

## **Interfacial structures of acidic and basic aqueous solutions**

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### **Abstract**

Phase-sensitive sum-frequency vibrational spectroscopy was used to study water/vapor interfaces of HCl, HI, and NaOH solutions. The measured imaginary part of the surface spectral responses provided direct characterization of OH stretch vibrations and information about net polar orientations of water species contributing to different regions of the spectrum. We found clear evidence that hydronium ions prefer to emerge at interfaces. Their OH stretches contribute to the “ice-like” band in the spectrum. Their charges create a positive surface field that tends to reorient water molecules more loosely bonded to the topmost water layer with oxygen toward the interface, and thus enhances significantly the “liquid-like” band in the spectrum. Iodine ions in solution also like to appear at the interface and alter the positive surface field by forming a

narrow double-charge layer with hydronium ions. In NaOH solution, the observed weak change of the “liquid-like” band and disappearance of the “ice-like” band in the spectrum indicates that OH<sup>-</sup> ions must also have excess at the interface. How they are incorporated in the interfacial water structure is however not clear.

## **Introduction**

Water/vapor interfaces of acidic and basic aqueous solutions play a key role in environmental chemistry and atmospheric science.<sup>1,2</sup> They have been the topics of extensive theoretical and experimental studies in recent years,<sup>3-8</sup> but good understanding of the water interfacial structure at the molecular level is still lacking. The most concerned question is whether H<sup>+</sup> and OH<sup>-</sup> ions would emerge at the interface and affect the interfacial hydrogen-bonding network of water. Molecular dynamics (MD) simulations predicted that protons (H<sup>+</sup>) could appear at the interface in the form of hydronium(H<sub>3</sub>O<sup>+</sup>), but OH<sup>-</sup> should be repelled from the water surface.<sup>3,9-12</sup> The details, such as the depth profile of ion concentrations, depend very much on the molecular model and interaction potentials assumed.<sup>9-12</sup> Experiments carried out with scanning tunneling microscopy (STM)<sup>13</sup>, X-ray spectroscopy<sup>14,15</sup>, and attenuated total reflection (ATR)<sup>8</sup>

have been used to verify the theoretical prediction. They however suffer from either the water surface being too dynamic or the techniques not being sufficiently surface-specific.

Sum-frequency vibrational spectroscopy (SFVS) has been proven to be a highly surface-specific and versatile probe for liquid interfaces, and is the only technique available to acquire surface vibrational spectra of liquids.<sup>5,6,16</sup> Using SFVS, several research groups have successfully obtained vibrational spectra of water/vapor interfaces of acid, basic and salt solutions.<sup>5-8,17,18</sup> In all cases, the SFVS spectrum appears to roughly consist of three spectral features in the OH stretch region: a relatively sharp peak at  $3700\text{ cm}^{-1}$  attributed to the dangling OH protruding at the surface, and two broad bands at  $\sim 3200$  and  $\sim 3450\text{ cm}^{-1}$  from bonded OH often labeled as ice-like and liquid-like bands, respectively.<sup>16</sup> When the acid concentration in water was sufficiently high ( $\text{pH} \leq 2$  with HCl), strong enhancement of both ice-like and liquid-like bands were observed.<sup>7,8,11,18</sup> Appearance of hydronium ions at the surface was used to explain the enhancement.<sup>7,8,11</sup> In basic solution, only the liquid-like band displayed slight changes when pH is sufficiently high ( $\text{pH} \geq 13$ ).<sup>7</sup> It was believed that at high pH,  $\text{OH}^-$  anions might have emerged at the interface with enough concentration to significantly distort the interfacial hydrogen-bonding network of water.<sup>7</sup> Salt solutions have also been investigated. Results showed that ions of small size like to stay in the

bulk, while negative ions with large radius, such as Br<sup>-</sup> and I<sup>-</sup> prefer to stay close to the surface.<sup>6</sup>

How the water interfacial structure would change upon emergence of various types of ions at the water/vapor interface is however still not clear. Interpretation of the SF spectrum for the same interface often varies from group to group. The problem arises because the conventional SFVS yields only an intensity spectrum, proportional to the absolute square of the surface nonlinear susceptibility,  $|\chi_S^{(2)}(\omega_{IR})|^2$ , with  $\chi_S^{(2)}(\omega_{IR})$  being complex. To deduce information on resonances from  $|\chi_S^{(2)}(\omega_{IR})|^2$ , one usually assumes discrete resonances and fits the spectrum.<sup>6-8,19</sup> Unfortunately, such fitting is often not unique. The reason is that OH stretch resonances of a water interface are not discrete. They form a broad continuum because of the existence of widely varying geometry and strength of hydrogen bonds connecting interfacial water molecules to their neighbors. Properly characterizing the continuum resonances from fitting of  $|\chi_S^{(2)}(\omega_{IR})|^2$  is generally not possible. One could approximate the continuum resonances by discrete resonances, but without specifying *a priori* the resonance frequencies and the signs of their resonant amplitudes, the fitting would not be unique. Thus when different groups fit the same SF intensity spectrum for a water interface with discrete resonances, they often obtained different results, and accordingly,

different interpretations.<sup>7,8</sup> Obviously the situation calls for a direct measurement of  $\text{Im } \chi_S^{(2)}(\omega_{IR})$ , which playing the same role as the imaginary part of the dielectric constant for absorption or emission spectroscopy, contains the desired resonant information.

We have recently developed a phase-sensitive (PS) SFVS technique that allows us to measure spectra of both the amplitude and the phase of  $\chi_S^{(2)}(\omega_{IR})$ , and hence the spectra of  $\text{Re } \chi_S^{(2)}(\omega_{IR})$  and  $\text{Im } \chi_S^{(2)}(\omega_{IR})$ .<sup>20,21</sup> We have applied it to the neat water/vapor interface and obtained more detailed understanding on the structure of the interface.<sup>22</sup> We can now use the neat water/vapor interface as a reference in our SFVS study of water/vapor interfaces of acid and base solutions. From the spectral changes resulting from dissolving acid or base into water, we can learn how various types of ions appearing at the interface can perturb the interfacial water structure. We shall focus on the  $\text{Im } \chi_S^{(2)}(\omega_{IR})$  spectra of HCl, NaOH, and HI solutions in which protons, hydroxyls and iodine ions like to come to the interface.

