Interactions of Water With the Nonionic Surfactant Polyoxyethylene Glycol Alkyl Ethers Studied by Phase-Sensitive Sum Frequency Generation and Molecular Dynamics Simulation

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Zaure
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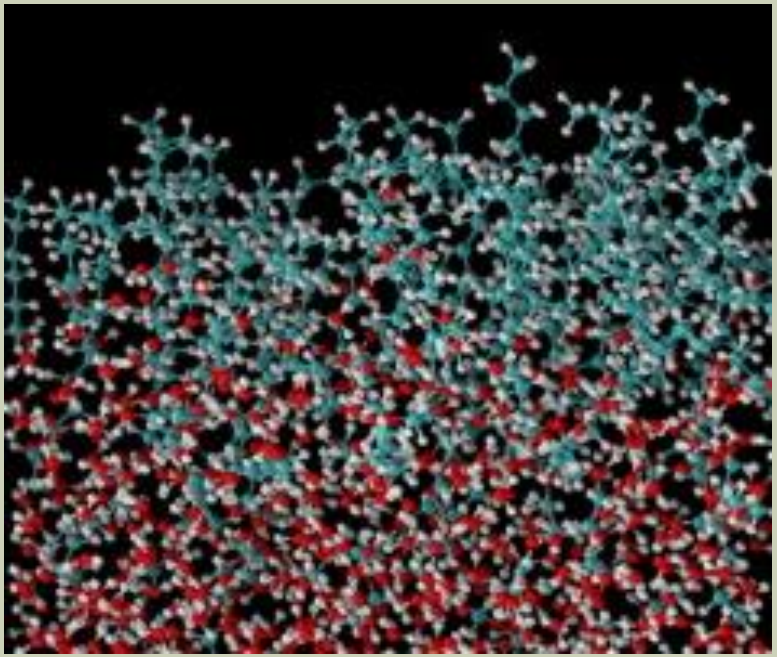
Interactions of water with the nonionic surfactant

Polyoxyethylene glycol alkyl ether

C_mH_{2m+1}-$(OCH_2CH_2)_n$-OH

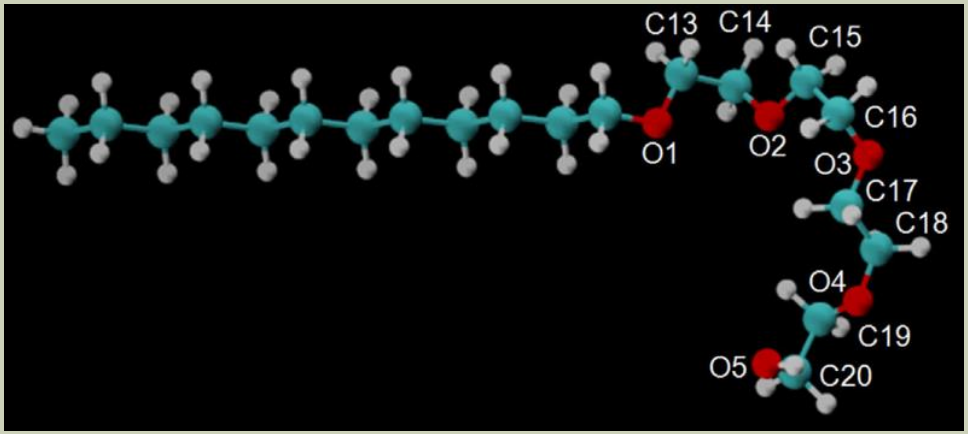
C_mE_n

- m: the number of carbon in hydrophobic carbon chain
- n: the number the ethylene oxide units



Sample

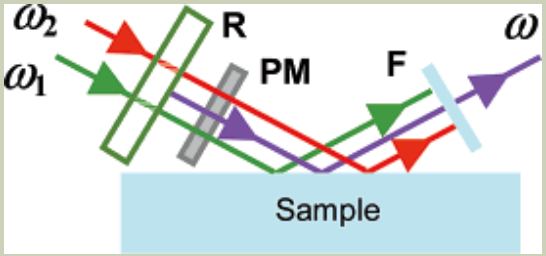
- Tetraethylene glycol monododecyl ether ($C_{12}E_4$)



