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Water Hydrogen Bond Structure near Highly Charged Interfaces Is Not Like Ice

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Charged interfaces such as electrochemical, colloidal and membrane interfaces are ubiquitous and important in life and science. These charged interfaces are in contact with an aqueous counter subphase in most cases. Thus, understanding of charge−water interaction is essential. However, even a fundamental question has not been answered; does an electric field at a charged interface induce the "ice-like" hydrogen (H-) bond structure at water interfaces? The simplest way to examine this problem is to compare vibrational spectra of water at interfaces to that of the bulk water. This apparently straightforward approach has turned out to be challenging to realize.

To obtain vibrational spectra of aqueous interfaces, vibrational sum frequency generation (VSFG) has been widely utilized.[1−3] However, conventional VSFG spectroscopy employs a homodyne detection and probes the absolute square of the second order nonlinear susceptibility ($|\chi^{(2)}|^2$). This results in a significant spectral distortion due to the interference between a nonresonant background ($\chi^{(2)}_{NR}$) and multiple neighboring resonances.[4] Thus, analysis of VSFG spectra requires Lorenzian model fit to isolate individual resonances but the fitting does not always give a unique solution.[5] In addition, H-bonded OH bands are believed to involve inhomogeneous broadening so that the Lorenzian model is not more than a rough approximation. These problems can be solved by measuring a complex $\chi^{(2)}$ spectrum with use of phase-sensitive or heterodyne detection techniques.[6−9] The imaginary part of $\chi^{(2)}$ spectrum ($\mathrm{Im}\chi^{(2)}$) is essentially the quantity that one can compare with a linear absorption spectrum, which is given by the imaginary part of the linear susceptibility ($\mathrm{Im}\chi^{(1)}$).

Another problem arises from intramolecular coupling of HOH (DOD) vibration, which splits the OH stretch into the symmetric and antisymmetric modes. The symmetric stretch is further split by the Fermi resonance (FR) coupled with the bending overtone.[10] Bonn and co-workers pointed out that the effect of FR is significant in a VSFG spectrum and questioned the ice-like structure at the water surface.[11,12] In addition, intermolecular coupling is also believed to modulate the vibrational spectra.[13] The stretch bands of H_2O are broad and overlapped and therefore difficult to be analyzed. To avoid this complication, an isotopically diluted water (HOD) has been used to study water structure.[11,14−16] Due to the absence of intramolecular coupling and FR, HOD has only one vibrational normal mode in the OH stretch region in both Raman[17] and IR[18] spectra. The $\mathrm{Im}\chi^{(2)}$ spectrum of HOD is the one to be compared with the bulk HOD Raman/IR spectra.

At the air/neat water interface, Tian and Shen have reported the complex $\chi^{(2)}$ spectrum of HOD deduced from phase-sensitive VSFG.[15] The $\mathrm{Im}\chi^{(2)}$ spectra showed a positive band at 3300 cm^{-1} and a negative band at 3480 cm^{-1} in the H-bonded OH stretch region. They concluded that the positive lower frequency band is the signature of the "ice-like" structure.[15] Other assignments
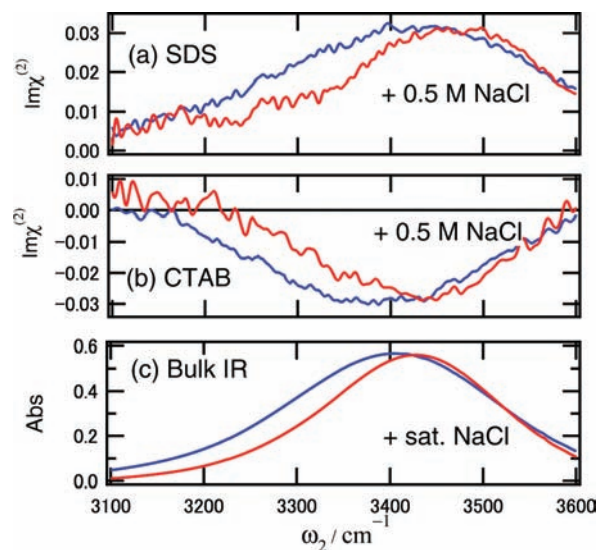

Figure 1. Complex $\chi^{(2)}$ spectra of airy interfaces of aqueous (a) 0.5 mM SDS and (b) 0.1 mM CTAB solutions of HOD (H_2O/HOD/D_2O = 1:12:33) in the absence (blue lines) and presence (red lines) of 0.5 M NaCl. The red curves were magnified by 2 for (a) and 3 for (b). The SF, ω_1, and ω_2 beams were s-, s-, and p- polarized, respectively. (c) Bulk absorption spectra of HOD (H_2O/HOD/D_2O = 1:12:33) (blue) and that of saturated NaCl HOD solution (red).

concerning collective motion have been suggested by theorists.[19−21] Here, we label this band "OH(x)".