## **Background of Phase-Sensitive Sum-Frequency Vibrational Spectroscopy**

Consider two input beams overlapping at a surface, one at a fixed visible frequency and the other tunable over vibrational resonances in the

infrared. The SF output is given by  $I(\omega_{SF}) \propto |\chi_{eff}^{(2)}|^2$ , with <sup>23</sup>

$$\chi_{eff}^{(2)} = [\vec{L}(\omega_{SF}) \cdot \hat{e}(\omega_{SF})] \cdot \vec{\chi}_S^{(2)} : [\hat{e}(\omega_{vis}) \cdot \vec{L}(\omega_{vis})][\hat{e}(\omega_{IR}) \cdot \vec{L}(\omega_{IR})] \quad (1)$$

where  $\vec{\chi}_S^{(2)}$  is the surface nonlinear susceptibility, and  $\vec{L}(\omega)$  and  $\hat{e}(\omega)$  are the transmission Fresnel factor and the polarization unit vector of the beam at  $\omega$ , respectively. With  $\omega_{IR}$  near resonances, we can write

$$\vec{\chi}_S^{(2)} = \vec{\chi}_{NR}^{(2)} + \sum_q \frac{\vec{A}_q}{\omega_{IR} - \omega_q + i\Gamma_q} \quad (2)$$

if the resonances are discrete, and

$$\vec{\chi}_S^{(2)} = \vec{\chi}_{NR}^{(2)} + \int \frac{\vec{A}_q \rho(\omega_q)}{\omega_{IR} - \omega_q + i\Gamma_q} d\omega_q \quad (3)$$

if the resonances form a continuum. Here,  $\vec{\chi}_{NR}^{(2)}$  describes the nonresonant contribution.  $\vec{A}_q$ ,  $\omega_q$ , and  $\Gamma_q$  represent the amplitude, frequency, and damping constant of the  $q^{\text{th}}$  vibrational resonance, respectively, and  $\rho(\omega_q)$  is the density of modes at  $\omega_q$ .

In general, it is difficult to properly deduce characteristics of the resonances from fitting a  $|\vec{\chi}_S^{(2)}|^2$  spectrum using Eq.(2) or (3) if the resonances strongly overlap or form a continuum. For characterization of the resonances, one would like to know  $\text{Im} \vec{\chi}_S^{(2)}$ , instead of  $|\vec{\chi}_S^{(2)}|^2$ . This requires knowledge of both the amplitude,  $|\vec{\chi}_S^{(2)}|$ , and the phase,  $\Phi_S$ , of  $\vec{\chi}_S^{(2)}$ , both of which should be obtained directly from measurement. It is clear that  $\Phi_S$  can be deduced from interference of the SF signal from the sample with that from a reference.

Depicted in Fig. 1 is a possible scheme for the phase measurement of  $\tilde{\chi}_S^{(2)}$ .<sup>21</sup> It involves insertion of a reference crystal and a phase plate in the incoming beam path of a SFVS setup using the collinear beam geometry. The SF output generated from both the reference and the sample is given by

$$\begin{aligned}
S(\omega_{IR}) &\propto \left| \chi_S^{(2)}(\omega) + C e^{i\Phi} \chi_{Ref}^{(2)}(\omega) \right|^2 \\
&= \left| \chi_S^{(2)}(\omega_{IR}) \right|^2 + \left| C \chi_{Ref}^{(2)}(\omega_{IR}) \right|^2 + 2 \left| C \chi_S^{(2)} \chi_{Ref}^{(2)} \right| \cos \left[ \Phi_S(\omega_{IR}) - \Phi_{Ref}(\omega_{IR}) - \Phi(\omega_{IR}) \right]
\end{aligned}
\tag{4}$$

where  $\chi_S^{(2)} = \left| \chi_S^{(2)} \right| e^{i\Phi_S}$ ,  $\chi_{Ref}^{(2)} = \left| \chi_{Ref}^{(2)} \right| e^{i\Phi_{Ref}}$ ,  $C$  is a constant depending on the beam profiles and  $\Phi$  is a relative phase that can be adjusted by the phase plate. Because  $\left| \chi_S^{(2)}(\omega_{IR}) + C e^{i\Phi} \chi_{Ref}^{(2)}(\omega_{IR}) \right|^2$ ,  $\left| \chi_S^{(2)}(\omega_{IR}) \right|^2$ , and  $\left| C \chi_{Ref}^{(2)}(\omega_{IR}) \right|^2$  can be measured separately, and  $\Phi_{Ref}(\omega_{IR})$  and  $\Phi(\omega_{IR})$  are known,  $\Phi_S(\omega_{IR})$  can be readily deduced. The spectra of  $\text{Re } \tilde{\chi}_S^{(2)}(\omega_{IR})$  and  $\text{Im } \tilde{\chi}_S^{(2)}(\omega_{IR})$  can then be obtained.

The details of our PS-SFVS setup are described in Ref. 21. As seen in Fig. 1, a green beam (532nm) and a tunable IR beam (2.5-3.6  $\mu\text{m}$ ) derived from a picosecond Nd:YAG laser/optical parametric amplifier system propagated collinearly through a y-cut quartz plate and then onto the sample. The SF signal generated from the y-cut quartz, serving as a reference, interfered with that from the sample in the reflected direction.

The interference signal was detected by a photomultiplier/gated integrator system after spectral filtering. A fused silica phase plate inserted between the sample and the y-cut quartz was used to vary  $\Phi$ . The SF output was normalized against that from a z-cut quartz plate.

The nonvanishing elements of  $\tilde{\chi}_s^{(2)}$  for water/vapor interfaces are

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

where Z is along the surface normal. We shall focus on  $\chi_{S,YYZ}^{(2)}$  which can be measured by the SSP polarization combination (denoting S-, S-, and P-polarized SF output, visible input, and IR input, respectively). We note that the SF signal is proportional to  $|\chi_{eff}^{(2)}|^2$ , and  $\chi_{eff}^{(2)}$  in Eq.(1) is related to  $\chi_s^{(2)}$  through the Fresnel factors that depend on the beam geometry. In order to avoid confusion and be able to compare our spectra with those reported in the literature, we shall present our spectra with the Fresnel factors removed, i.e., we shall focus our discussion on  $\chi_s^{(2)}$  instead of  $\chi_{eff}^{(2)}$ .