- Phase-sensitive SFG
- MD simulation

Phase-Sensitive SFG

- Fm Ti-sapphire laser (120 fs, 800 nm, 1 kHz, and 2 mJ/pulse)
- The energy of the 800 nm ~ 10 μJ/pulse and IR beam ~ 3 μJ/pulse



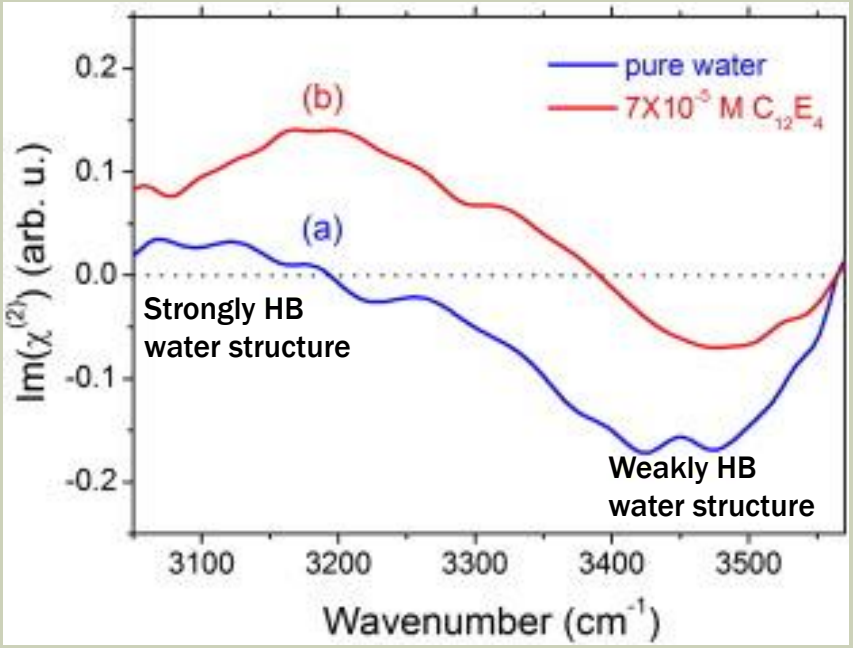
$$S_S(\omega_2) = A\left\{\left|\left[\left|\chi_S^{(2)}(\omega_2)\right| e^{i\phi(\omega_2)} + a\left|\chi_R^{(2)}\right| e^{i\theta(\omega_2)}\right]\right|^2 + b^2\left|\chi_R^{(2)}\right|^2\right\}$$

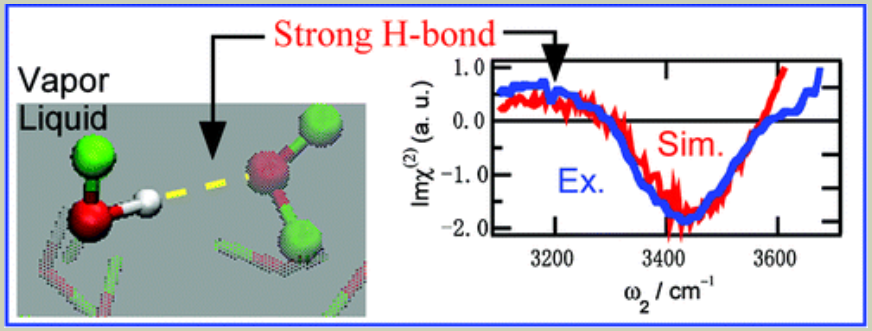
- $S_{S1}(\omega_2)$ & $S_{S2}(\omega_2)$ with the phase of the reference SF field at $\theta(\omega_2)$ & $\theta(\omega_2)$ $+\pi/2$

$$\phi(\omega_2) - \theta(\omega_2) = \tan^{-1}\left[\frac{S_{S2} - A\left|\chi_S^{(2)}\right|^2 - A(a^2+b^2)\left|\chi_R^{(2)}\right|^2}{S_{S1} - A\left|\chi_S^{(2)}\right|^2 - A(a^2+b^2)\left|\chi_R^{(2)}\right|^2}\right]$$

J. AM. CHEM. SOC. 2007

$Im\chi^{(2)}$ spectra of water (a)

