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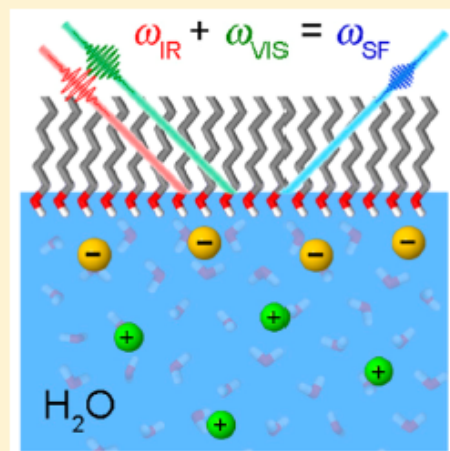
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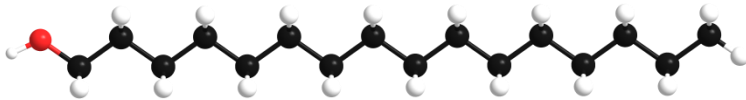
## Supporting Information

**ABSTRACT:** Phase-sensitive sum-frequency vibrational spectroscopy was used to probe interfaces of a long-chain alcohol monolayer with various electrolytic solutions, chosen as a prototype for *nonionic* organic/water interfaces. Spectra in the OH stretching range were observed to be under the influence of ions emerging at the interfaces. Analysis of the spectra with the help of Levin's theory allowed us to quantitatively find the surface densities of various ions and, hence, the ion affinities and surface pH/pOH at the alcohol/water interface. For the ions studied, the interface affinity has the ranking order of  $\text{OH}^- > \text{I}^- > \text{Cl}^- \sim \text{H}_3\text{O}^+ > \text{Na}^+$ , the same as that at the air/water interface except that  $\text{OH}^-$  and  $\text{H}_3\text{O}^+$  have their places interchanged. Significantly stronger affinity of  $\text{OH}^-$  than  $\text{H}_3\text{O}^+$  with the result of surface pH/pOH extrapolating to bulk pH 7 suggests that the alcohol/neutral water interface is weakly basic.