Aqueous solutions were held in a glass cell. Beams interrogating the water/vapor interface went through holes in the top cover of the cell. In preparing the samples, the cell was soaked in strong acid (98%  $\text{H}_2\text{SO}_4$  + NoChromix) for more than two days, then rinsed thoroughly with distilled water (18.3  $\text{M}\Omega \cdot \text{cm}$ ), and finally blow-dried with nitrogen gas.

With such treatment, the sample surfaces were found free of detectable contaminants. Because HI in water is sensitive to room light, we prepared and kept the HI solution always in dark.

## Results

We present in Figs. 2-4 the measured spectra of  $|\chi_s^{(2)}|^2$ ,  $\text{Re } \chi_s^{(2)}$ , and  $\text{Im } \chi_s^{(2)}$ , for water/vapor interfaces of aqueous solutions of 1.2M HCl, HI, and NaOH, respectively. For comparison, we also plotted in each figure the spectra for the neat water/vapor interface. In all cases, our  $|\chi_s^{(2)}|^2$  spectra, which have the Fresnel coefficients removed, agree well with those obtained by others.<sup>7,8,11</sup> The spectra of all cases appear qualitatively similar, all having an ice-like and a liquid-like feature peaked at  $\sim 3200$  and  $\sim 3400$   $\text{cm}^{-1}$ . Comparison with the neat water case shows that both features are significantly enhanced for HCl and HI solutions and only weakly altered for NaOH solution. In contrast, the corresponding  $\text{Im } \chi_s^{(2)}$  spectra exhibit little changes above  $3500$   $\text{cm}^{-1}$  in all cases, but significant changes below  $3450$   $\text{cm}^{-1}$  for HCl and HI solutions, including a stronger negative liquid-like band for HCl and HI solutions, and a flip of sign in the ice-like region. Comparison of the  $\text{Im } \chi_s^{(2)}$  spectra for HCl and HI solutions shows a stronger negative strength for HCl in the  $\sim 3200$ - $3500$   $\text{cm}^{-1}$  region and a stronger negative strength for HI in the  $\sim 3100$ - $3200$   $\text{cm}^{-1}$  region. For the NaOH solution, the  $\text{Im } \chi_s^{(2)}$  spectrum is

somewhat less negative between 3200 and 3500  $\text{cm}^{-1}$  compared to the neat water case and shows a negative, but nearly vanishing, ice-like band below 3200  $\text{cm}^{-1}$ .

## Discussion

For water/vapor interfaces of HCl, HI, and NaOH solutions, the spectral changes observed in Figs. 2-4 with respect to the neat water case must come from ions appearing at the interfaces. It is believed that  $\text{H}^+$ ,  $\text{I}^-$ , and perhaps also  $\text{OH}^-$  can preferentially reside at a water/vapor interface. They could disturb the interfacial hydrogen(H)-bonding structure of water either by their physical presence or by the surface field they create.<sup>7,8,12,18,24</sup>

In the following discussion, we shall use the neat water/vapor interface always as a reference. To facilitate the discussion, therefore, we need to briefly review the spectra and structure of the neat water/vapor interface deduced from our earlier PS-SFVS measurement.<sup>22</sup> We have found that while the  $|\chi_s^{(2)}|^2$  spectrum for neat water/vapor interface (displayed in Figs. 2a, 3a, and 4a as reference) is the same as those reported by others, the  $\text{Im } \chi_s^{(2)}$  spectrum (in Figs. 2c, 3c, and 4c) is very different from those of others obtained from fitting of the  $|\chi_s^{(2)}|^2$  spectrum.<sup>7,8</sup> 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. These molecules are largely responsible for the observed SF spectra because further down into the liquid, molecular ordering at the surface rapidly decays away and approaches that of the isotropic bulk. In the  $\text{Im } \chi_s^{(2)}$  spectrum, the sharp peak at  $3700 \text{ cm}^{-1}$  can be identified as the OH stretch of the dangling OH at the surface, the  $3450\text{-}3700 \text{ cm}^{-1}$  region mainly as donor-bonded OH stretches of DDA and DAA molecules, the  $3200\text{-}3450 \text{ cm}^{-1}$  region mainly as asymmetrically D-bonded DDAA molecules, and  $3000\text{-}3200 \text{ cm}^{-1}$  regions mainly as symmetrically donor-bonded DDAA molecules. We emphasize here that the overall spectrum results from a continuous band of OH stretch resonances of interfacial water molecules that are H-bonded to neighbors with a wide variety of different geometries and strengths. Therefore, the above description is only a crude approximation. Molecules ascribed here to the specific spectral regions also contribute to some extent to the neighboring spectral regions. For example, both symmetrically and asymmetrically bonded DDAA molecules should contribute to the  $\text{Im } \chi_s^{(2)}$  spectrum around  $3200 \text{ cm}^{-1}$ , one positively and the other negatively so that the

combined  $\text{Im } \chi_s^{(2)}$  is nearly zero.