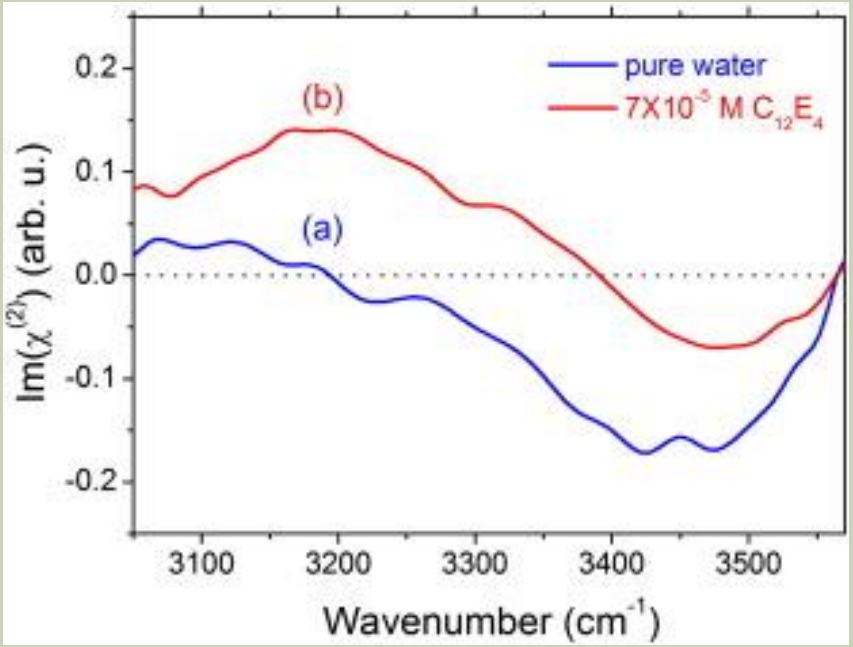




J. Am. Chem. Soc., 2011

- a positive OH band near 3100 cm^{-1}
- a negative OH band near 3450 cm^{-1}

$Im\chi^{(2)}$ spectra of mixture (b)



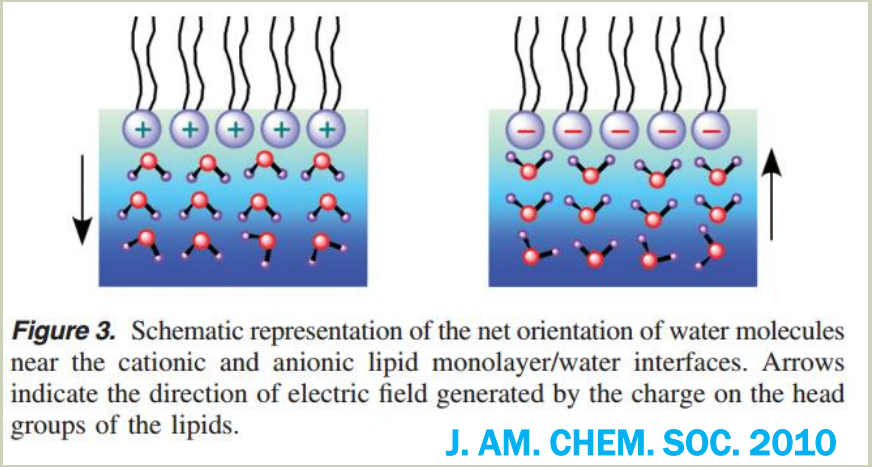
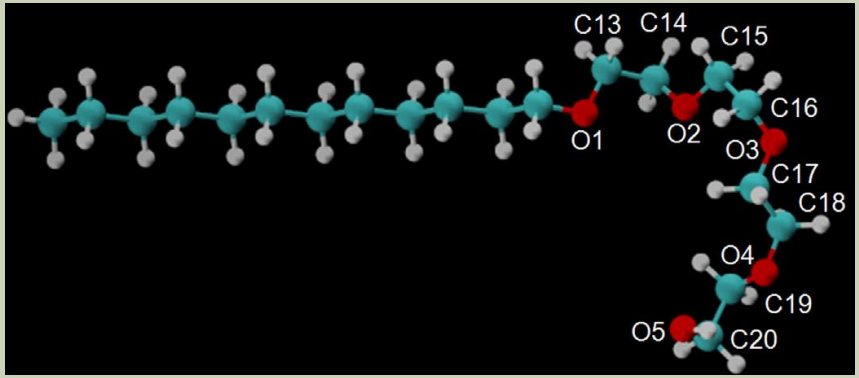


Figure 3. Schematic representation of the net orientation of water molecules near the cationic and anionic lipid monolayer/water interfaces. Arrows indicate the direction of electric field generated by the charge on the head groups of the lipids.