Recently, we have developed multiplex heterodyne-detected VSFG (HD-VSFG) that can provide the real and imaginary parts of $\chi^{(2)}$.[22] In a previous paper, we determined the up/down orientation of water molecules at air/charged surfactant/H_2O interfaces by the complex $\chi^{(2)}$ spectra.[22] Unlike the pure water surface, where positive and negative OH bands are observed, two OH bands observed at the surfactant/H_2O interfaces showed the same sign. This implies that the water structure at the highly charged interfaces is significantly different from that of the pure water surface. In this letter, we report $\chi^{(2)}$ spectra of HOD at charged surfactant/aqueous interfaces, which provides decisive information on H-bond structure at charged interfaces. The $\mathrm{Im}\chi^{(2)}$ spectra of HOD at the charged interfaces do not show the OH(x) band and are almost identical to the IR spectrum of the bulk HOD. The OH band of HOD at the charged interfaces blue-shifts upon adding salt in the same way as in the bulk saline water. These findings strongly suggest that the surface electric field does not induce the ice-like structure even though it enhances orientational order along the field.

Figure 1a and b (blue lines) shows the $\mathrm{Im}\chi^{(2)}$ spectra of the air/HOD solution interfaces containing 0.5 mM sodium dodecyl-sulfate (SDS) and 0.1 mM cetyltrimethylammonium bromide (CTAB), respectively, in the mixture of H_2O/HOD/D_2O = 1:12:33. At the

given concentrations, the surface excesses of SDS and CTAB were reported to be ca. 0.8/nm^2,[23] and ca. 0.9/nm^2,[24] respectively. The broad bands centered around 3400 cm^{-1} in Figure 1a and b are due to the OH stretching of HOD water molecules near the charged surfactant/water interface. The Im$\chi^{(2)}$ of the OH band is positive for SDS and negative for CTAB because water molecules orient with their H up at the negatively charged SDS interface while water orients with their H down at the positively charged CTAB interface.[22] $\chi_{NR}^{(2)}$ of the aqueous interfaces appears only in the real part (see Suporting Information).

Importantly, the OH band in Figure 1a and b is essentially a single band. In other words, the OH(x) band, which is observed at the neat HOD surface,[15] is absent or very small compared to the OH band at ∼3400 cm^{-1} in the present condition. As mentioned above, the Im$\chi^{(2)}$ spectra can be directly compared with the bulk IR spectrum shown in Figure 1c. The IR spectrum of the bulk HOD is essentially identical to the previously reported ones[17,18] and shows a broad band at 3400 cm^{-1}, while those of bulk HOD ice show an intense narrow band at 3300 cm^{-1} with broad shoulder around 3400 cm^{-1}.[25] The spectral shape and center frequency of the OH band in the Im$\chi^{(2)}$ spectra (Figures 1a and 1b) resemble the IR spectrum of the liquid HOD (Figure 1c) and there is no signature of the distinct "ice-like" structure. Clearly, the H-bond structure of the charged interfaces is not like ice but similar to that in the bulk liquid water. The OH band frequencies of the Im$\chi^{(2)}$ spectra of SDS are slightly higher than those of CTAB. This is probably due to the different charge of the head groups. A similar trend was observed for AOT[26] and CTAB[27] micelles.

It is known that the bulk IR absorption band blue-shifts in a concentrated salt HOD solution[12] (Figure 1c, red curve). Similar but more substantial blue-shifts are observed in the HOD Im$\chi^{(2)}$ spectra with 0.5 M NaCl (Figure 1a and b, red curves). These band shifts together with the absence of OH(x) band in the Im$\chi^{(2)}$ spectra indicate that the water structure near the charged interface is described by the continuum model in which a broad continuum of states changes the center frequency depending on the environment,[12] rather than the "ice/liquid" model in which distinct ice- and liquid-like structures change their ratio.[1]

