

Interfacial Structures of Acidic and Basic Aqueous Solutions

Chuanshan Tian, Na Ji, Glenn A. Waychunas, and Y. Ron Shen

*Department of Physics, UniVersity of California, Berkeley, California 94720, and
Earth Sciences DiVision, Lawrence Berkeley National Laboratory, Berkeley,
California 94720*

J. AM. CHEM. SOC. XXXX, xxx, 000

Introduction

Using Sum-frequency vibrational spectroscopy (SFVS)

- studied vibrational spectra of water/vapor interfaces of acid, basic, and salt solutions

The SFVS spectrum in the OH stretch region:

- 3700 cm^{-1} : sharp Peak
- $\sim 3200\text{ cm}^{-1}$: ice-like broad band
- $\sim 3450\text{ cm}^{-1}$: liquid-like broad band

Using **phase-sensitive (PS) SFVS** technique (a recent technique)

- measured spectra of both the amplitude and the phase of $\chi_s^{(2)}(\omega_{\text{IR}})$
- obtained the spectra of **Re** $\chi_s^{(2)}(\omega_{\text{IR}})$ and **Im** $\chi_s^{(2)}(\omega_{\text{IR}})$.

We focus on the $\chi_s^{(2)}(\omega_{\text{IR}})$ spectra of HCl, NaOH, and HI solutions in which protons, hydroxyls, and iodine ions like to come to the interface.

Sum-frequency generation- second-order nonlinear optical process

The SF output : $I(\omega_{\text{SF}}) \propto |\chi_{\text{eff}}^{(2)}|^2$

$$\chi_{\text{eff}}^{(2)} = \underbrace{\left[\vec{L}(\omega_{\text{SF}}) \cdot \hat{e}(\omega_{\text{SF}}) \right]}_{\text{transmission Fresnel factor}} \cdot \vec{\chi}_S^{(2)} : \underbrace{\left[\hat{e}(\omega_{\text{vis}}) \cdot \vec{L}(\omega_{\text{vis}}) \right] \left[\hat{e}(\omega_{\text{IR}}) \cdot \vec{L}(\omega_{\text{IR}}) \right]}_{\text{Polarization unit vector}}$$

transmission Fresnel factor

Polarization unit vector

Symmetry-allowed surface vibrations appear as resonances in $\chi_s^{(2)}$

$$\chi_S^{(2)}(\omega_2) = \chi_{\text{NR}}^{(2)} + \sum_q \frac{A_q}{\omega_2 - \omega_q + i\Gamma_q} \quad : \text{formed a band with continuously varying frequencies}$$

$\chi_{\text{NR}}^{(2)}$: nonresonant contribution

A_q : strength

ω_q : resonant frequency

Γ_q : damping coefficient
(q th vibrational mode)

consider discrete



$$\chi_S^{(2)}(\omega_2) = \chi_{\text{NR}}^{(2)} + \int d\omega_q \frac{A_q}{\omega_2 - \omega_q + i\Gamma_q} \rho(\omega_q) \quad \rho(\omega_q) : \text{density of modes at } \omega_q$$

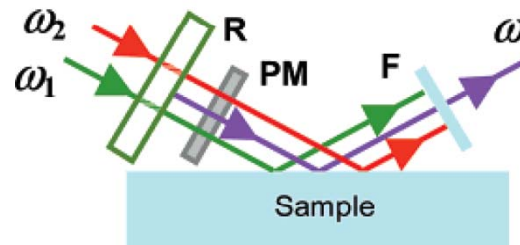
complex conjugation



$$\text{Im } \chi_s^{(2)}(\omega_2) = - \int d\omega_q \frac{A_q \Gamma_q}{(\omega_2 - \omega_q)^2 + \Gamma_q^2} \rho(\omega_q)$$

To find $\text{Im } \chi_s^{(2)}(\omega_2)$

Need to the phase of $\chi_s^{(2)}(\omega_2) \rightarrow$ interference method provide phase



(phase-sensitive sum-frequency vibrational spectrometer)

