7	803.9	799	811.5
1045.0	1209.5	1066	1227
1128.1	1123.9	1158	1155

Probing these modes optically (IR or Raman) depends on:

1. Mode symmetry
2. Tranverse (couples to IR) v. longitudinal (does not)

Gonze, Allan, Teter (1992) Physical Review Letters, 68(24), 3603

VSF phonon spectroscopy in bulk α-qtz



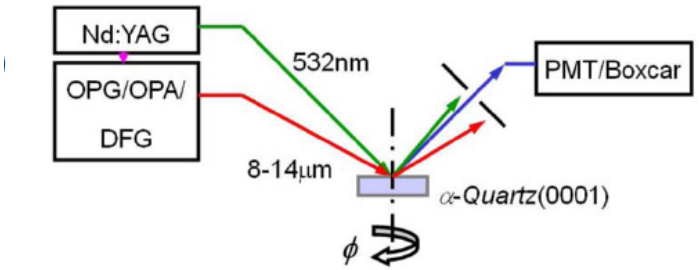
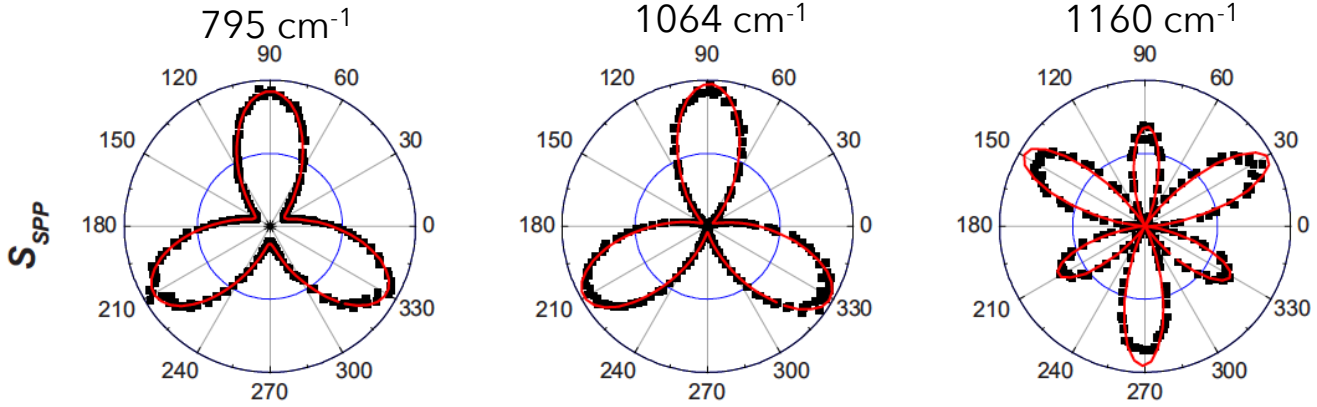


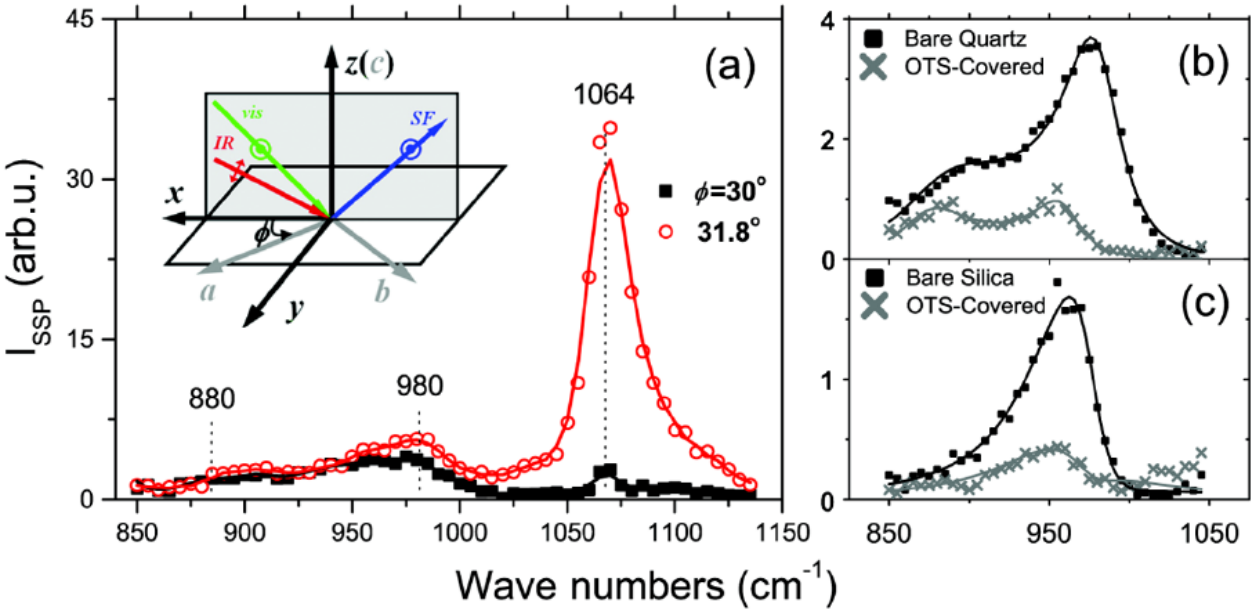
FIG. 2. (Color online) SF phonon spectra from α-quartz with (a) SSS and (b) SPP beam polarization combinations for different azimuthal angles ϕ_0. The solid lines are theoretical fits using Eq. (9).