We now compare the spectra of water/vapor interfaces of aqueous solutions with those of neat water. The spectral change then allows us to learn how ions emerging at the interfaces perturb the interfacial structure. We consider first the HCl acid solution. It was found earlier that there was no detectable structural change of the water/vapor interface with addition of up to 1.7M NaCl in water.<sup>25</sup> This indicates that both  $\text{Na}^+$  and  $\text{Cl}^-$  are largely repelled from the interface. In HCl solution, however, protons are likely to have excess at the interface as suggested by molecular dynamics simulations.<sup>9-11</sup> They can be readily incorporated into the interfacial H-bonding network as hydrated ions in the form of  $\text{H}_3\text{O}^+$  (Eigen form, hydronium) and/or  $\text{H}_5\text{O}_2^+$  (Zundel form,  $\text{H}_2\text{O}-\text{H}-\text{OH}_2^+$ ).<sup>7,8,11,18</sup> 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. Recent SFVS studies<sup>7</sup> showed enhancement of both ice-like and liquid-like bands in the  $|\chi_s^{(2)}|^2$  spectrum due to solvation of HCl in water, which was an indication that  $\text{H}^+$  ions had emerged at the interface to modify the water interfacial structure. Shultz and coworkers understood the enhancement as due to reorientation of interfacial water molecules by the  $\text{H}^+$ -created surface field.<sup>18</sup> Richmond and coworkers decomposed the

$|\chi_s^{(2)}|^2$  spectrum into discrete resonances, and attributed the enhancement of the 3200 and 3330  $\text{cm}^{-1}$  modes to effects of the strong surface field and strong electrostatic interactions between hydrated protons ( $\text{H}_3\text{O}^+$  and  $\text{H}_5\text{O}_2^+$ ) and water molecules at the interface.<sup>7</sup> Allen and coworkers fitted the spectrum with a different set of discrete resonances and suggested that the enhancement at 3200  $\text{cm}^{-1}$  came from the surface field effect as well as contributions from OH stretch vibrations of  $\text{H}_3\text{O}^+$  and  $\text{H}_5\text{O}_2^+$  at the interface.<sup>8,11</sup> Ishiyama and Morita recently reported their MD simulations on the water/vapor interface of HCl solution.<sup>12</sup> Their calculated  $|\chi_s^{(2)}|^2$  spectrum agree qualitatively with the experimental one, and the calculated  $\text{Im } \chi_s^{(2)}$  spectra also resemble that deduced from decomposition of the  $|\chi_s^{(2)}|^2$  spectrum by Richmond's group.<sup>7</sup> (See Fig.5, where we compare the  $\text{Im } \chi_s^{(2)}$  spectra obtained by different groups. The signs of the resonant amplitudes were not specified in Ref. 8. In composing the  $\text{Im } \chi_s^{(2)}$  spectrum from the information given in Ref. 8, we assume that all the bonded OH modes have negative amplitude as we have measured.)

Our  $|\chi_s^{(2)}|^2$  spectrum in Fig. 2a for the water/vapor interface of a 1.2M HCl solution is essentially the same as that obtained by other groups, but the measured  $\text{Im } \chi_s^{(2)}$  spectrum is different from those of others deduced from the  $|\chi_s^{(2)}|^2$  spectrum assuming discrete resonances,<sup>7,8</sup> and also from

that of MD simulation<sup>12</sup>, as shown in Fig. 5. (We note that significant differences, including the difference in the signs of the resonant amplitudes, between our directly measured  $\text{Im } \chi_s^{(2)}$  spectrum and those of others are also evident for the neat water/vapor interface.) In comparison with the spectrum of the neat water/vapor interface also displayed in Fig. 2c, the dangling OH peak at  $\sim 3700 \text{ cm}^{-1}$  hardly changes, but the broad band due to bonded OH stretches in the  $|\chi_s^{(2)}|^2$  spectrum is significantly enhanced. From the spectra of  $\text{Re } \chi_s^{(2)}$  and  $\text{Im } \chi_s^{(2)}$ , it is obvious that the enhancement in the higher frequency region ( $\geq 3200 \text{ cm}^{-1}$ ) comes from enhancement of  $\text{Im } \chi_s^{(2)}$  and enhancement in the lower frequency region ( $\leq 3250 \text{ cm}^{-1}$ ) comes from  $\text{Re } \chi_s^{(2)}$ .

The  $\text{Im } \chi_s^{(2)}$  spectra are more informative because it directly reflects the resonance profile as described in Eq.(3). Comparing the  $\text{Im } \chi_s^{(2)}$  spectra of HCl solution and neat water, we find (1) there is hardly any change above  $3500 \text{ cm}^{-1}$  except for a slight increase of the shoulder around  $3600 \text{ cm}^{-1}$ , (2) the negative liquid-like band between  $3200$  and  $\sim 3450 \text{ cm}^{-1}$  becomes significantly stronger for the HCl solution, and (3) the ice-like band below  $3200 \text{ cm}^{-1}$  flips from positive to negative with HCl in water and terminates at  $\sim 3100 \text{ cm}^{-1}$ .

Using the  $\text{Im } \chi_s^{(2)}$  spectrum in relation to the structure of neat water/vapor interface as references, we can deduce information on how

the interfacial structure of the HCl solution differs from that of neat water from the spectral changes. As mentioned earlier,  $H^+$  likes to emerge at the interface. Knowing that the spectrum above  $3500\text{ cm}^{-1}$  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. This is supported by the result of MD simulation that the excess proton concentration at the surface should be less than 4% of a monolayer.<sup>12</sup> 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  $O\rightarrow H$  toward the bulk liquid, thus enhancing the negative liquid-like band between  $3200$  and  $3500\text{ cm}^{-1}$ . 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.<sup>26</sup> The observed flip of the ice-like band below  $3200\text{ cm}^{-1}$  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  $O\rightarrow H$  pointing into the liquid and therefore contribute negatively to the respective spectral region. In recent years, there has been a great deal of discussion on the existence of hydronium ions and their OH stretch frequencies. Infrared spectroscopic studies on clusters ( $n = 5$ )<sup>27</sup> and bulk HCl solutions<sup>28</sup> suggest the presence of

hydronium ions with a stretch frequency around  $\sim 2900\text{ cm}^{-1}$ . Raman studies found a very broad band (called proton continuum) below  $\sim 3200\text{ cm}^{-1}$  which was attributed to  $\text{H}_3\text{O}^+$  and  $\text{H}_5\text{O}_2^+$ .<sup>8,29</sup> 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.