SF signal reflected from the sample :

$$S_S(\omega_2) = A\{[|\chi_S^{(2)}(\omega_2)|e^{i\phi(\omega_2)} + a|\chi_R^{(2)}|e^{i\theta(\omega_2)}]^2 + b^2|\chi_R^{(2)}|^2\} \quad (4)$$

$A(a^2 + b^2)|\chi_R^{(2)}|^2$: total reference SF signal

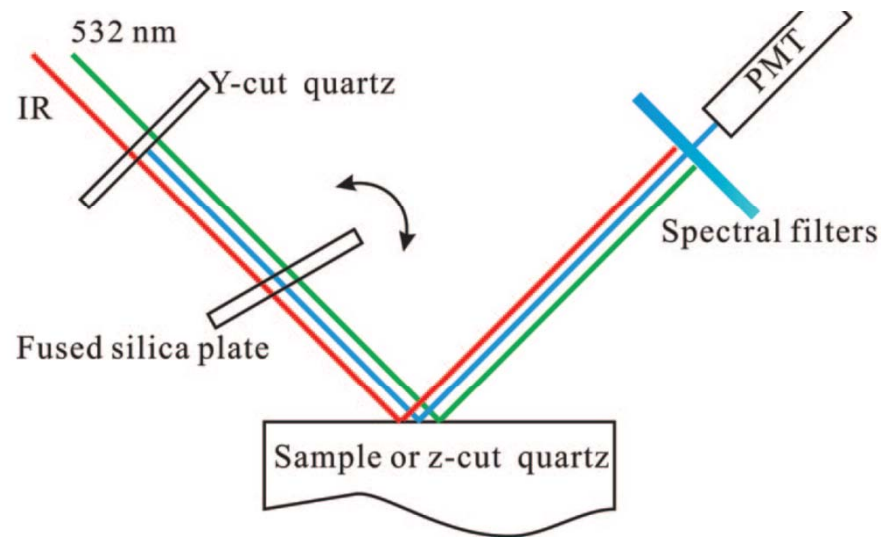
we make two scans:

- $S_{S1}(\omega_2)$ with the phase of the reference SF field at $\theta(\omega_2) \rightarrow \text{Re}\chi_s^{(2)}$
- $S_{S2}(\omega_2)$ with the phase of the reference SF field at $\theta(\omega_2) + \pi/2 \rightarrow \text{Im}\chi_s^{(2)}$

Using eq 4, we find

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

PS-SFVS Setup



The nonvanishing elements of $\vec{\chi}_S^{(2)}$ or water/vapor interfaces :

$$\chi_{S,YYZ}^{(2)} = \chi_{S,XXZ}^{(2)}, \chi_{S,YZY}^{(2)} = \chi_{S,XZX}^{(2)}, \chi_{S,ZYY}^{(2)} = \chi_{S,ZXX}^{(2)} \text{ and } \chi_{S,ZZZ}^{(2)}$$

(Z : the surface normal)

Focus on: $\chi_{s,YYZ}^{(2)}$ the SSP polarization combination

(SF output visible input IR input)

Result

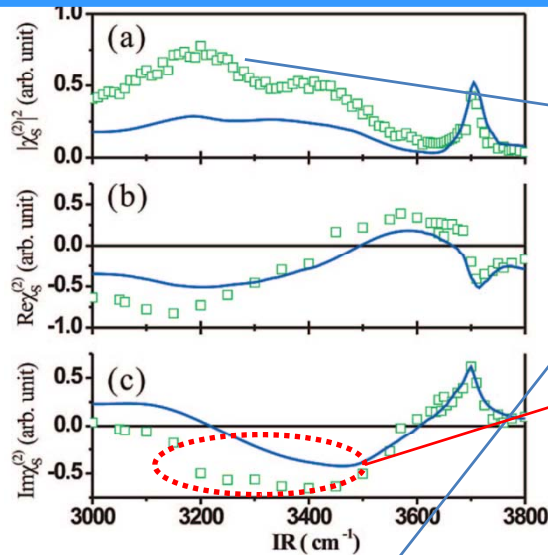


Figure 2. Spectra of (a) $|\chi_s^{(2)}|^2$, (b) $\text{Re} \chi_s^{(2)}$, and (c) $\text{Im} \chi_s^{(2)}$ for the water/vapor interfaces of 1.2 M HCl solution (symbols) and neat water (lines).