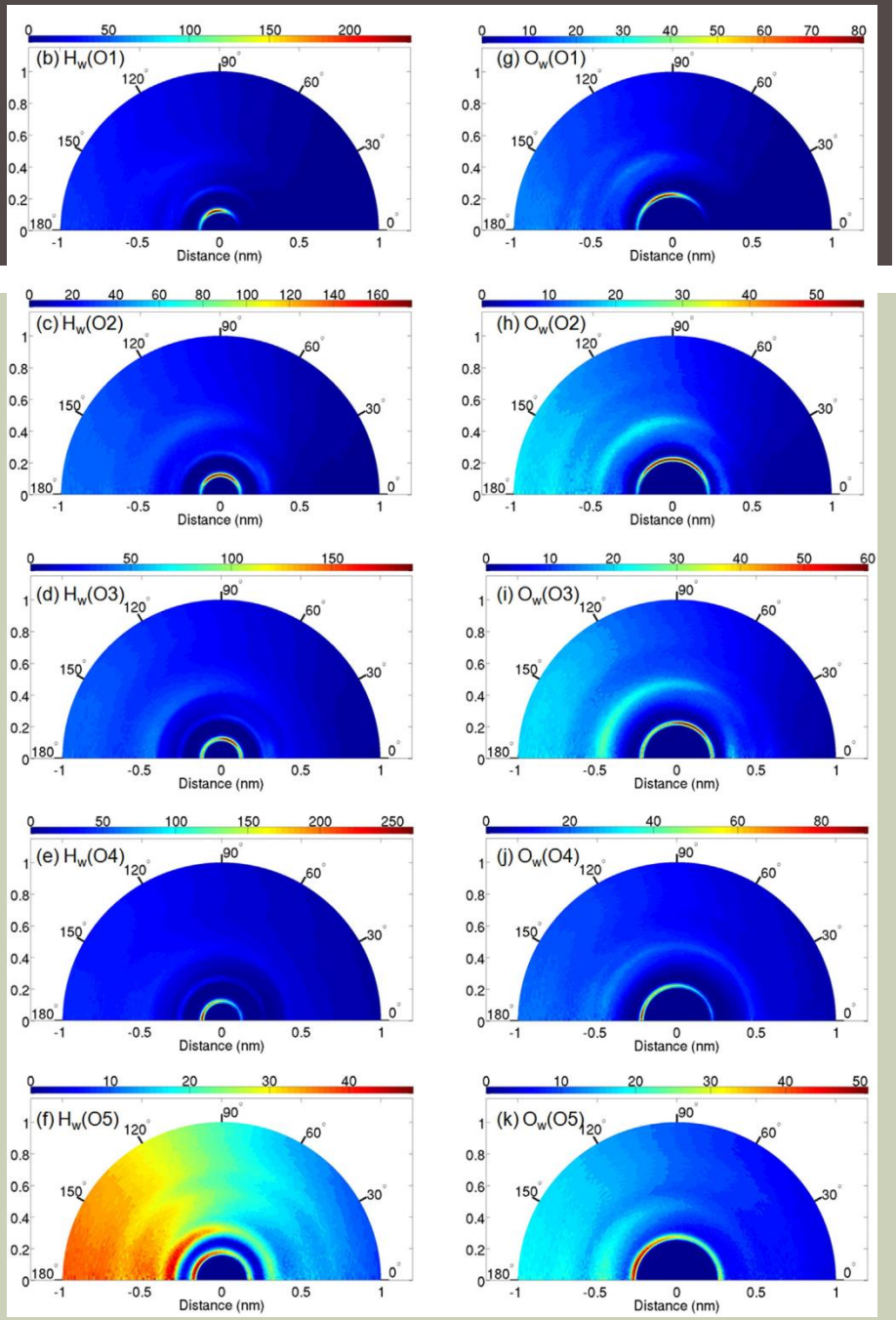
J. AM. CHEM. SOC. 2010

- Even though the surfactant is overall neutral, the effect of $C_{12}E_4$ on the orientation of water is more anionic-like