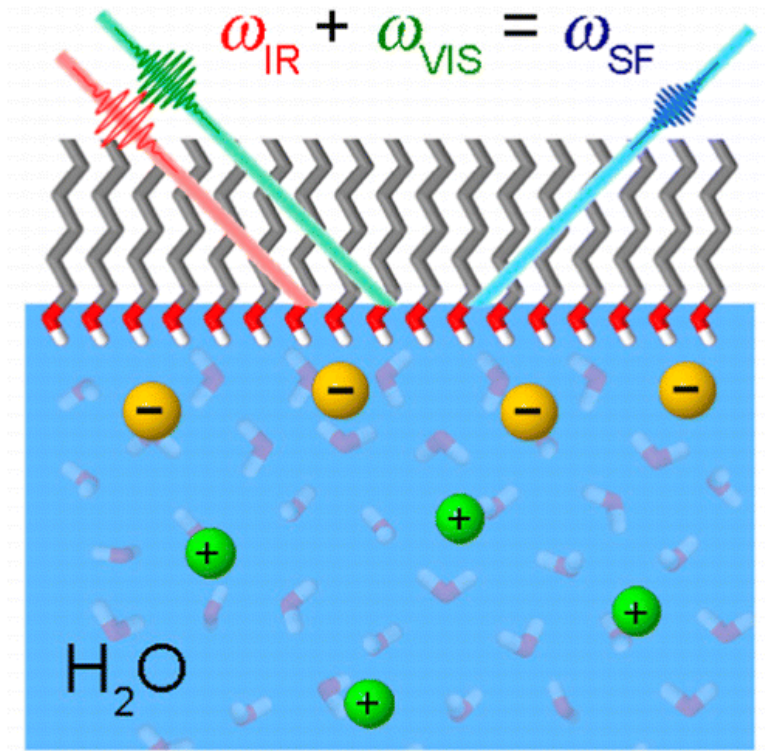


# Introduction

- Hexadecanol/water interface



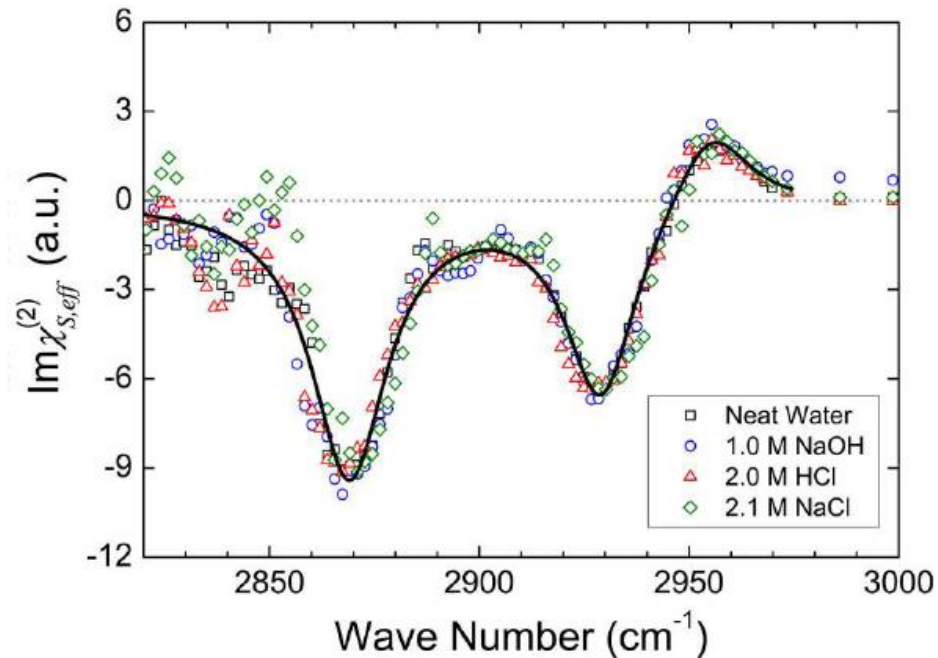
- PS-SFVS (SSP, 30fs, 1kHz Ti:Sapphire laser)
- Ranking order:  $\text{OH}^- \gg \text{I}^- > \text{Cl}^- \sim \text{H}_3\text{O}^+ > \text{Na}^+$



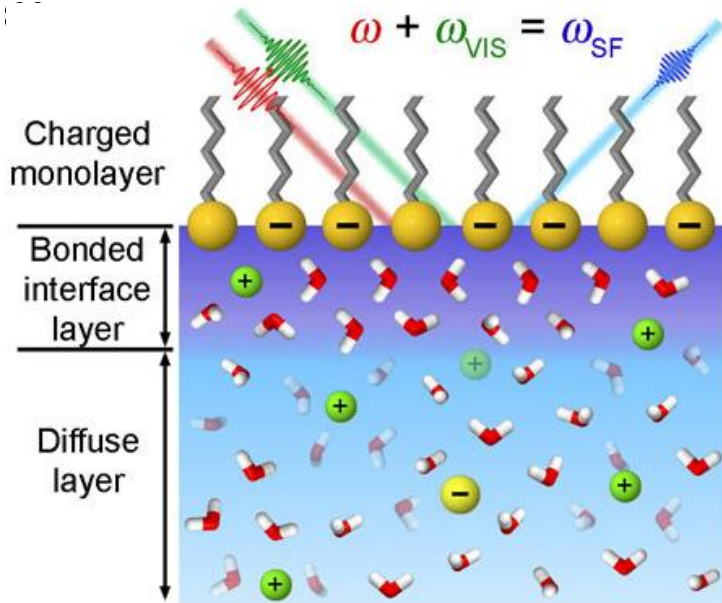
Fully packed monolayer of hexadecanol ( $\text{C}_{16}\text{H}_{33}\text{OH}$ , with a mean molecular area of  $\sim 20 \text{ \AA}^2$ )

# CH-stretch spectra

- The monolayer chain structure was unaffected by ions at the interface.



# Interfacial structure model: BIL and EDL



$$\vec{\chi}_{\text{S,eff}}^{(2)} = \vec{\chi}_{\text{S,eff},0}^{(2)} + \Delta\vec{\chi}_{\text{S,eff}}^{(2)}$$