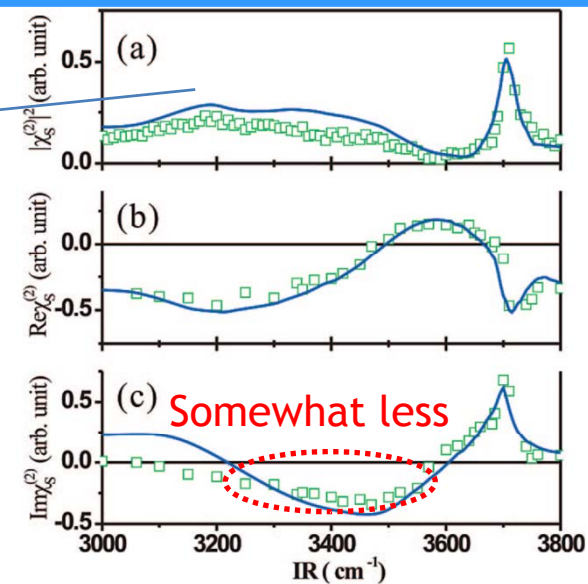


Figure 4. Spectra of (a) $|\chi_s^{(2)}|^2$, (b) $\text{Re} \chi_s^{(2)}$, and (c) $\text{Im} \chi_s^{(2)}$ for the water/vapor interfaces of 1.2 M NaOH solution (symbols) and neat water (lines).

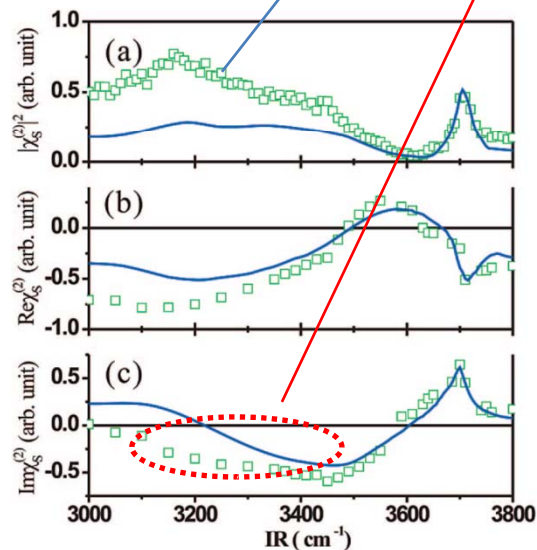


Figure 3. Spectra of (a) $|\chi_s^{(2)}|^2$, (b) $\text{Re} \chi_s^{(2)}$, and (c) $\text{Im} \chi_s^{(2)}$ for the water/vapor interfaces of 1.2 M HI solution (symbols) and neat water (lines).

enhanced

stronger negative strength
→ A flip of sign

Somewhat less

- spectra exhibit little changes above 3500 cm⁻¹ in $\text{Im} \chi_s^{(2)}$ spectra

Discussion

The $\text{Im } \chi_s^{(2)}$ spectrum allows us to construct a qualitative picture of the interfacial structure: The water surface appears as a highly distorted ice surface.

The **topmost layer** is covered with DAA and DDA molecules. (Here, D and A denote donor and acceptor H-bonds, respectively, with which water molecules connect to the neighbors.)