To check the validity of the above assignment, we tried to single out contribution from hydronium to the spectrum by removing the surface field effect. This can be done by comparing the spectrum of 1.2M HCl solution with a linear combination of spectra for HCl and NaI solutions. From previous SFVS studies of NaI solution,<sup>22</sup> it is known that  $\text{I}^-$  ions prefer to come to the surface and create a negative surface field. The spectral change with respect to the neat water interface mainly comes from the surface field reorienting the interfacial DDA water molecules.<sup>22</sup> On the other hand, in HCl solution, the surface field created by excess  $\text{H}^+$  is positive and induces a spectral change opposite to that in NaI solution. Thus if we choose a proper linear combination of the two spectra for HCl and NaI solutions, we can expect cancellation of the surface field effect in the combined spectrum. Then, in comparing the

combined spectrum with that of neat water, the observed difference would have to come from OH stretches of the hydronium ions. In Fig. 6a, we show separately the  $\text{Im} \chi_s^{(2)}$  spectra for 1.2M HCl and 2.1M NaI solutions. The two are obviously different in the 3000-3600  $\text{cm}^{-1}$  region. We then present in Fig. 6b the combined  $\text{Im} \chi_s^{(2)}$  spectrum composed of the average of the two spectra in Fig. 6a for 1.2M HCl and 2.1M NaI solutions and compare it with that of neat water. The two spectra in Fig. 6b differ only below 3250  $\text{cm}^{-1}$  and around 3600  $\text{cm}^{-1}$ ; the surface field effect that affects mainly the spectral region 3200-3500  $\text{cm}^{-1}$  has indeed been suppressed. The difference spectrum of the two, also shown in Fig. 6b, displays a negative band below 3250  $\text{cm}^{-1}$  that can be attributed to OH stretches of interfacial hydronium ions and a small positive bump presumably arising from disturbance of interfacial DAA water molecules by the hydronium ions.<sup>30</sup> Figure 6c shows a cartoon describing the water/vapor interfacial structure of HCl solution.

We next consider the water/vapor interface of the HI acid solution. Both  $\text{H}^+$  and  $\text{I}^-$  would have excess at the surface. However,  $\text{H}^+$  must have more surface excess because as we described earlier, it takes 2.1M NaI in water to produce enough surface excess  $\text{I}^-$  ions to create the same field strength as that of surface excess  $\text{H}^+$  ions produced by 1.2M HCl. For an HI solution with equal bulk concentrations of  $\text{H}^+$  and  $\text{I}^-$ , more  $\text{H}^+$  than  $\text{I}^-$

must appear at the water/vapor interface. This is supported by MD simulation.<sup>12</sup> The surface ions form a double-charge layer with a positive surface field that could reorient DDAA molecules with O→H pointing towards the liquid bulk and enhance the negative liquid-like band in the  $\text{Im } \chi_s^{(2)}$  spectrum.

Our  $|\chi_s^{(2)}|^2$  spectrum for the 1.2M HI solution in Fig. 3a is the same as those obtained by others, but our  $\text{Im } \chi_s^{(2)}$  spectrum is again different from those of others deduced from fitting of the  $|\chi_s^{(2)}|^2$  spectrum.<sup>8</sup> Compared to that of neat water, the  $\text{Im } \chi_s^{(2)}$  spectrum of the HI solution shows little change above 3500  $\text{cm}^{-1}$  except for the shoulder at  $\sim 3600 \text{ cm}^{-1}$ , but an enhanced negative strength in the 3200-3500  $\text{cm}^{-1}$  liquid-like region. Below 3200  $\text{cm}^{-1}$ , the ice-like band becomes negative. The result supports the picture that more  $\text{H}^+$  than  $\text{I}^-$  appear at the surface, producing a positive surface field that changes the liquid-like spectral feature through reorientation of the asymmetrically bonded DDAA water molecules. This picture differs from the one predicted by MD simulation of Dang et al<sup>4</sup> that shows a negative surface field formed by  $\text{H}^+$  than  $\text{I}^-$ , but agrees with the MD simulations of Morita et al<sup>12</sup>. The hydronium ions formed by  $\text{H}^+$  at the interface again make the ice-like band appear negative and the positive shoulder at 3600  $\text{cm}^{-1}$  stronger.

Compared to the  $\text{Im } \chi_s^{(2)}$  spectrum of the 1.2M HCl solution (see

Fig.7a), the enhancement in the liquid-like region is somewhat less, but the negative ice-like band is stronger and so is the positive shoulder at  $\sim 3600\text{ cm}^{-1}$ . This is an indication that there are more hydronium ions at the interface of the HI solution than the HCl solution, but the surface field is weaker. We can understand the observation as follows. Due to Coulomb interaction, the presence of  $\text{H}^+$  (or hydronium ions) at the interface helps attract  $\text{I}^-$  ions to the interface and vice versa.<sup>31</sup> Therefore, for the same molar concentration of HI, HCl, and NaI in solutions, more  $\text{H}^+$  and  $\text{I}^-$  ions are expected at the interface of the HI solution than  $\text{H}^+$  and  $\text{I}^-$  ions at the interfaces of the HCl and NaI solutions, respectively. Saykally and coworkers using second harmonic generation to monitor the amount of  $\text{I}^-$  ions at the vapor/water interfaces of NaI and HI solutions, and indeed found more  $\text{I}^-$  ions in the HI case.<sup>31</sup> However, since both  $\text{H}^+$  and  $\text{I}^-$  preferentially appear at the surface, they are likely to be close to each other, forming a relatively thin double-charge layer. Compared to the HCl case, even though the surface concentration of  $\text{H}^+$  is higher, the surface field effect could still be weaker, as actually seen from the weaker liquid-like band in the  $\text{Im}\chi_s^{(2)}$  spectra. MD simulations support the above description.<sup>11,12</sup> Morita et al shows that the HI solution has a larger surface excess density of  $\text{H}^+$  ( $\rho/\rho_{bulk}=2.3$ ) than the HCl solution ( $\rho/\rho_{bulk}=1.55$ ), and the average gap between  $\text{H}^+$  and  $\text{I}^-$  is only 1.5 Å, much smaller than that between  $\text{H}^+$  and  $\text{Cl}^-$  (4.5 Å). Thus the surface

potential is lower at the interface of the HI solution. We present in Fig. 7b a cartoon describing the interfacial water structure of the HI solution.