At the charged interface, an electric double layer (EDL) is formed, where water molecules are oriented along the electric field, resulting in the large $\chi^{(2)}$ compared to the neat water surface (Figure 2). In this context, "oriented" means that an ensemble average of the water orientation is not zero, but it does not refer to a crystalline-like structure. At the low ionic strength, the EDL is dominated by the Gouy−Chapman (GC) layer, which consists of the surface charge and thermally diffused counterions.[28] Thus, the spectra shown in Figures 1 (blue lines) indicate that the H-bond of water in the GC layer is similar to that in the bulk of pure water, although they are oriented in average. Because the counterion in the GC layer is diffused in a few nm thick layer, the local concentration of the counterion near the interface is not so high (see Supporting Information). Thus, most of water molecules in the EDL are considered to be free from the ions, being allowed to form water−water H-bonds. In this sense, it is reasonable to observe the bulk-like H-bond structure in the GC layer. It has been claimed on the basis of the homodyne VSFG spectra that the electric field induces the "ice-like" structure upon the reorientation of the interfacial water molecules.[14,29] In contrast, our data indicate that the water reorientation due to the electric field does not enhance or promote the "ice-like" H-bond structure.

The signal intensity decreases when the salt concentration increases because EDL and the oriented water layer become thinner.[30] At the high ionic strength, the EDL is dominated by the
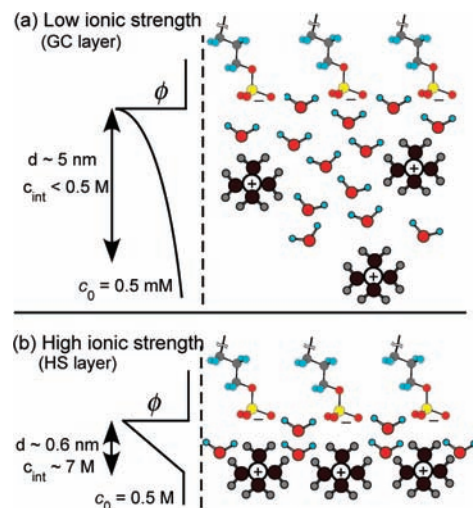

Figure 2. Schematic drawings of the electric double layer at (a) low and (b) high ionic strengths. The hydration shell of the counterion is assumed to be spherical and therefore SFG inactive for symmetrical reason. The decay of the potential ϕ is nearly exponential in GC model and linear in HS model.
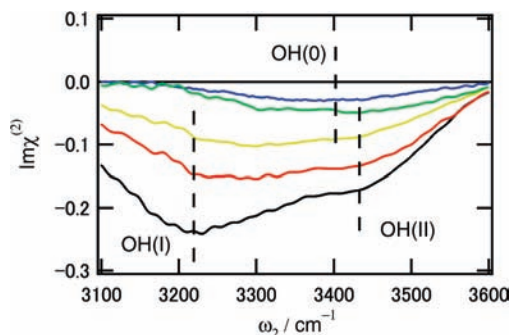

Figure 3. The complex $\chi^{(2)}$ spectra of airy interfaces of aqueous 0.1 mM CTAB solutions at variuos isotopic concentrations (black, H$_2$O; red, H$_2$O/HOD/D$_2$O = 9:6:1; yellow, 1:2:1; green, 1:6:9; blue, 1:12:33). The SF, ω_1, and ω_2 beams were s-, s-, and p- polarized, respectively.

Helmholtz-Stern (HS) layer, in which the counterions are adsorbed in the vicinity of the surface charge. Assuming the thickness of the EDL being 0.6 nm, the ion density in the EDL is estimated to be as high as 7 M (see Supporting Information). Although this estimation is highly model dependent, the situation is very similar to that in the bulk of a concentrated salt solution. Thus, the water structure in the HS layer is expected to be affected by the presence of the dense surface charge and the counterions. The structure of HS layer highly depends on the nature of ions in the system.[31] At the given condition, water molecules exist in between the surfactant headgroup and the counterions as evident by the nonzero OH band intensity of the Im$\chi^{(2)}$ spectra.