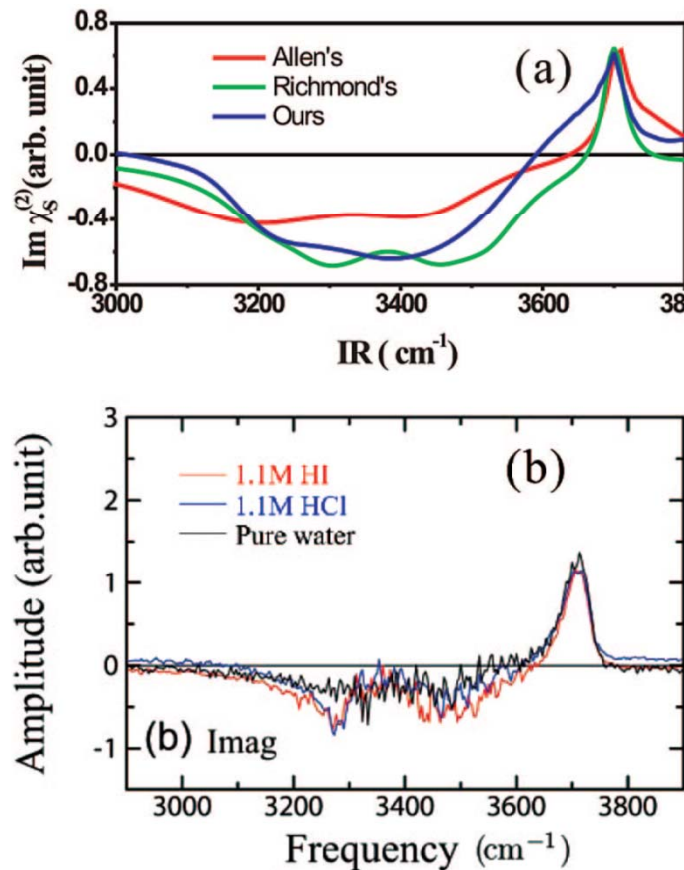
The **subsequent layer** has DDAA molecules symmetrically or asymmetrically donor-bonded or singly donor-bonded to molecules in the topmost layer.

In the $\text{Im } \chi_s^{(2)}$ spectrum,

- sharp peak at 3700 cm^{-1} : the OH stretch of the dangling OH at the surface
- $3450\text{-}3700 \text{ cm}^{-1}$ region : donor-bonded OH stretches of DDA and DAA molecules
- $3200\text{-}3450 \text{ cm}^{-1}$ region : asymmetrically donor-bonded DDAA molecules
- $3000\text{-}3200 \text{ cm}^{-1}$ regions : symmetrically donor-bonded DDAA molecules

compare the spectra of water/vapor interfaces of aqueous solutions with those of neat water.

In HCl solution



protons are likely to be concentrated at the interface as suggested by molecular dynamics simulations.

protons can be readily incorporated into the interfacial H-bonding network as hydrated ions in the form of H_3O^+ (Eigen form, hydronium) and/or H_5O_2^+ (Zundel form, $\text{H}_2\text{O}-\text{H}-\text{OH}_2^+$).

These hydrated ions can influence the interfacial spectra directly through their own OH stretches and less directly through reorientation of interfacial water molecules by the surface field they create.

Figure 5. (a) Comparison of $\text{Im } \chi_s^{(2)}$ spectra of the water/vapor interface of 1.2 M HCl solution obtained (or deduced from spectral information given) by different groups. (b) $\text{Im } \chi_s^{(2)}$ spectra obtained by MD simulation of Ishiyama and Morita presented in ref 12.

- enhancement of both ice-like and liquid-like bands in the $|\chi_s^{(2)}|^2$ spectrum due to solvation of HCl in water
- H^+ ions had emerged at the interface to modify the water interfacial structure.