$$\vec{\chi}_{\text{S,eff},0}^{(2)} = \vec{\chi}_{\text{BIL},0}^{(2)}$$

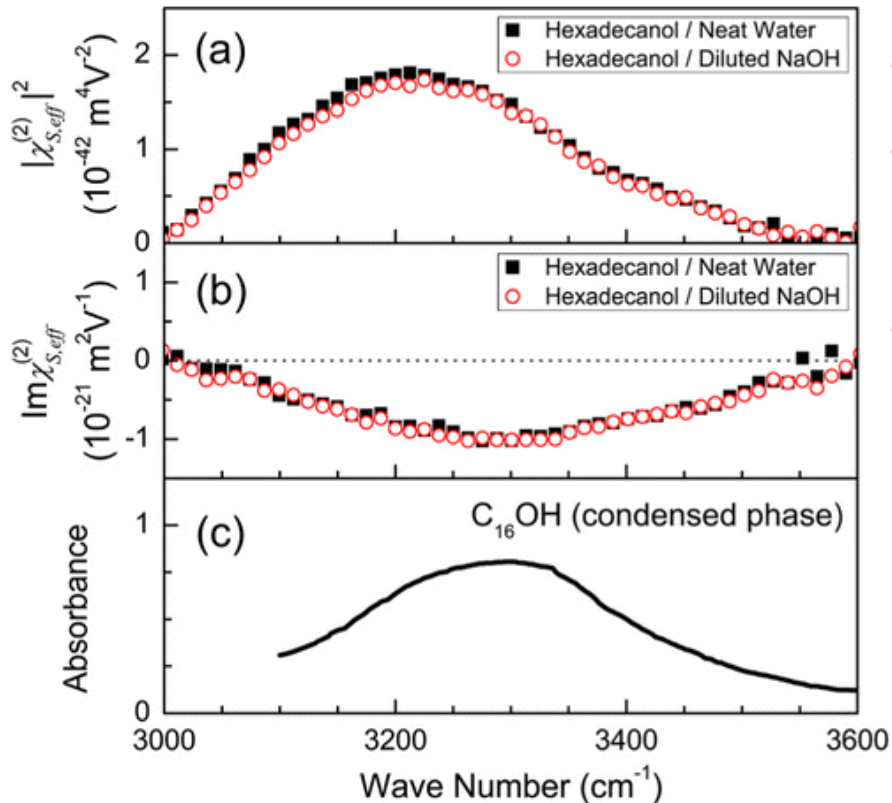
$$\Delta\vec{\chi}_{\text{S,eff}}^{(2)} = \Delta\vec{\chi}_{\text{BIL}}^{(2)} + \vec{\chi}_{\text{EDL}}^{(2)}$$

$$\vec{\chi}_{\text{EDL}}^{(2)} \equiv \int_0^\infty [\vec{\chi}_{\text{B}}^{(3)}(z') \cdot \hat{z} E_0(z')] e^{i\Delta k_z z'} dz' \cong \vec{\chi}_{\text{B}}^{(3)} \cdot \hat{z} \Psi$$

$$\text{with } \Psi \equiv \int_0^\infty E_0(z') e^{i\Delta k_z z'} dz',$$

- BIL: Water molecules strongly interacting with charged headgroups and counter cations.
- EDL: Water molecules reoriented by surface electric field.

# OH-stretch range



- $\text{pH}_1 = \text{pH } 5.8$ ;  $\text{pH}_2 = \text{pH } 7.5$
- $\sigma$  due to adsorption of  $\text{H}^+$  and  $\text{OH}^-$  should vary by at least a factor of  $10^{|\text{pH}_2 - \text{pH}_1|} = 10^{1.7}$
- $\sigma$  is negligibly small so that

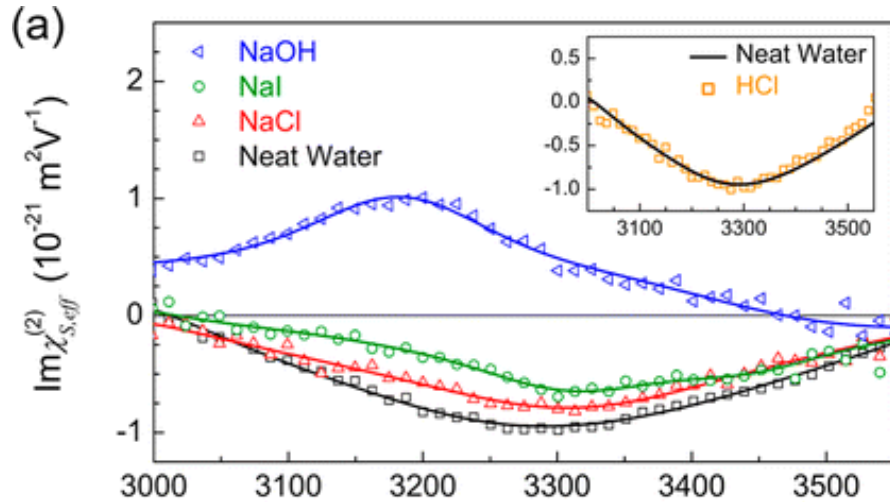
$$\chi_{S,eff}^{(2)}(\omega_{IR}) \cong \chi_{BIL,0}^{(2)}(\omega_{IR})$$