We also measured Im$\chi^{(2)}$ spectra of a charged interface under various H$_2$O/HOD/D$_2$O concentrations (Figure 3). The Im$\chi^{(2)}$ spectrum of the charged H$_2$O interface (black line) exhibits two broad OH bands around 3200 cm^{-1} (OH(I)) and 3400 cm^{-1} (OH(II)), which were assigned to the "ice-like" and "liquid-like" structures, respectively, in former homodyne VSFG studies.[14,29] As clearly seen, the OH(I) and OH (II) bands merge into one band (OH(0), blue line) as H$_2$O is replaced by HOD. Note that almost no Im$\chi^{(2)}$ signal was observed below 3200 cm^{-1} at H$_2$O/HOD/D$_2$O = 1:12:33, which assures that the contribution of the H$_2$O molecule is sufficiently low at this condition. These data confirm that the two OH bands observed for the charged H$_2$O interface are not due

to different water structures, because the interfacial water structure is essentially the same for H_2O and HOD. Therefore, we can conclude that the OH(I) and OH(II) bands have the same structural origin and they are split by intramolecular[12,32] and/or intermolecular[13,33] couplings. We note that a similar doubly peaked feature is also observed for the OH stretch band in the bulk H_2O Raman spectra. The temperature and salt concentration dependences of this feature of the bulk spectra have been explained with intra- or intermolecular couplings.[34,35]

Bonn and co-workers have shown that the two peaks in the homodyne VSFG spectrum of both neat and charged aqueous surfaces merged upon isotopic dilution. Based on this, they concluded that the two bands are associated with FR splitting and hence the ice-like model is incorrect.[12] In response, however, Tian and Shen showed that $\text{Im}\chi^{(2)}$ spectra of air/HOD interfaces exhibit a positive OH(x) band ($\sim$3300 cm^{-1}) and a negative band ($\sim$3480 cm^{-1}) in the region in question, although the $|\chi^{(2)}|^2$ spectrum apparently shows only a single band.[15] This means that the merging of the two bands in $|\chi^{(2)}|^2$ spectrum upon isotopic dilution can NOT exclude the presence of the OH(x) band even though it discerns the presence of FR in the H_2O VSFG spectrum. Therefore, the measurement of $\text{Im}\chi^{(2)}$ spectra is crucial.

The key finding in the present study is the absence of the OH(x) band in the $\text{Im}\chi^{(2)}$ spectra of charged HOD interfaces, which allowed straightforward discussion on the OH band position, being free from the distortion due to the overlap of the positive OH(x) and negative OH(0) bands. This enabled us to unambiguously observe the blue-shift of the OH band upon addition of the salt and to directly compare it with the shift of the IR absorption of the bulk water. These results are obtainable only by HD-VSFG and led us to conclude that the water structure near highly charged interfaces is similar to that in bulk liquid water. It is worth stressing that, although homodyne VSFG spectra of both air/charged surfactant/ H_2O solution and air/H_2O interfaces show a broad band around 3200 cm^{-1},[11,14] their origins are different, as revealed by the significantly different $\text{Im}\chi^{(2)}$ spectra. The one at the charged interface arises from the FR of the OH stretch band of the liquid water while the other at the neat water surface is due to the OH(x) band interfered with the FR band.[36] This essential difference is indistinguishable in the homodyne VSFG spectra.

In conclusion, the $\text{Im}\chi^{(2)}$ spectra of HOD near the highly charged interfaces are very similar to the IR absorption spectrum of the bulk HOD water and have no OH(x) band. The interfacial OH band blue-shifts in the presence of dense salt ions in the same way as that of the bulk water. These facts demonstrate that the H-bond of the water in the GC layer is essentially the same as in the bulk water while that in the HS layer is similar to that in the bulk of concentrated salt solutions. Note that our conclusion is limited to the highly charged interfaces and should not be extended to weakly charged interfaces such as I^- aqueous surfaces where the positive OH(x) band is observed.[37]