Enhancement cause

- Shultz and co-workers : reorientation of interfacial water molecules by the H^+Cl^- created surface field.
- Richmond and co-workers :
effects of the strong surface field and strong electrostatic interactions between hydrated protons (H_3O^+ and $H_5O_2^+$) and water molecules at the interface (3200 and 3330 cm^{-1} modes)
- Allen and co-workers :surface field effect as well as contributions from OH stretch vibrations of H_3O^+ and $H_5O_2^+$ at the interface.

the spectrum above 3500 cm^{-1} comes mainly from DAA and DDA water molecules in the topmost layer at the surface, its **insignificant change** indicates that the surface concentration of H^+ or hydrated H^+ is not high enough to physically perturb the structure of the topmost layer

The surface field created by interfacial H^+ ions cannot affect DAA and DDA molecules in the topmost layer, but can reorient the **more loosely H-bonded** DDAA molecules in the adjacent layer with $\text{O} \rightarrow \text{H}$ toward the bulk liquid, thus enhancing the negative liquid-like band between 3200 and 3500 cm^{-1} .

It is less likely to be able to reorient DDAA molecules contributing to the ice-like band because of their **stronger H-bonding** to neighbors.

The observed flip of the ice-like band below 3200 cm^{-1} from positive to negative could be due to contribution of OH stretches of hydronium (H_3O^+) ions appearing at the interface. They have preferred orientation with $\text{O} \rightarrow \text{H}$ pointing into the liquid.

The spectral change we observe in the ice-like band region suggests that the surface hydronium ions do exist and should have their OH stretch frequencies in the range of $3000\text{-}3250\text{ cm}^{-1}$. It is possible that hydronium ions at the interface with no acceptor bond and **weaker donor bonds** to neighbors would have higher OH stretch frequencies than in the bulk.