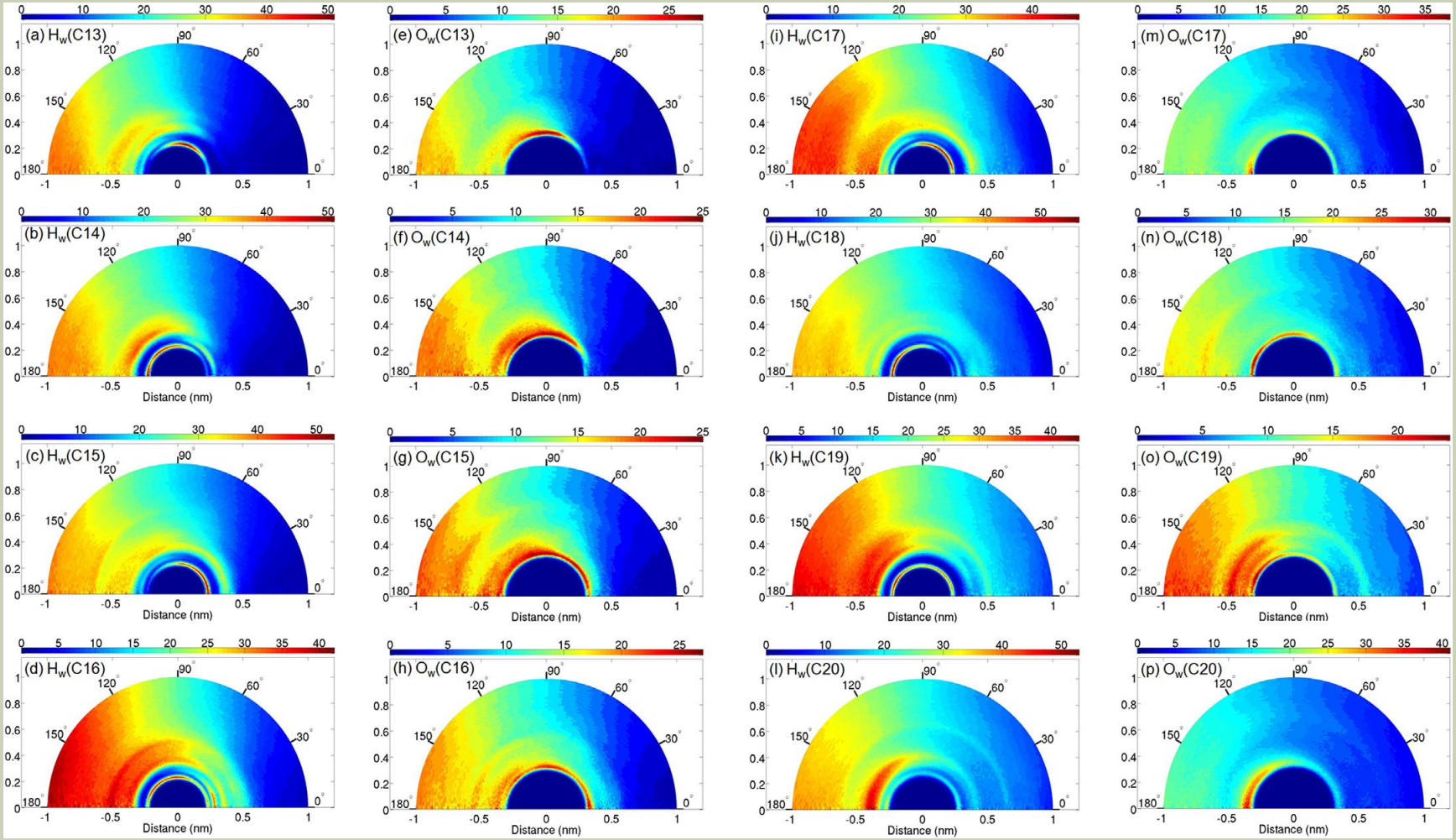
MD: H_W and O_W near the O



- The water molecules are rearranged such that the H_W are closer to the surfactant's oxygen no matter if the water is located above or below the surfactant.
- the water molecules above the O atoms of $C_{12}E_4$ have their OH pointing down, and the water molecules below the O atoms of $C_{12}E_4$ have their OH pointing up.



