

On the Structure of Water at the Aqueous/Air Interface

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Introduction

Three pronounced peak(at OH stretch range) in the Vibrational sum frequency (VSF) spectrum :

- ~3200 cm^{-1} : first broad feature, ice-like peak
- ~3450 cm^{-1} : second broad, water-like peak
- ~3700 cm^{-1} : sharp peak , dangling OH bond,

Peak amplitude value in the phase-sensitive VSFS :

- 3700 cm^{-1} peak : Positive amplitude (or **negative amplitude**)
- 3200 ~ 3600 cm^{-1} : negative amplitude (or **Positive amplitude**)

→ the sign returns to a positive value below 3200 cm^{-1} .

agreement is generally found above 3200 cm^{-1}

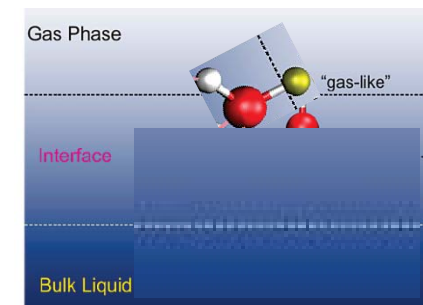
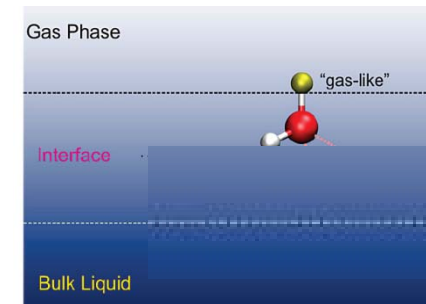
agreement is not below 3200 cm^{-1}

motivation

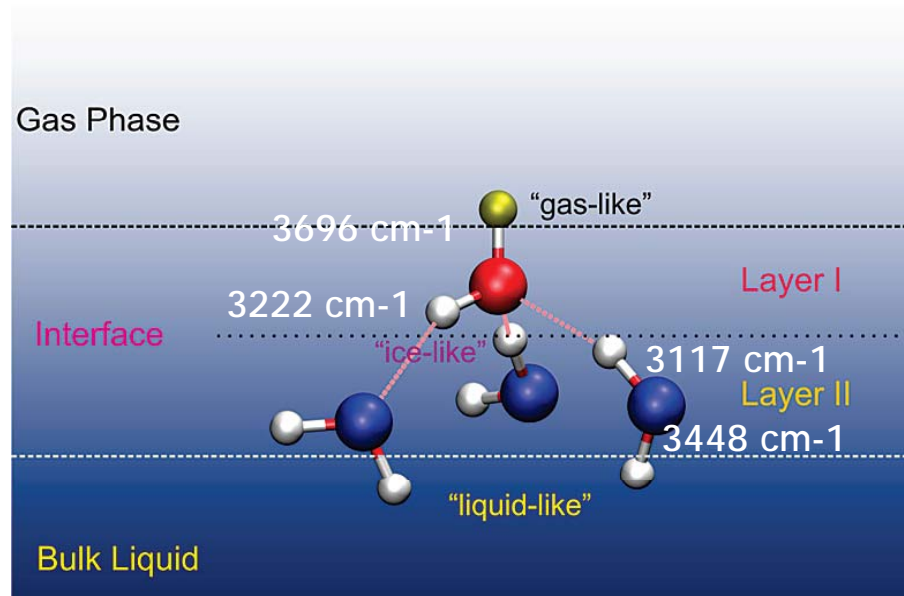
Interfacial water molecules forms :

- a single dangling OH bond (“single-donor” water) support VSFS experiment

- two dangling OH bonds (“acceptor-only” water) support X-ray absorption spectroscopy



molecular structure and hydrogen bonding of the air/water interface investigate with
→ Vibrational sum frequency spectroscopy (VSFS) , phase-sensitive VSFS
→ molecular dynamics (MD) simulations