removed the contribution from the surface field effect

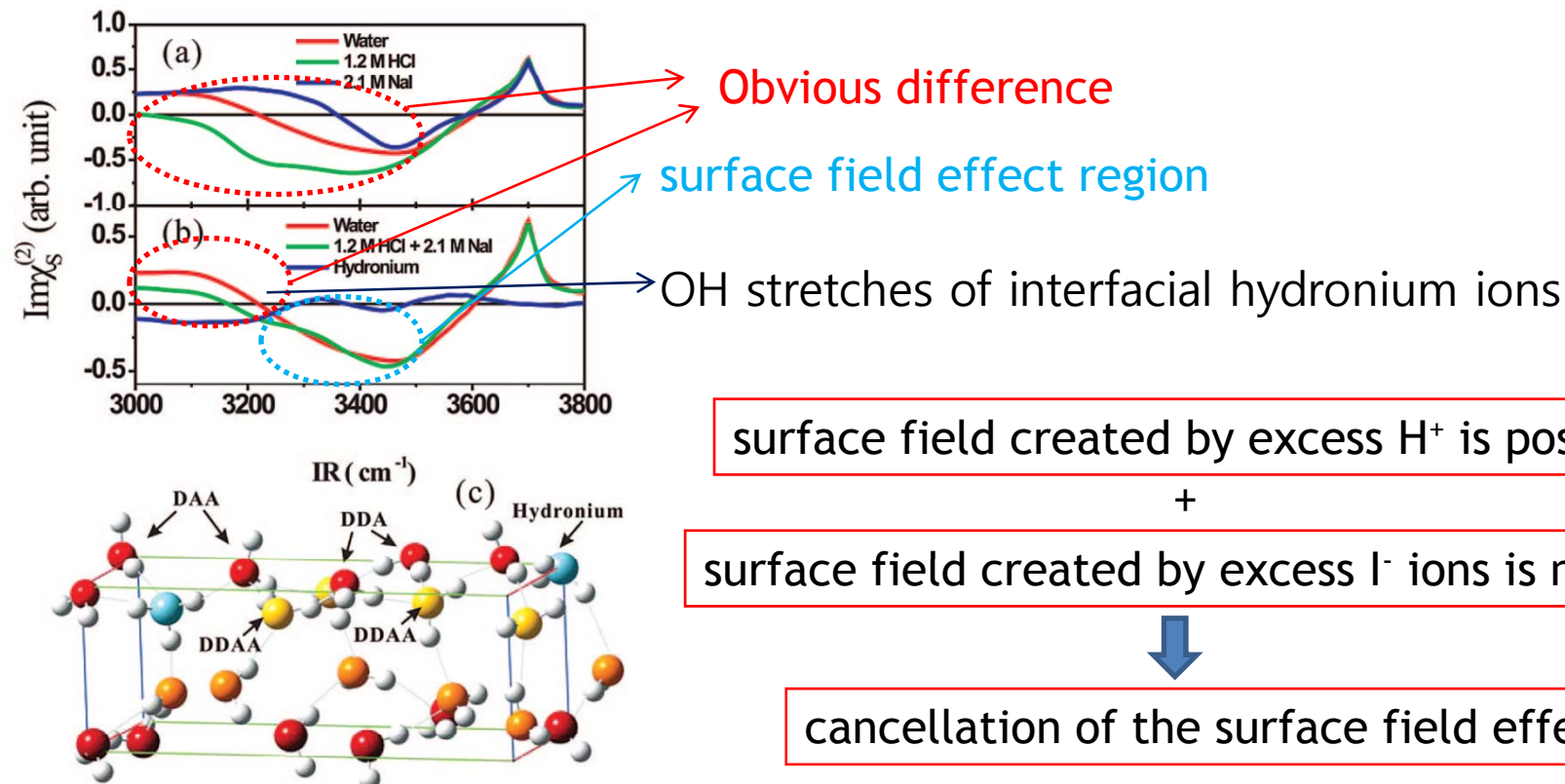


Figure 6. (a) $\text{Im} \chi_S^{(2)}$ spectra of water/vapor interfaces of neat water (red line), 1.2 M HCl solution (green line), and 2.1 M NaI solution (blue line). (b) $\text{Im} \chi_S^{(2)}$ spectrum of water/vapor interfaces of neat water (red line), average of $\text{Im} \chi_S^{(2)}$ spectra for 1.2 M HCl and 2.1 M NaI solutions (green line), and the difference spectrum deduced from the above two (blue line). (c) Cartoon depicting the water/vapor interfacial structure of the HCl solution with hydronium ions (oxygen painted blue) close to the surface. Water molecules in different interfacial layers have their oxygen coded with different colors: DAA and DDA molecules in the topmost layer colored with red, DDAA molecules in the second layer colored with gold, and DDAA molecules in the third and fourth layers colored with orange and red, respectively.

consider the water/vapor interface of the HI acid solution.

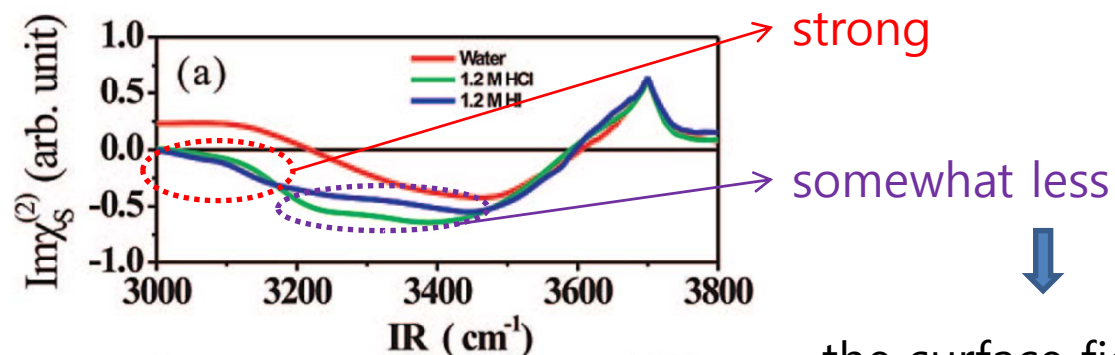
For an HI solution,

More H^+ than I^- must appear at the water/vapor interface.

The surface ions form a double-charge layer with a positive surface field that could reorient DDAA molecules with $\text{O} \rightarrow \text{H}$ pointing toward the liquid bulk and enhance the negative liquid-like band in the $\text{Im } \chi_s^{(2)}$ spectrum.

In HI solution

Compared spectrum of the 1.2 M HCl with spectrum of the 1.2 M HI



the surface field effect is weaker.