MD: H_W and O_W near the C



Conclusion

- The effect of $C_{12}E_4$ was found to be more anionic-like.
- The presence of $C_{12}E_4$ increases the thickness of water's surface layer and the average number of HB per water molecule.
- The O atoms in $C_{12}E_4$ have more influence on the orientation of water.

Water orientation at hydrophobic interfaces

Simona Strazdaite, Jan Verslui, Huib J. Bakker
J. Chem. Phys. 143, 084708 (2015)

Water/air, water/hexane, water/heptane, water/PDMS interfaces

HD-VSFG

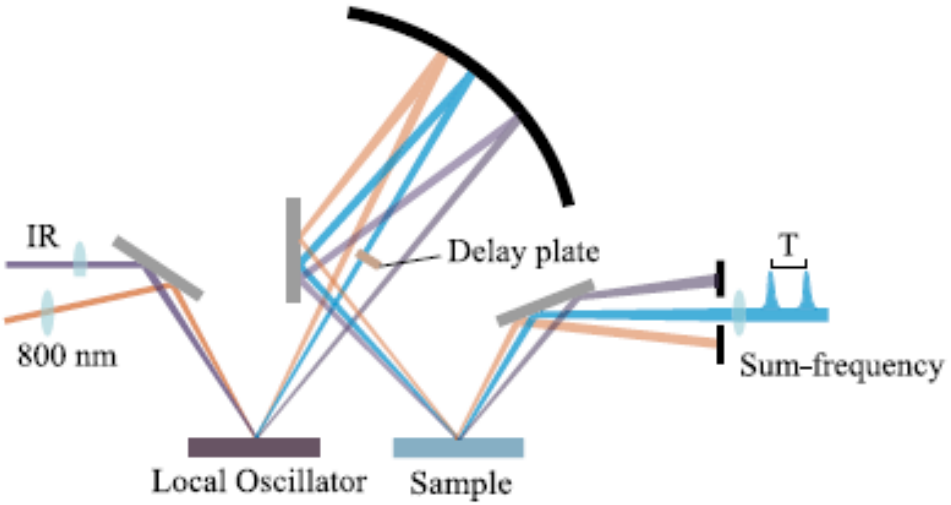
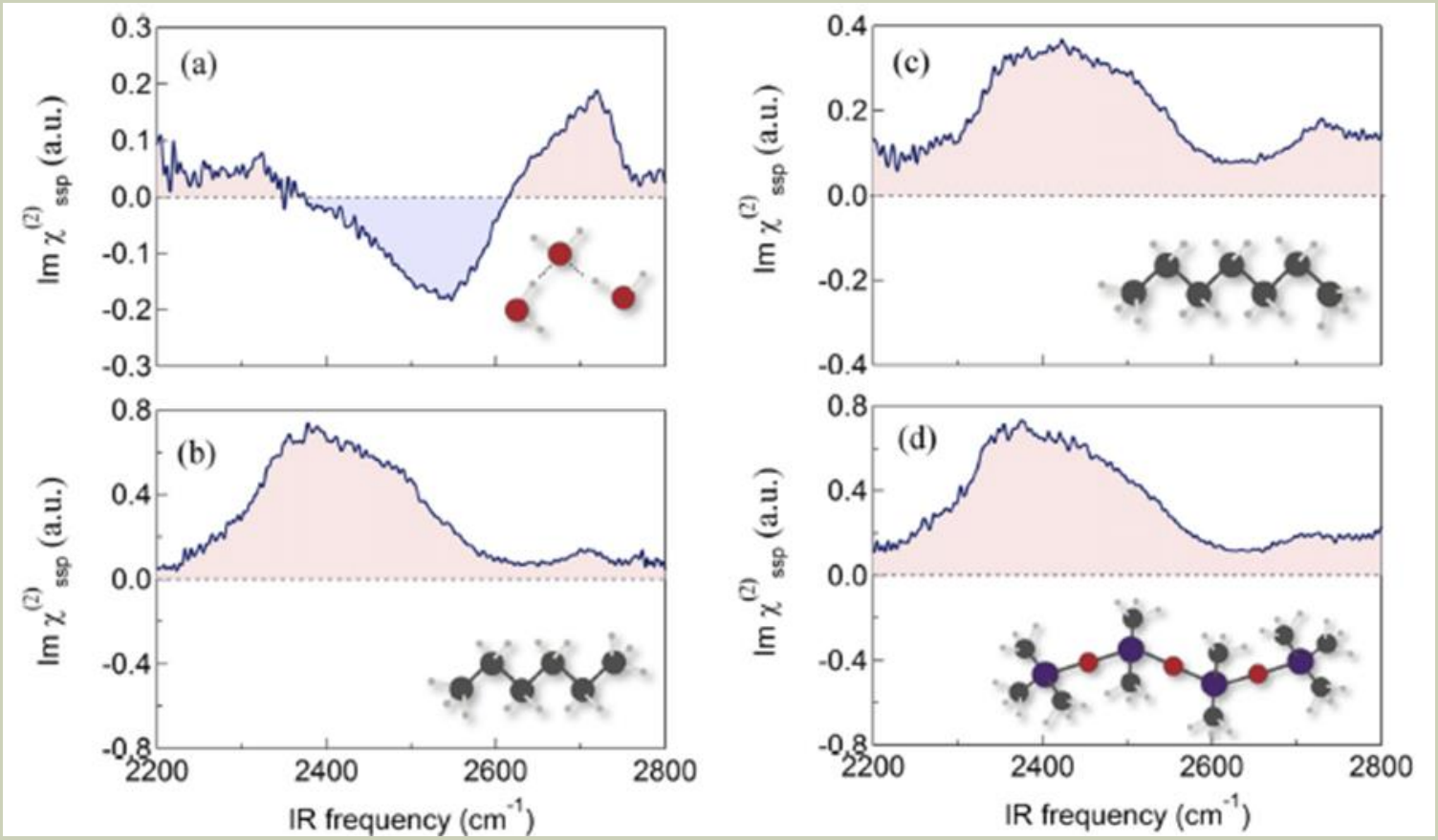