Finally, we consider the water/vapor interface of 1.2M NaOH solution. This is a case more difficult to understand. Even in the bulk, how OH<sup>-</sup> is incorporated in an hydrogen-bonding structure of water is not very clear<sup>32</sup>. Traditionally, OH<sup>-</sup> is thought of being a “mirror image” of H<sup>+</sup> in water, capable of hydrogen-bonding to four neighboring water molecules by three acceptor bonds and one donor bond. However, this picture has been challenged by recent theoretical and experimental works, which proposed that OH<sup>-</sup> could have one donor and four acceptor bonds<sup>32,33</sup>. The bonding structure of OH<sup>-</sup> at the water/vapor interface is even less clear. MD simulation predicts that OH<sup>-</sup> should be repelled from the interface<sup>11</sup>. SFVS studies on 1.3M NaOH solution, on the other hand, found clear reduction of the liquid-like band in the  $|\chi_s^{(2)}|^2$  spectrum<sup>7,11</sup>, indicating that OH<sup>-</sup> had emerged at the interface. The reduction was attributed to OH<sup>-</sup> inducing random orientation of water molecules at the interface<sup>7</sup>.

Our  $|\chi_s^{(2)}|^2$  spectrum of an 1.2M NaOH in Fig. 4 is the same as those of others seeing a reduction of the liquid-like band, but the Im  $\chi_s^{(2)}$  spectrum in comparison with the neat water case shows more clearly a change in the disappearance of the ice-like band below 3200 cm<sup>-1</sup>, in addition to the weak reduction of the negative liquid-like band. The latter can be understood to be due to the surface field effect created by excess OH<sup>-</sup> at

the interface that tends to reorient interfacial water molecules with O→H toward the interface. This rather small change, in comparison with those observed in NaI, HCl, and HI solutions, indicates that the field resulting from surface excess of OH<sup>-</sup> is much less than in the other cases, but it is still opposite to the prediction of MD simulation that there should be a surface depletion of OH<sup>-</sup>. The disappearance of the ice-like band must also be due to appearance of OH<sup>-</sup> at the interface. It is not likely that the weak surface field can reorient the symmetrically bonded DDAA water molecules responsible for the ice-like band, and is presumably the result of how OH<sup>-</sup> is incorporated into the hydrogen-bonding structure of water at the interface. Randomization of interfacial structure by five-coordinated OH<sup>-</sup> probably is probably not the reason because changes in other spectral regions are very weak. Since DDAA molecules symmetrically donor-bonded to the topmost DDA and DAA molecules mainly contribute to the ice-like band in the neat water case, we suspect that in NaOH solution, OH<sup>-</sup> ions may have come to the interface to replace such DDAA molecules and thus reduce the ice-like band. It is also possible that incorporation of OH<sup>-</sup> 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. However, these are pure conjectures. Theoretical help is clearly needed to understand the interfacial structure of NaOH solution.

## Conclusions

We used the PS-SFVS technique to study water/vapor interfaces of 1.2M HCl, HI and NaOH solutions, and obtained in the OH stretch region not only the  $|\chi_s^{(2)}|^2$  spectrum, but also the spectra of  $\text{Re } \chi_s^{(2)}$  and  $\text{Im } \chi_s^{(2)}$ . The  $\text{Im } \chi_s^{(2)}$  spectrum directly reveals the resonance characteristics, and is therefore more informative. While our  $|\chi_s^{(2)}|^2$  spectra are essentially identical to those obtained by others, our  $\text{Im } \chi_s^{(2)}$  spectra are different from those deduced from fitting of the  $|\chi_s^{(2)}|^2$  spectra by others. Accordingly, our understanding of the water interfacial structures of these solutions is also different.

With the neat water/vapor interface taken as a reference, we found that protons in HCl solution like to appear in the form of hydronium ions at the interface and create a positive surface field, which tends to reorient the interfacial water molecules and alters the liquid-like band of the spectrum. The hydronium ions themselves oriented with O→H toward the liquid contribute to the negative ice-like band in the  $\text{Im } \chi_s^{(2)}$  spectrum and an enhanced shoulder below the dangling OH peak. In the case of HI solution, both  $\text{H}^+$  and  $\text{I}^-$  prefer to appear at the interface. They form a double-charge layer creating again a positive surface field that changes the liquid-like band in the spectrum. The hydronium ions at the

interface also affect the spectrum the same way as in the HCl case. For the NaOH solution, the  $\text{Im}(2) S \chi$  spectrum indicates preferential appearance of OH<sup>-</sup> at the interface, contrary to the prediction of MD simulation. How OH<sup>-</sup> gets incorporated in the hydrogen-bonding structure of the water interface and alters the spectrum is however difficult to visualize.

This work demonstrates how PS-SFVS is needed to study water interfaces. The experimentally determined  $\text{Im}(2) S \chi$  spectrum properly describes the extremely broad band of OH stretch resonances originating from continuously varying bonding geometry and strength interfacial water molecules connect with neighbors. It is more of a challenge to theoretical studies of water interfaces. Hopefully, theoretical reproduction of the spectrum could also provide information on how different interfacial water species contribute to different spectral regions. Results from this work will also be used as the basis and references for future studies of other water interfaces including water/liquid and water/solid interfaces.

### **Acknowledgement**

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**Figures:**

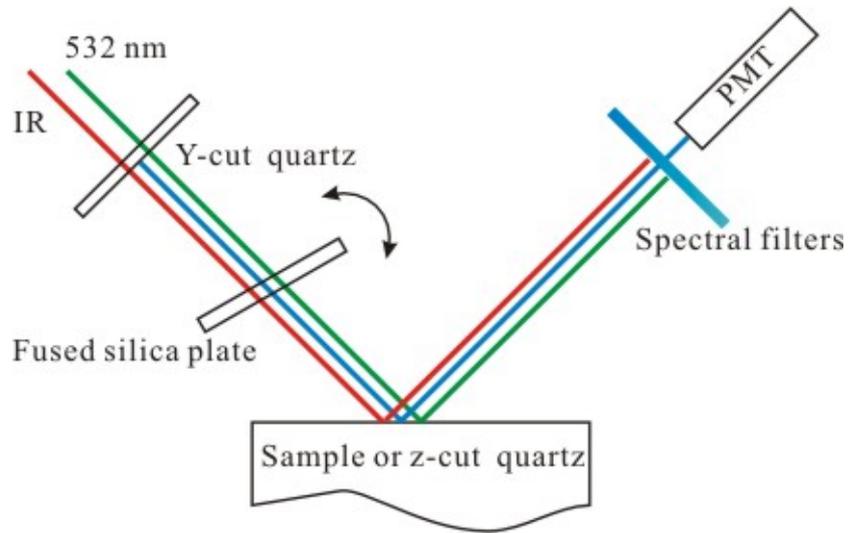


Figure 1. Schematic of the PS-SFVS setup.