Four VSFS resonances in the OH stretch region

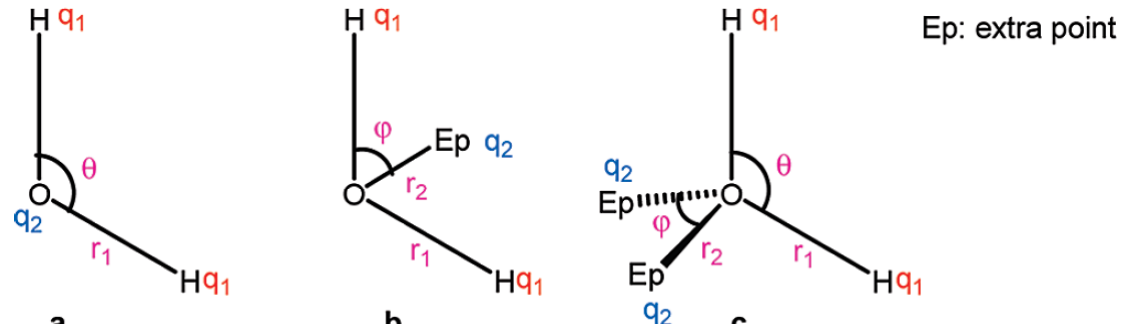
correspond 

Four chemically distinct OH moieties in the top two water layers at the interface

Methods

Molecular Dynamics Simulations

TABLE 1: Force Field Parameters for Water Models

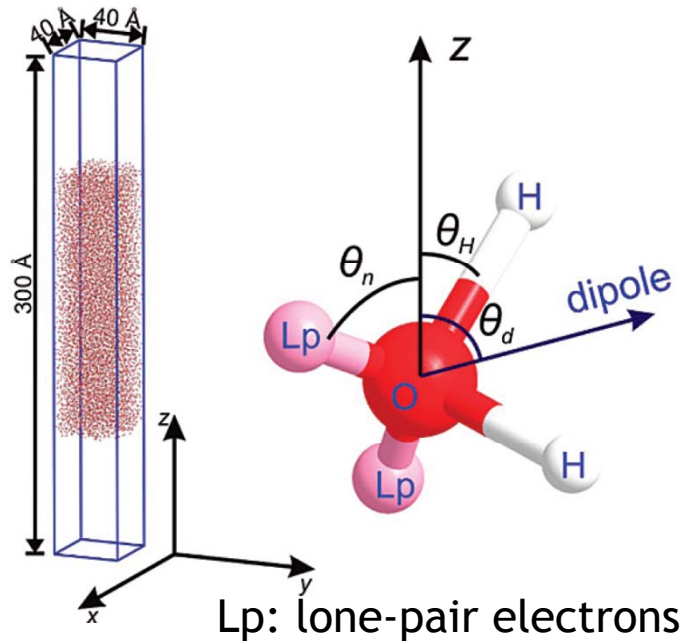


model	type	r_0 (Å)	ϵ (kcal/mol)	r_1 (Å)	r_2 (Å)	q_1 (e)	q_2 (e)	θ (deg)	φ (deg)
SPC/E	a	1.7767	0.1553	1.0000		0.4238	-0.8476	109.47	
TIP3P	a	1.7683	0.152	0.9572		0.417	-0.834	104.52	
POL3	a	1.798	0.156	1.0000		0.365	-0.730	109.47	
TIP4P-Ew	b	1.775931	0.16275	0.9572	0.1250	0.52422	-1.04844	104.52	52.26
TIP5P	c	1.7510	0.160	0.9572	0.70	0.241	-0.241	104.52	109.47
mTIP5P	c	1.7510	0.160	0.850	0.850	0.241	-0.241	109.47	109.47

In this water models

the protons and the negative charges occupy the apexes of a perfect tetrahedron

SCHEME : Cuboid Water Slab and the Definitions of the Orientations of the O-H Bond, O-Lp and the Water Dipole



the orientation defined by the angles between vectors and the *z axis*

(Vector: O-H bond, O-Lp (lone pair), water dipole)