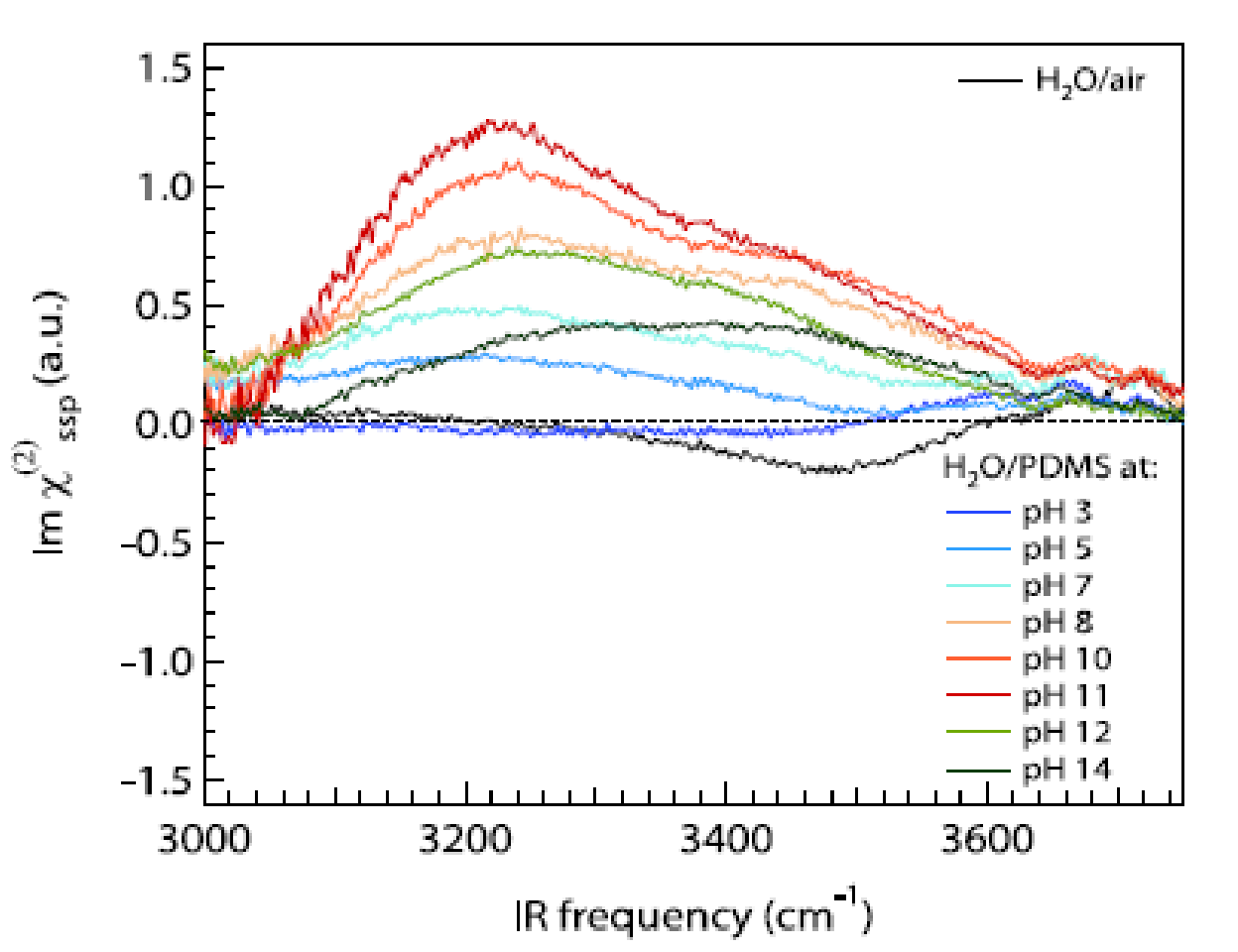
FIG. 1. Experimental layout of heterodyne-detected vibrational sum-frequency generation (HD-VSFG). A broadband femtosecond IR light pulse and a narrowband 800 nm pulse are focused onto a metal surface, generating an intense local oscillator SFG (LO-SFG) response that is delayed by a silica plate. The three beams are refocused onto the sample, producing a SFG signal that interferes with the LO-SFG signal on the CCD camera.