$$\text{Im} \chi_{S,eff}^{(2)} \cong \text{Im} \chi_{BIL,0}^{(2)}$$

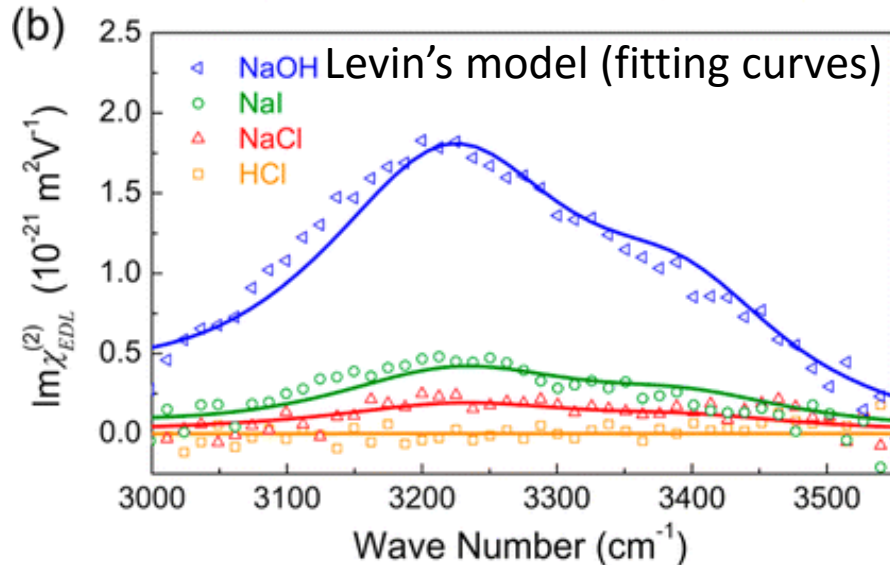
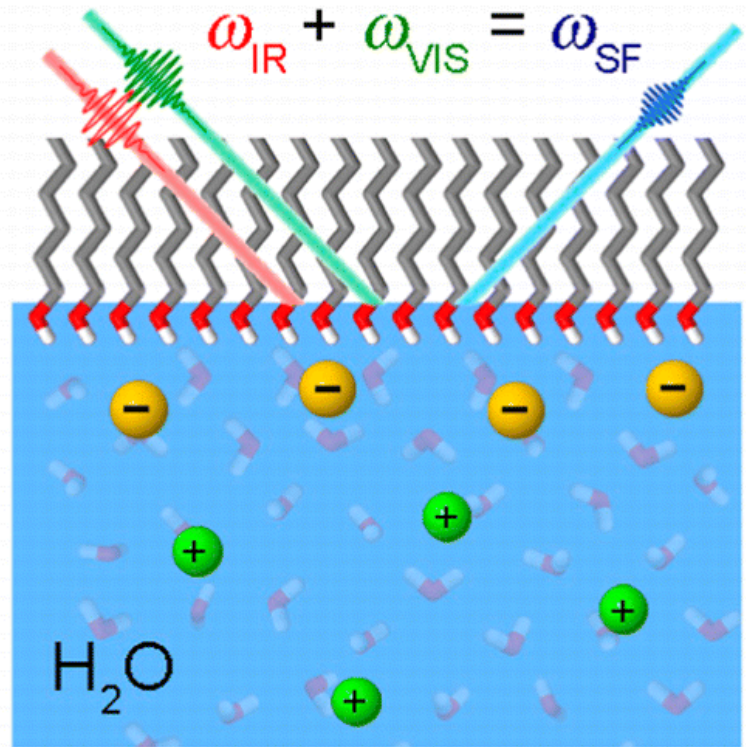