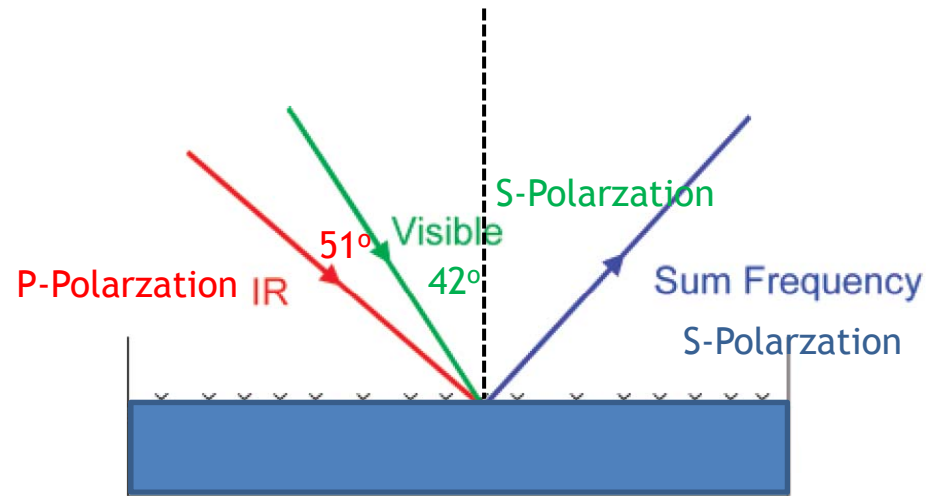
AMBER 9 suite of programs:

Initial structure : box size was approximately $40 \times 40 \times 155 \text{ \AA}^3$

extend

later structure : box size was approximately $40 \times 40 \times 300 \text{ \AA}^3$

Vibrational Sum-Frequency Spectroscopy (VSFS)



$$I_{\text{SFG}} \propto |\chi_{\text{eff}}^{(2)}|^2 I_{\text{vis}} I_{\text{IR}}$$

I_{vis} : intensities of the incoming visible beam

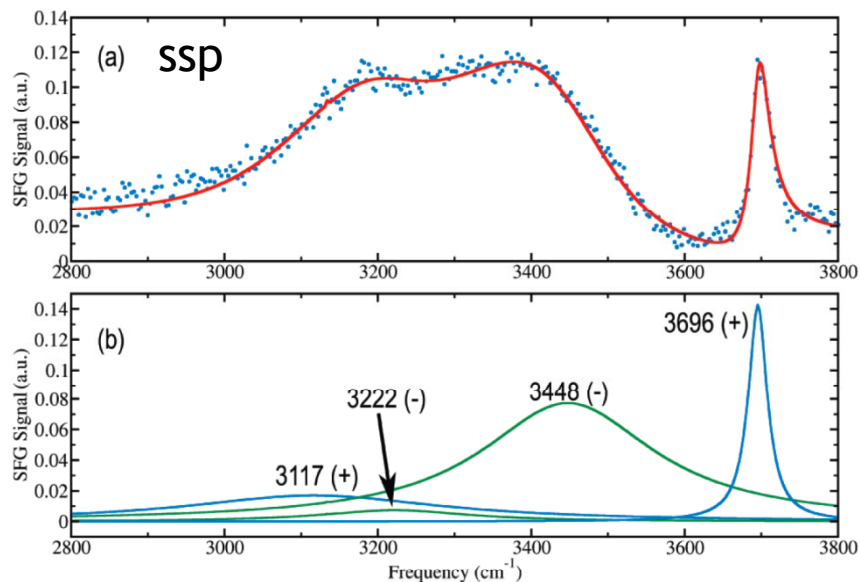
I_{IR} : intensities of the incoming infrared laser beams

$\chi_{\text{eff}}^{(2)}$: effective second-order nonlinear susceptibility

$$\chi_{\text{eff}}^{(2)} = \chi_{\text{NR}}^{(2)} + \chi_{\text{R}}^{(2)} = \chi_{\text{NR}}^{(2)} + \sum_q \frac{A_q}{\omega_{\text{IR}} - \omega_q + i\Gamma_q}$$

Results

VSFS



- (a) VSFS of the air/water interface
- (b) Four component peaks are derived from the fit in part a.