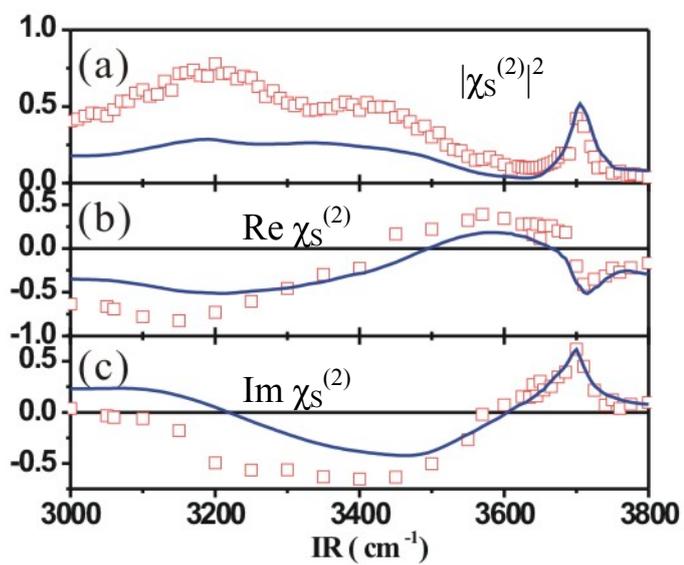


Figure 2. Spectra of (a)  $|\chi_s^{(2)}|^2$ , (b)  $\text{Re } \chi_s^{(2)}$  and (c)  $\text{Im } \chi_s^{(2)}$  for the water/vapor interfaces of 1.2 M HCl solution (symbols) and neat water (lines).

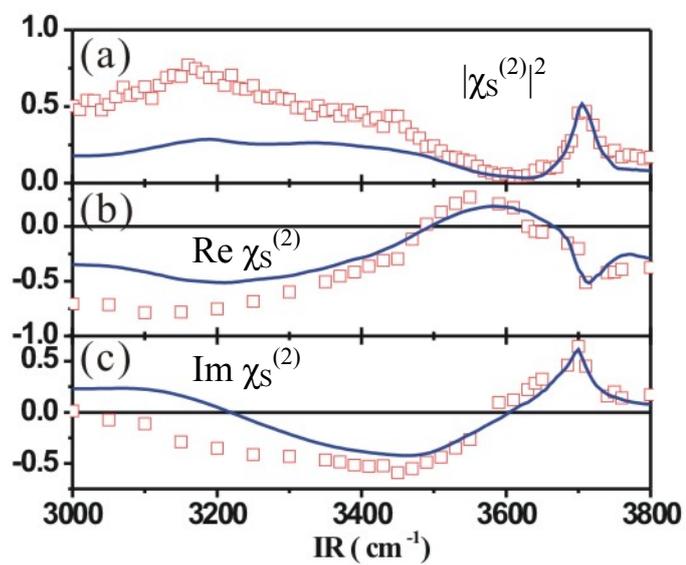


Figure 3. Spectra of (a)  $|\chi_s^{(2)}|^2$ , (b)  $\text{Re } \chi_s^{(2)}$  and (c)  $\text{Im } \chi_s^{(2)}$  for the water/vapor interfaces of 1.2 M HI solution (symbols) and neat water (lines).

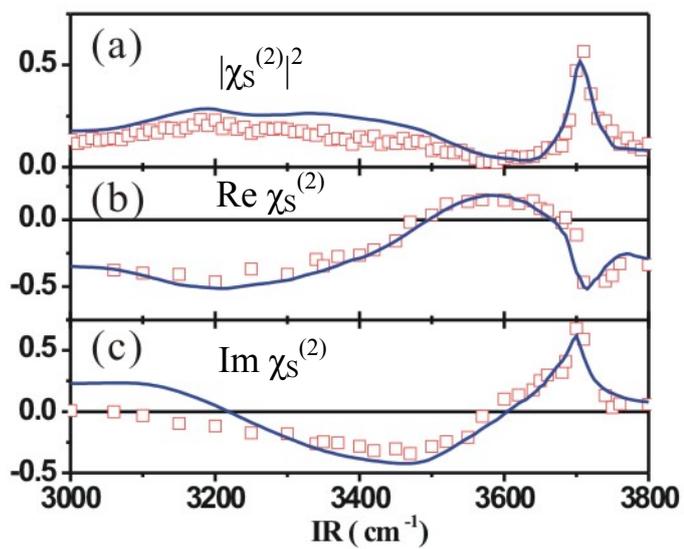


Figure 4. Spectra of (a)  $|\chi_s^{(2)}|^2$ , (b)  $\text{Re } \chi_s^{(2)}$  and (c)  $\text{Im } \chi_s^{(2)}$  for the water/vapor interfaces of 1.2 M NaOH solution (symbols) and neat water (lines).