# OH-stretch range

0.1 M - NaCl, NaI, HCl; 0.03 M – NaOH

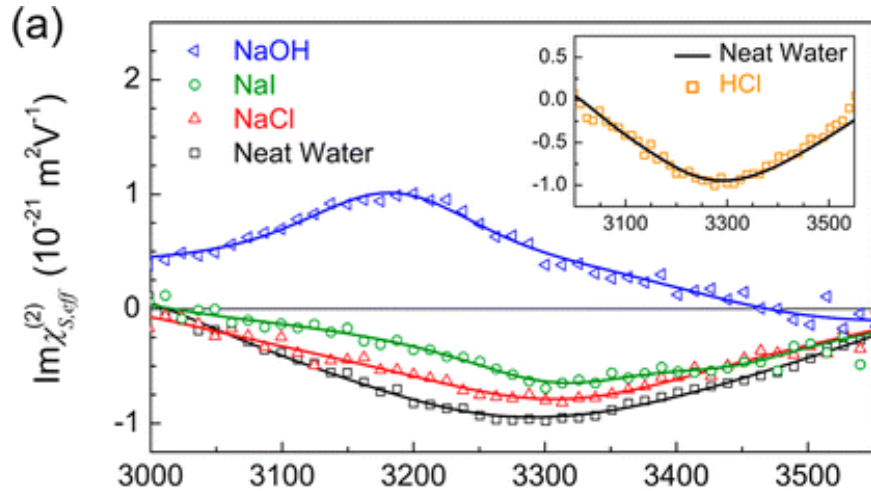


$$Im \chi_{EDL}^{(2)}(\omega_{IR}) \sim Im \chi_{S,eff}^{(2)}(\omega_{IR}) - Im \chi_{BIL,0}^{(2)}(\omega_{IR})$$



# OH-stretch range

0.1 M - NaCl, NaI, HCl; 0.03 M – NaOH

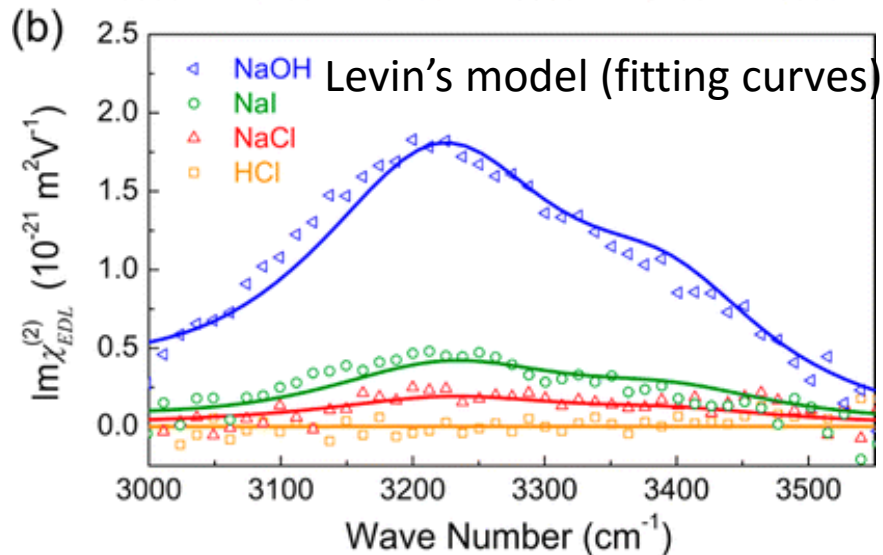


HCl in water = neat water

$$Im \chi_{EDL}^{(2)}(\omega_{IR}) \sim Im \chi_{S,eff}^{(2)}(\omega_{IR}) - Im \chi_{BIL,0}^{(2)}(\omega_{IR})$$

accordingly,  $Im \chi_{EDL}^{(2)}(\omega_{IR}) \approx 0$

indicating,  $\sigma \approx 0$ , so  $H^+$  (or  $H_3O^+$ ) and  $Cl^-$  must be in equal probability.



So, the affinity of ions at the alcohol/water interface appears to follow the ranking order of  
 $OH^- > I^- > Cl^- \approx H^+ > Na^+$ .



# Levin's theory

$$\nabla^2 \phi(z) = -\frac{q}{\varepsilon_W} [\rho_+(z) - \rho_-(z)],$$

$$\rho_+(z) = c_1 \cdot e^{[-\beta q \phi(z) - \beta U_+(z)]},$$

$$\rho_-(z) = c_2 \cdot e^{[\beta q \phi(z) - \beta U_-(z)]},$$

where  $\phi$  is the electrostatic potential,  $\rho_+$  ( $\rho_-$ ) is the concentration profile of cation (anion),  $\varepsilon_W$  is the dielectric constant of water,  $q$  denotes the elementary charge,  $\beta = 1/k_B T$ , and  $c_1$  and  $c_2$  are normalization constants determined by the boundary conditions  $\rho_{\pm}(z \rightarrow \infty) = \rho_B$  and