HD-VSFG $Im\chi^{(2)}$

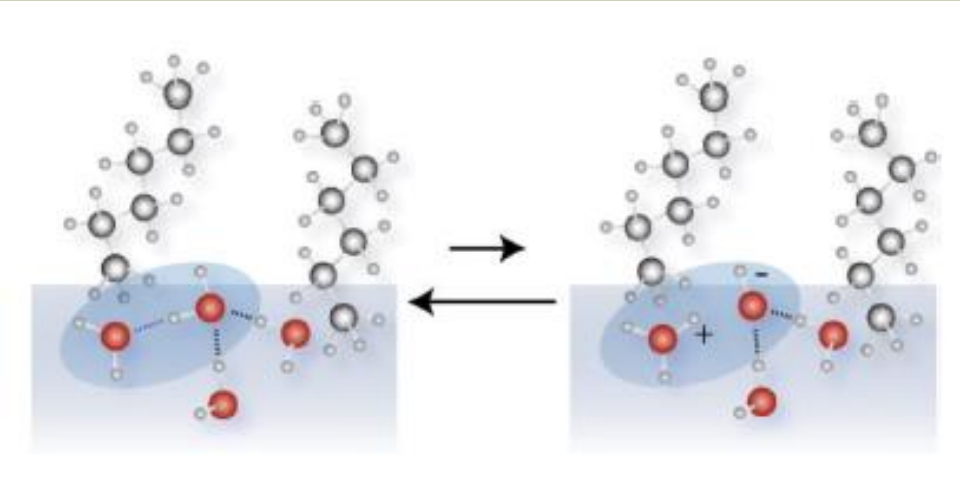


- The hydrogen-bonded O–D groups show a strong net orientation towards the hydrophobic phase

Im $\chi^{(2)}$ of H_2O/PDMS interface at different pH values



Introduction



- Enhanced $H_2O^+H\cdots OH^-$ valence-bond character

Conclusion

- The water HB structure is stronger than that at the water/air interface.
- The water molecules show a net orientation with their O–H groups pointing towards the hydrophobic phase.
- At the water/air interface, the orientation depends on the O–H stretch frequency and most hydrogen-bonded water molecules have their O–H groups pointing towards the water phase.