Liu and Shen (2008) Physical Review B, 78(2), 024302

VSF probes both IR and Raman active transverse optical phonons: a simplified phonon spectrum that reflects bulk symmetry.

VSF surface phonon spectroscopy on α-qtz and amorphous SiO_2



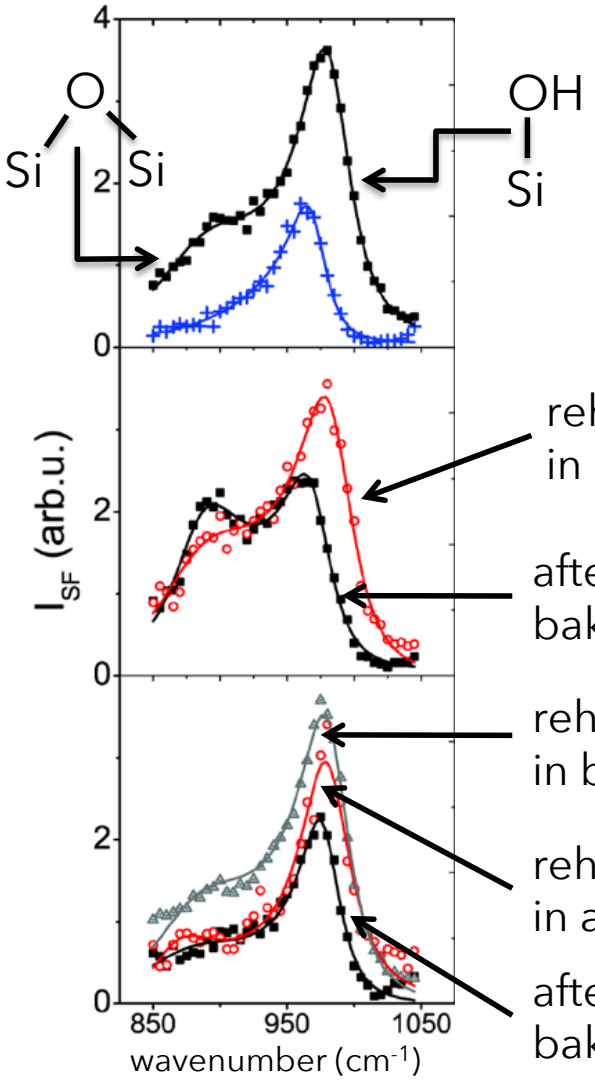
Liu and Shen (2008) Physical Review Letters, 101(1), 016101

Resonances appear in VSF response at,

1. nonbulk frequencies
2. nonbulk symmetries
3. for amorphous material
4. and are perturbed by surface chemistry

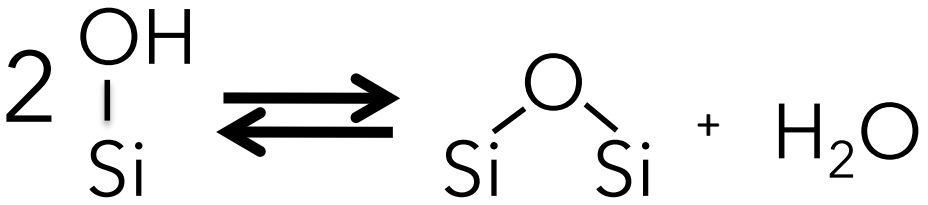
VSF surface phonon spectroscopy on α-qtz for tracking surface reconstruction

Liu and Shen (2008) Physical Review Letters, 101(1), 016101



■ = quartz

\+ = amorphous silica



surface *damage*

Conclusions

1. Using VSF spectroscopy one can probe *both* interfacial solvent (most work on water) *and* surface phonons at *buried interfaces*.

2. Adding additional pulses to VSF experiments makes it possible to probe structural and energy relaxation dynamics with interfacial specificity.

3. Future work: optically probing the association of interfacial molecules with particular surface sites.

Related Publications (from our previous work the results of which were discussed above)

1. Sovago, Campen, Wurpel, Müller, Bakker, Bonn (2008) *Vibrational Response of Hydrogen-Bonded Interfacial Water is Dominated by Interfacial Coupling*, Physical Review Letters, 100, 173901
2. Sovago, Campen, Bakker, Bonn (2009) *Hydrogen bonding strength of interfacial water determined with surface sum-frequency generation*, Chemical Physics Letters, 470, 7
3. Hsieh, Campen, Vila Verde, Bolhuis, Nienhuys, Bonn (2011) *Ultrafast Reorientation of Dangling OH Groups at the Air-Water Interface Using Femtosecond Vibrational Spectroscopy*, Physical Review Letters, 107(11), 116102
4. Vila Verde, Bolhuis, Campen (2012) *Statics and Dynamics of Free and Hydrogen-Bonded OH Groups at the Air/Water Interface*, Journal of Physical Chemistry B, 116(31), 9467