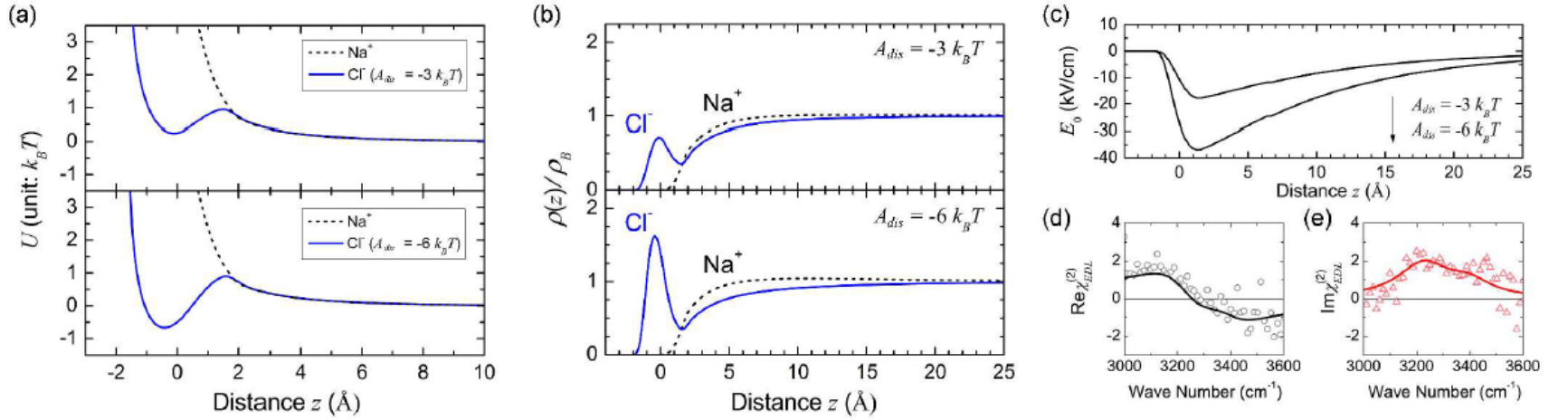
$$\phi(z \rightarrow \infty) = \frac{d\phi}{dz}(z \rightarrow \infty) = 0.$$

# Levin's theory

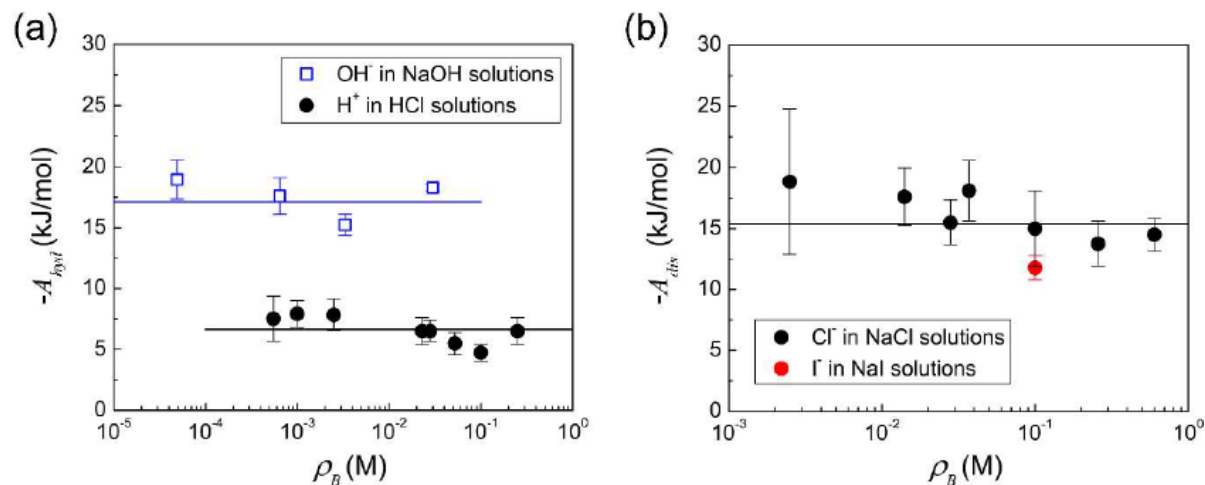
$$U = U_{pol} + U_{im} + U_{cav} + U_{int}$$

$U(z)$  consists of four parts:

- (1) the electrostatic self-energy,  $U_{pol}(z)$ , arising from redistribution of charges on the surface of a polarizable ion as the ion emerges toward the interface;
- (2) the cavitation energy,  $U_{cav}(z)$ , resulting from the energy cost required to disrupt the water H-bonding network in order to dissolve the ion;
- (3) the image potential,  $U_{im}(z)$ , near the interface;
- (4) interaction potential,  $U_{int}(z)$ , of the ion with the surface (alcohol headgroups in our case).