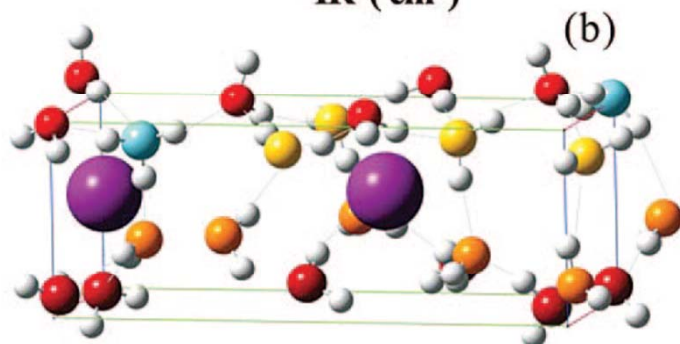
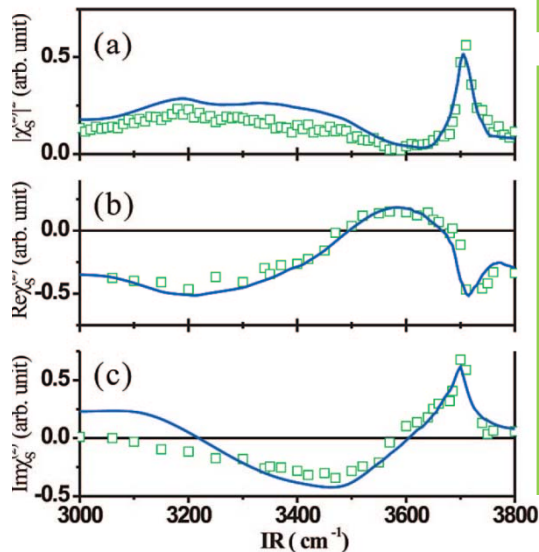


Figure 7. (a) Comparison of $\text{Im}\chi_s^{(2)}$ spectra of water/vapor interfaces of neat water (red line), 1.2 M HCl (green line), and HI (blue line) solutions. (b) Cartoon depicting the water/vapor interfacial structure of the HI solution. The color codes for interfacial water molecules in different layers are the same as those given in Figure 6. Oxygens of hydronium ions close to the surface are painted blue, and iodine ions are painted purple.

In NaOH solution

- This is a case more difficult to understand.
- Even in the bulk, how OH^- is incorporated in an hydrogen-bonding structure of water is not very clear.
- the disappearance of the ice-like band below 3200 cm^{-1} .
- the weak reduction of the negative liquid-like band.
- This rather small change indicates that the field resulting from surface excess of OH^- is much less than in NaI, HCl, and HI solutions cases

pure conjectures



- OH^- ions may have come to the interface to replace such DDAA molecules and thus reduce the ice-like band.
- Incorporation of OH^- ions in the interfacial hydrogen-bonding structure may affect the OH stretches of water molecules bonded to them and contribute to the change of the ice-like band.

Conclusion

Using **phase-sensitive (PS) SFVS** technique (a recent technique)

- measured spectra of $|\chi_s^{(2)}(\omega_{IR})|^2$ in the OH stretch region
- obtained the spectra of **Re** $\chi_s^{(2)}(\omega_{IR})$ and **Im** $\chi_s^{(2)}(\omega_{IR})$.
- studied water/vapor interfaces of 1.2 M HCl, HI, and NaOH solutions

In HCl solution,

- Protons like to appear in the form of hydronium ions at the interface.
- positive surface field changes the liquid-like band of the spectrum.
- The hydronium ions contribute to the negative ice-like band in the spectrum.

In the case of HI solution,

- both H^+ and I^- prefer to appear at the interface.
- double-charge layer form.
- positive surface field changes the liquid-like band in the spectrum.
- The hydronium ions change the ice-like band the spectrum.

For the NaOH solution,

- Im $\chi_s^{(2)}$ spectrum indicates appearance of OH^- at the interface.
- the spectrum is difficult to visualize.