Fitting Parameters and Peak Assignments for the Spectrum

frequency (cm ⁻¹)	strength	width (cm ⁻¹)	assignment
3696	+5.6	15	gas-like
3448	-38.2	137	liquid-like
3222	-10.0	117	ice-like
3117	+26.4	202	ice-like

Table provided absolute orientation information, oscillator strength data, and peak width values for each of the four resonances

The assignment of a peak at 3117 cm^{-1} is new

- Come from an ice-like structure.
- the peak exist the lower end of the IR absorption band for ice.
- the peak is much highest than the Raman spectrum for ice peak(3085 cm^{-1})



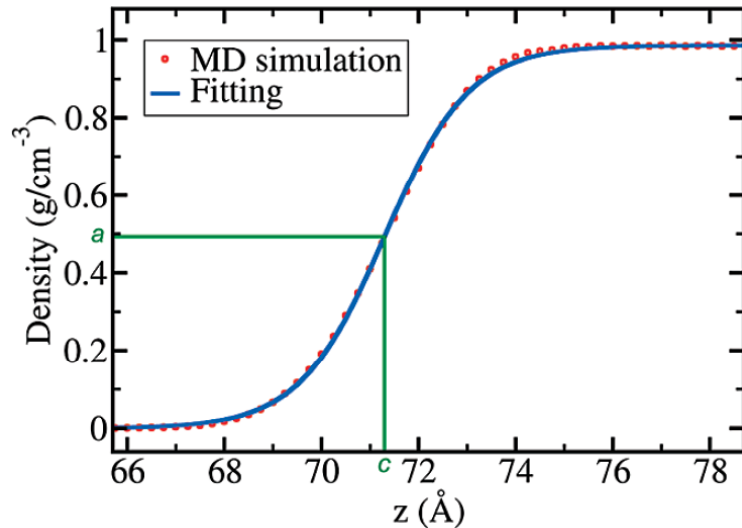
Why so?

there are multiple absorption peaks in the IR and Raman spectra of ice as well as many other solid forms of water.

MD Simulations

Density Profile :
(use the SPC/E model)

the thickness of the air/liquid interface is about 4 Å
(the interface is defined as the region between 5% and 95% of the bulk liquid density)



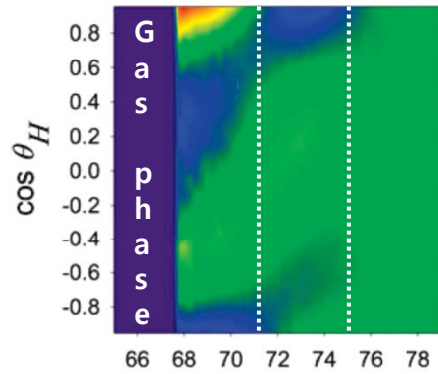
a hyperbolic tangent function:

$$\rho(z) = a\{1 + \tanh[b(z - c)]\}$$

$a = 0.493 \text{ g/cm}^3$, $b = 0.5735 \text{ \AA}^{-1}$, $c = 71.296 \text{ \AA}$
 c : the position of the Gibbs dividing surface

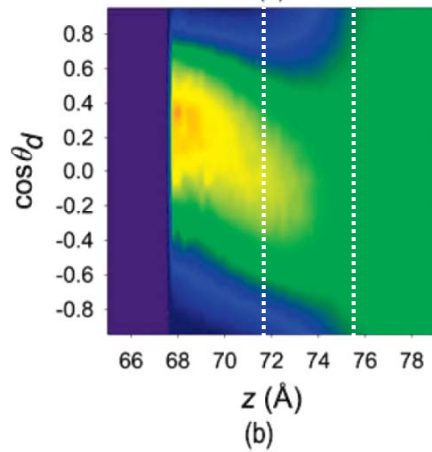
Figure 2. Density profile along the z-direction of the water slab.

Layered Structures at the Air/Water Interface



the uneven distribution of $P(\cos \theta_H)$, $P(\cos \theta_d)$ and $P(\cos \theta_n)$:
Provide a partially ordered structure in interface

divide the interface into two distinct
Layer 1: 68 ~ 71 Å (5-50% of the bulk density) and
Layer 2: 71 ~ 75 Å (50-95% of the bulk density)



the water dipoles near the interface tend to be perpendicular to the surface normal,