**Figure S2.** (a)  $U(z)$  for  $\text{Na}^+$  and  $\text{Cl}^-$  near the interface of an alcohol monolayer with a 0.1 M NaCl solution. Top and bottom panels are results with  $A_{dis}(\text{Cl}^-)$  of  $-3k_B T$  and  $-6k_B T$ , respectively. (b) Normalized ion distributions,  $\rho(z)/\rho_B$ , for  $\text{Na}^+$  and  $\text{Cl}^-$ . (c) Surface electric field  $E_0$ , calculated from Eq.(S1) and  $U(z)$  given in (a). (d) and (e) Fitting of theoretical spectra (lines) to the measured spectra (dots) of  $\text{Re}\chi_{EDL}^{(2)}(\omega_{IR})$  and  $\text{Im}\chi_{EDL}^{(2)}(\omega_{IR})$  for the interface of a hexadecanol monolayer with a 0.1 M NaCl solution.  $\chi_{EDL}^{(2)}(\omega_{IR})$  is plotted in unit of  $10^{-22} \text{ m}^2 \text{ V}^{-1}$ .



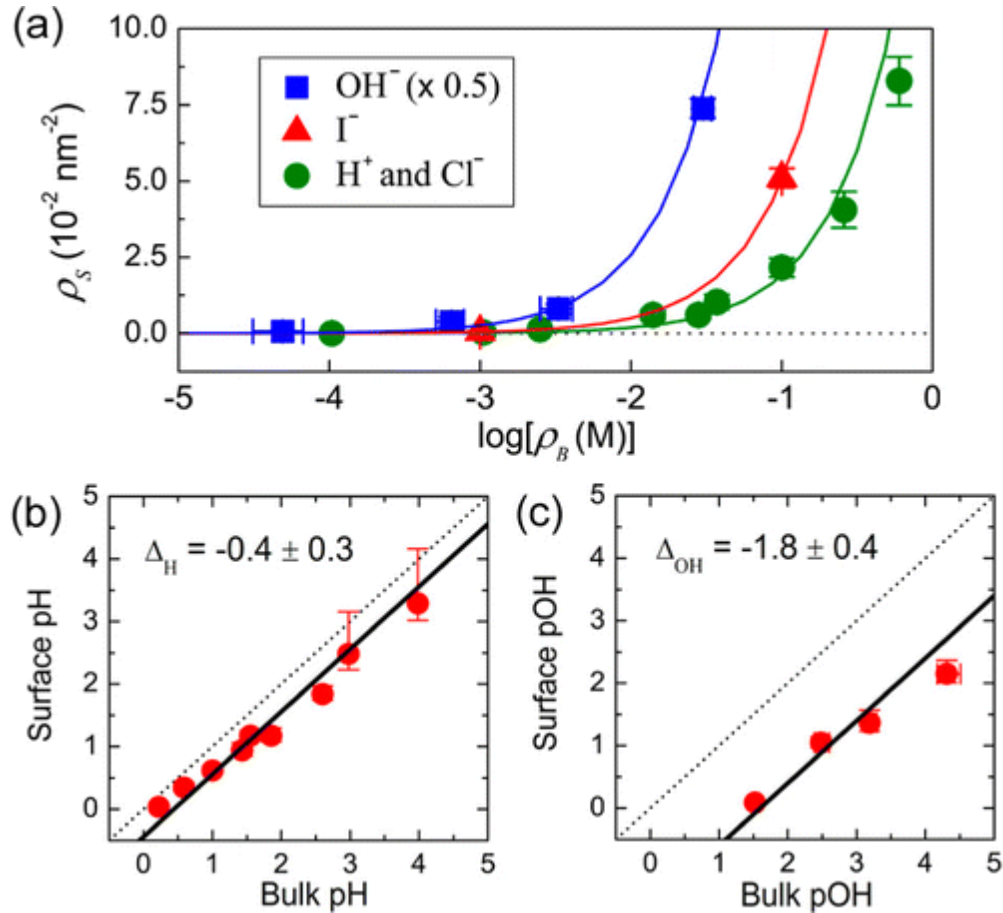
**Figure S4.** (a) Negative  $A_{hyd}$  for  $\text{H}^+$  and  $\text{OH}^-$  and (b) negative  $A_{dis}$  for  $\text{Cl}^-$  and  $\text{I}^-$ , deduced from the spectral analysis discussed in Sec. S3 for the alcohol monolayer/solution interfaces with various HCl, NaOH, NaCl, and NaI concentrations in water (dots). Lines denote the average values of  $A_{hyd}$  or  $A_{dis}$ .