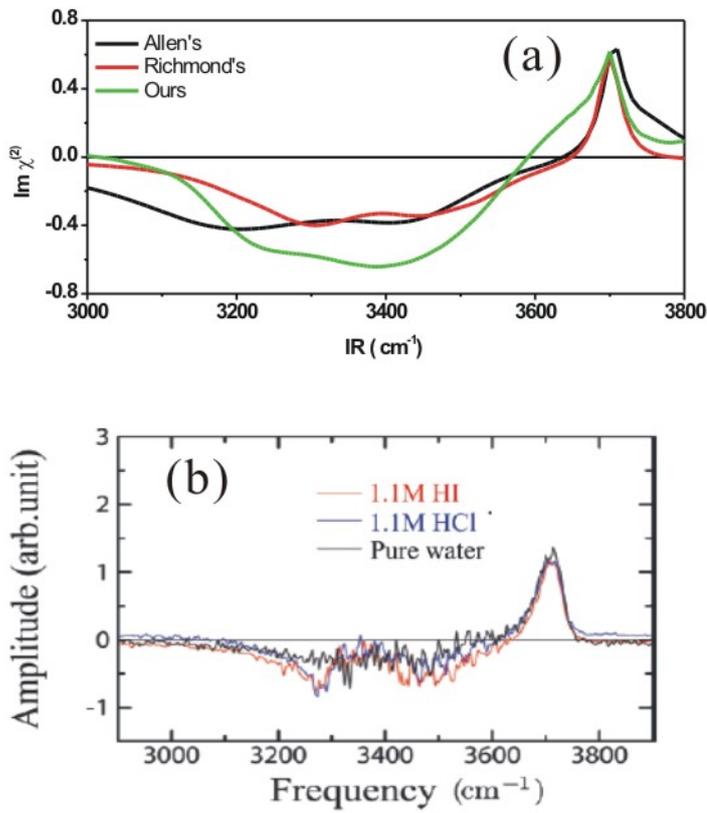


Figure 5. Comparison of  $\text{Im } \chi_s^{(2)}$  spectra of the water/vapor interface of 1.2 M HCl solution obtained (or deduced from spectral information given) by different groups. MD simulation by Morita's group is shown in (b).

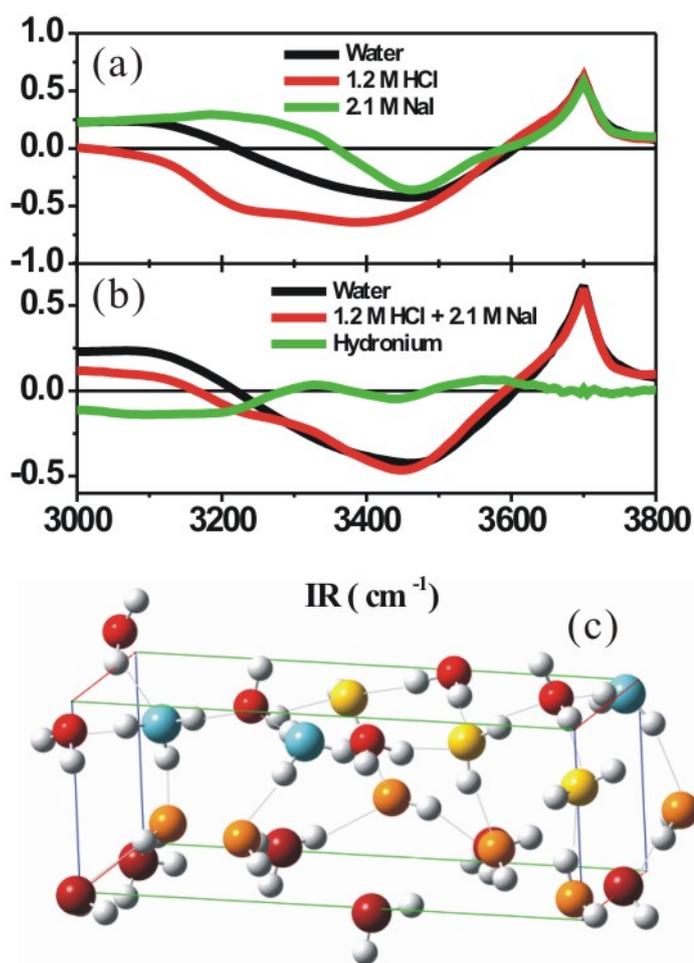


Figure 6. (a)  $\text{Im } \chi_s^{(2)}$  spectra of water/vapor interfaces of 1.2 M HCl solution (red line) and 2.1 M NaI solution (green line). (b)  $\text{Im } \chi_s^{(2)}$  spectrum of water/vapor interfaces of near water (black line), 1:1 linear superposition of  $\text{Im } \chi_s^{(2)}$  spectra for 1.2M HCl and 2.1M NaI solutions (red line) and the difference spectrum deduced from the above two (green line). (c) Cartoon depicting the water/vapor interfacial structure of the HCl solution. Water molecules in different layers are coded with different colors while oxygens of hydronium ions are painted blue.

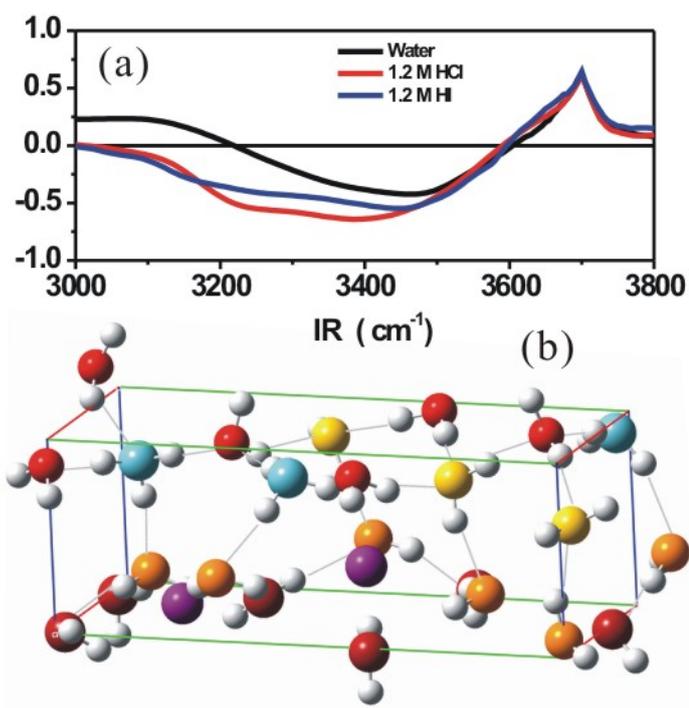


Figure 7. (a) Comparison of  $\text{Im } \chi_s^{(2)}$  spectra of water/vapor interfaces of 1.2 M HCl (red line) and HI (blue line) solutions. (b) Cartoon depicting the water/vapor interfacial structure of the HI solution. Water molecules in different layers are coded with different colors while oxygens of hydronium ions are painted blue and iodine ions painted purple.

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