Supporting Information Available: Detailed description of the experimental, the real part and absolute square of $\chi^{(2)}$ spectra and GC theory and estimation of Stern layer thickness. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Shen, Y. R.; Ostroverkhov, V. *Chem. Rev.* **2006**, *106*, 1140.
(2) Gopalakrishnan, S.; Liu, D. F.; Allen, H. C.; Kuo, M.; Shultz, M. J. *Chem. Rev.* **2006**, *106*, 1155.
(3) Eisenthal, K. B. *Chem. Rev.* **1996**, *96*, 1343.
(4) Bain, C. D. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 1281.
(5) Tian, C. S.; Shen, Y. R. *Chem. Phys. Lett.* **2009**, *470*, 1.
(6) Ji, N.; Ostroverkhov, V.; Chen, C. Y.; Shen, Y. R. *J. Am. Chem. Soc.* **2007**, *129*, 10056.
(7) Ji, N.; Ostroverkhov, V.; Tian, C. S.; Shen, Y. R. *Phys. Rev. Lett.* **2008**, *100*, 096102.
(8) Yamaguchi, S.; Tahara, T. *J. Chem. Phys.* **2008**, *129*, 101102.
(9) Stiopkin, I. V.; Jayathilake, H. D.; Bordenyuk, A. N.; Benderskii, A. V. *J. Am. Chem. Soc.* **2008**, *130*, 2271.
(10) Scherer, J. R.; Go, M. K.; Kint, S. *J. Phys. Chem.* **1974**, *78*, 1304.
(11) Sovago, M.; Campen, R. K.; Wurpel, G. W. H.; Muller, M.; Bakker, H. J.; Bonn, M. *Phys. Rev. Lett.* **2008**, *100*, 173901.
(12) Sovago, M.; Campen, R. K.; Bakker, H. J.; Bonn, M. *Chem. Phys. Lett.* **2009**, *470*, 7.
(13) Auer, B. M.; Skinner, J. L. *J.Chem. Phys.* **2008**, *128*, 224511.
(14) Gragson, D. E.; Richmond, G. L. *J. Phys. Chem. B* **1998**, *102*, 3847.
(15) Tian, C. S.; Shen, Y. R. *J. Am. Chem. Soc.* **2009**, *131*, 2790.
(16) Eftekhari-Bafrooei, A.; Borguet, E. *J. Am. Chem. Soc.* **2010**, *132*, 3756.
(17) Murphy, W. F.; Bernstein, H. J. *J. Phys. Chem.* **1972**, *76*, 1147.
(18) Kropman, M. F.; Bakker, H. J. *Chem. Phys. Lett.* **2003**, *370*, 741.
(19) Buch, V.; Tarbuck, T.; Richmond, G. L.; Groenzin, H.; Li, I.; Shultz, M. J. *J. Chem. Phys.* **2007**, *127*, 204710.
(20) Morita, A.; Ishiyama, T. *Phys. Chem. Chem. Phys.* **2008**, *10*, 5801.
(21) Ishiyama, T.; Morita, A. *J. Phys. Chem. C* **2009**, *113*, 16299.
(22) Nihonyanagi, S.; Yamaguchi, S.; Tahara, T. *J.Chem. Phys.* **2009**, *130*, 204704.
(23) Tajima, K. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3063.
(24) Barnes, G. T.; Lawrie, G. A.; Walker, K. *Langmuir* **1998**, *14*, 2148.
(25) Iglev, H.; Schmeisser, M.; Simeonidis, K.; Thaller, A.; Laubereau, A. *Nature* **2006**, *439*, 183.
(26) Dokter, A. M.; Woutersen, S.; Bakker, H. J. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 15355.
(27) Dokter, A. M.; Woutersen, S.; Bakker, H. J. *J. Chem. Phys.* **2007**, *126*, 124507.
(28) Luo, G. M.; Malkova, S.; Yoon, J.; Schultz, D. G.; Lin, B. H.; Meron, M.; Benjamin, I.; Vanysek, P.; Schlossman, M. L. *Science* **2006**, *311*, 216.
(29) Du, Q.; Freysz, E.; Shen, Y. R. *Phys. Rev. Lett.* **1994**, *72*, 238.
(30) Zhao, X. L.; Ong, S. W.; Eisenthal, K. B. *Chem. Phys. Lett.* **1993**, *202*, 513.
(31) Gurau, M. C.; Kim, G.; Lim, S. M.; Albertorio, F.; Fleisher, H. C.; Cremer, P. S. *Chemphyschem* **2003**, *4*, 1231.
(32) Henri-Rousseau, O.; Blaise, P.; Chamma, D. *Adv. Chem. Phys.* **2002**, *121*, 241.
(33) Green, J. L.; Lacey, A. R.; Sceats, M. G. *J. Phys. Chem.* **1986**, *90*, 3958.
(34) Rull, F.; Desaja, J. A. *J. Raman. Spectrosc.* **1986**, *17*, 167.
(35) Hare, D. E.; Sorensen, C. M. *J.Chem. Phys.* **1992**, *96*, 13.
(36) Three OH bands have been identified by fitting $\text{Im}\chi^{(2)}$ and $|\chi^{(2)}|^2$ of the neat water surface. See ref 12.
(37) Tian, C. S.; Ji, N.; Waychunas, G. A.; Shen, Y. R. *J. Am. Chem. Soc.* **2008**, *130*, 13033.

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