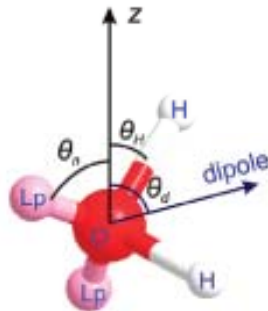
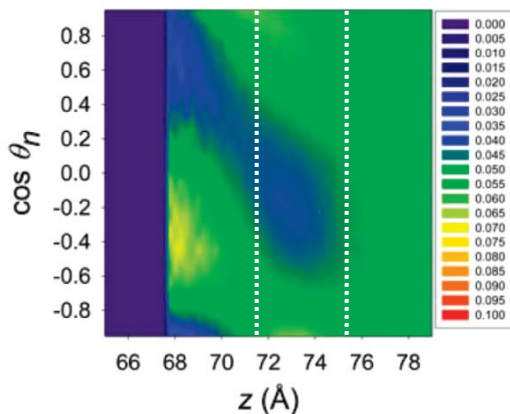
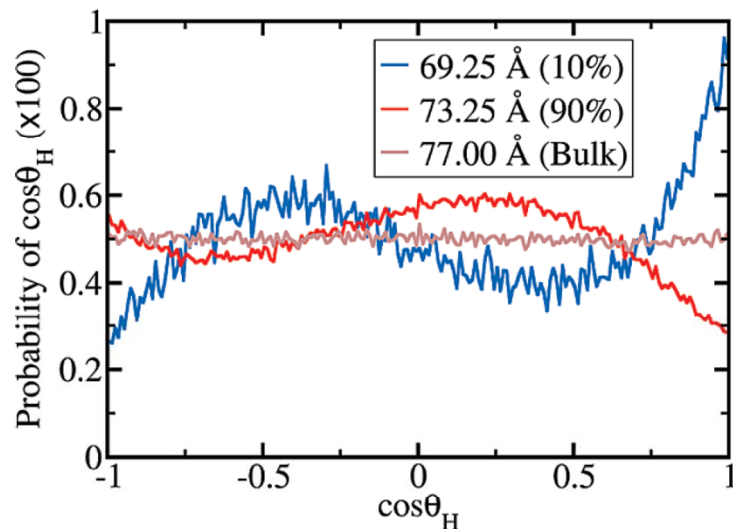
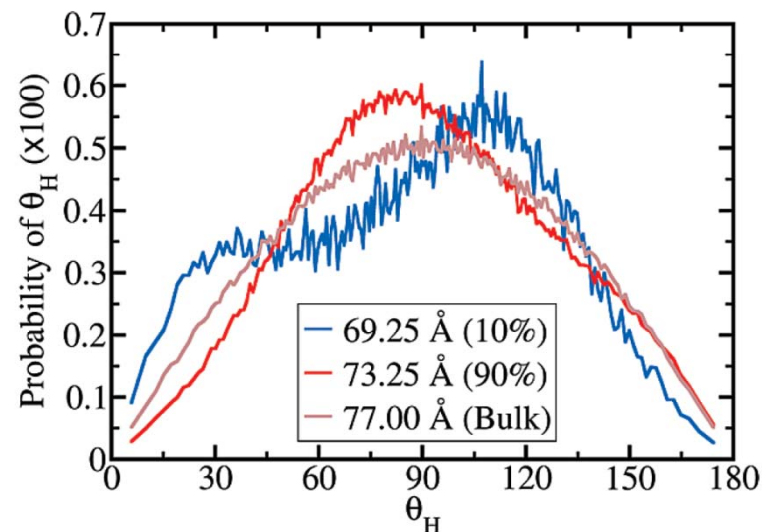


Figure 3. Probability distributions as a function of depth (z -axis) for the orientation of (a) the OH groups, (b) the water dipoles, and (c) O-Lp.



(a)



(b)

The distribution function for θ_H is shown in Figure 4 at three different depths, representing bulk water and the two interfacial layers

In the first layer
one OH bond pointing vertically out of the bulk liquid and the other OH bond at $\sim 110^\circ$

In the second layer,
one of the two OH bonds pointing into the bulk.

Free OH bond an angle is $\sim 30^\circ$

Figure 4. $P(\cos \theta_H)$ and $P(\theta_H)$ at three typical depths corresponding to the different interfacial layers.

conclusion

- we provide a first-order approximation for the connection between the phase of the spectrum and the averaged molecular orientation at the air/water interfaces.
- In the top layer the OH moiety prefers to point out of the bulk water