Fitting the SF spectra with Levin's theory yields the ion density distribution  $\rho_{\pm}(z)$ . We could then estimate the surface ion density,  $\rho_S$ , by defining it, somewhat arbitrarily, as the number of ions per unit area in a thin layer at the interface of thickness of the hydrogen bonding length for  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  or the ion size for  $\text{Cl}^-$ ,  $\text{I}^-$  and  $\text{Na}^+$ , with the expression:

$$\rho_S = \begin{cases} \int_0^{L_h} \rho(z) dz & \text{for } \text{H}_3\text{O}^+ \text{ and } \text{OH}^- \\ \int_{-R}^R \rho(z) dz & \text{for } \text{Cl}^-, \text{I}^-, \text{ and } \text{Na}^+ \end{cases}.$$

# The results of deduced $\rho_s$ versus $\rho_B$

The result of  $\text{pOH}_S < \text{pH}_S$  suggests that the interface is basic at bulk pH 7.



$$\text{pH}_S = \text{pH}_B + \Delta_H$$

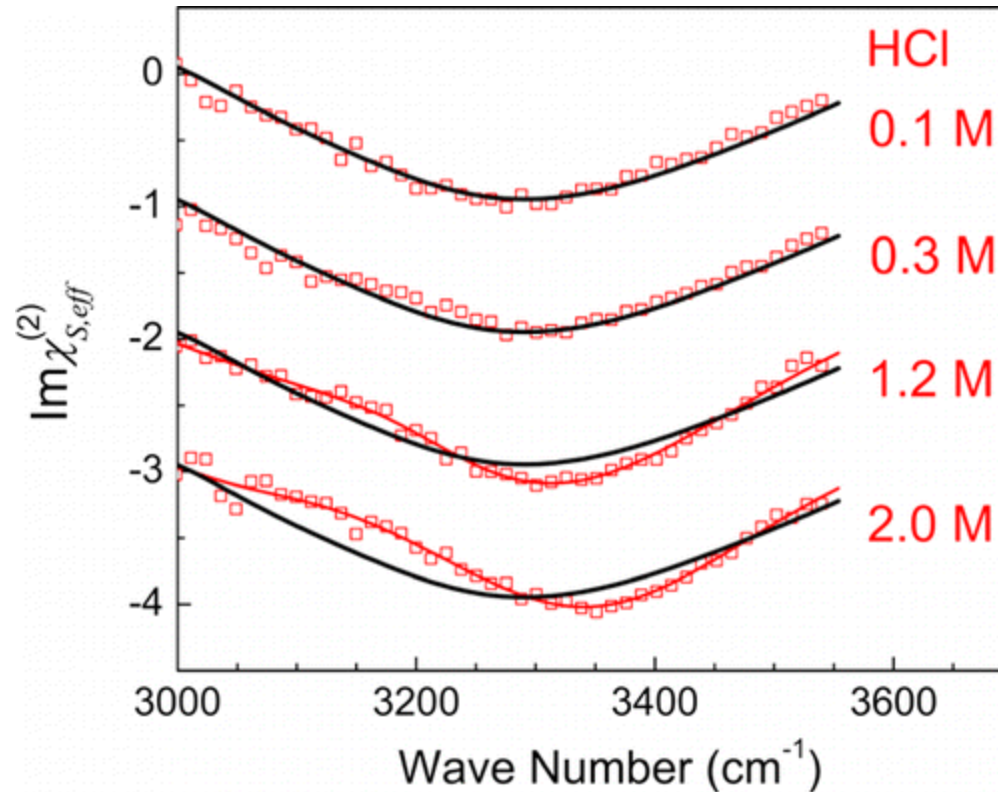
$$\text{pOH}_S = \text{pOH}_B + \Delta_{\text{OH}}$$



# Conclusion

- PS-SFVS study on ion affinity at the long-chain alcohol monolayer/water interface, chosen as a prototype for nonionic organic/water interfaces.
- The experimentally deduced vibrational spectra of the EDL, with the help of Levin's theory, allowed us to find the surface ion densities and surface pH/pOH at the alcohol interfaces with various electrolyte solutions.
- We found that  $\text{OH}^-$ ,  $\text{H}_3\text{O}^+$ , and halide ions could accumulate at the alcohol/water interface with the ranking order of:  $\text{OH}^- > \text{I}^- > \text{Cl}^- \sim \text{H}_3\text{O}^+ > \text{Na}^+$ .
- Adsorption of  $\text{OH}^-$  at the interface was most notable, and suggests that the interface with neat water is basic.

$Im \chi_{S,eff}^{(2)}$  of the hexadecanol/water (diff. HCl conc.)



- H<sup>+</sup> and Cl<sup>-</sup> may adsorb differently at the interface when  $\rho_B$  is high.