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Vibrational Spectrum of the Water Bend at the Charged Interfaces Probed by Heterodyne-Detected Sum Frequency Generation

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[Abstract]
　　　　We previously reported the $\text{Im}\chi^{(2)}$ (imaginary part of $\chi^{(2)}$, the second-order nonlinear susceptibility) spectra of water at the air/water and NaI aqueous solution interface in the bend region. They exhibit positive peaks at ~1660 cm^{-1}, and we concluded that the HOH bend band arises by the quadrupole mechanism that is beyond the conventional dipole approximation. In this study, we measured $\text{Im}\chi^{(2)}$ spectra in the HOH bend region at various charged surfactant and lipid monolayer interfaces. We found that the HOH bend vibrations at all these interfaces exhibit positive peaks, irrespective of the sign of the charge of the head group, and that the peak positions are different at different monolayers. This observation indicates that the $\text{Im}\chi^{(2)}$ spectrum in the bend region appear with the quadrupole mechanism but it originates from the water at the interface.

[Introduction]
　　　　Molecular-level understanding of structure and dynamics of interfacial water is of particular importance in fundamental and applied sciences. The structure and dynamics of water at air/water and charged interfaces has been intensively studied by measuring the OH stretching vibration of water using vibrational sum frequency generation (VSFG) spectroscopy [1]. However, the interpretation of OH stretch spectra is often complicated due to the Fermi resonance between the symmetric OH stretch vibration and the overtone of the HOH bending mode. Unlike the OH stretch band, the bending mode of water is free from such coupling and can provide complimentary information to that obtained from the OH stretch band. Vibrational spectra of the bending mode of water at the air/water interface and the aqueous interface of negatively charged sodium dodecylsulfate (SDS) were measured by using conventional VSFG spectroscopy [2,3]. The homodyne VSFG and previous MD simulation studies [3,5] claimed that the interfacial water molecules with "H-down" and "H-up" orientation show positive and negative peaks, respectively, in the bend region. A serious drawback of conventional VSFG is that it can only provide spectra of the absolute square of $\chi^{(2)}$. The $|\chi^{(2)}|^2$ spectra obtained with conventional homodyne detection is heavily deformed due to the interference between the resonant peak(s) and nonresonant background, which makes interpretation difficult and often generates misunderstanding. Unlike the conventional VSFG, heterodyne-detected VSFG (HD-VSFG) enables us to obtain $\text{Im}\chi^{(2)}$ spectra, which is free from spectral deformation by nonresonant background and provide direct information about the vibrational resonance of interfacial molecules [1]. We previously reported for the first time an experimentally obtained $\text{Im}\chi^{(2)}$ spectrum of the air/water interface in the HOH bend region [4]. The observed $\text{Im}\chi^{(2)}$ spectra of water at the air/water and negatively charged NaI aqueous solution interfaces show positive bands at 1660 cm^{-1} and the intensity of the $\text{Im}\chi^{(2)}$ spectrum of NaI aqueous solution interface is larger than that of the air/water interface, which is inconsistent to the flip-flop orientation of surface water established in the OH stretch region. These observations were elucidated by calculating quadrupole contributions beyond the conventional dipole approximation.
　　　　Here, we extend our study on the bending mode to various charged interfaces for

obtaining deeper understanding about the quadruple mechanism of water bending mode.

[Methods]

      The optical setup for HD-VSFG measurement was described in detail previously [4]. Briefly, a narrow-band visible ω_1 pulse (795 nm, *s*-polarized) and a broadband infrared ω_2 pulse (1500-1900 cm^{-1}, *p*-polarized) were first focused into a y-cut quartz crystal and then onto the sample surface to generate sum frequency ($\omega_1 + \omega_2$, *s*-polarized). The former SFG generated from the y-cut quartz was used as a local oscillator (LO) and passed through a glass plate (2 mm) to be delayed with respect to the latter SFG generated from the sample interface. The two SFG beams are collinearly guided into a polychromator where they were dispersed and temporally stretched to produce interference fringes in the frequency domain. The interference fringes were detected by a liquid-nitrogen cooled CCD. The Fourier analysis of the interference fringe from the sample combined with the calibration using the reference z-cut quartz allow us to obtain complex spectra of the second-order nonlinear susceptibility $\chi^{(2)}$.

[Results and Discussion]

      Figure 1 shows the experimentally obtained $Im\chi^{(2)}$ spectra of HOH bend at the air/ water interface as well as positively charged (CTAB and DPTAP) and negatively charged (SDS and DPPG) monolayer/water interfaces. The $Im\chi^{(2)}$ spectra in this Figure reveal two important features of the bend band of water. First, the bend band show positive peaks at all charged interfaces, irrespective of the sign of the head group. This provides a strong evidence for that quadruple mechanism gives rise to the $Im\chi^{(2)}$ band of water in the bend frequency region, being consistent with our previous conclusion [4]. The second key feature of the $Im\chi^{(2)}$ spectra is that the peak amplitude and frequency position are different for different monolayer. This spectral change indicates that the $Im\chi^{(2)}$ spectrum in the bend region somehow represents the properties of the interfacial water, even though it has the quadrupole origin. This implies that the origin of $Im\chi^{(2)}$ in the bend region is interface quadrupole induced by the large gradient of the electric field at the interface. We discuss the mechanism in detail in the poster.

Fig. 1. $Im\chi^{(2)}$ spectra of the air/ water (H_2O) (Black), CTAB/H_2O (Red), DPTAP/H_2O (Green), SDS/H_2O (Blue), DPPG/H_2O (Magenta) interfaces in the HOH bend frequency region. Solid lines show the Gaussian fit.

[References]

[1] S. Nihonyanagi *et al*. *Annu. Rev. Phys. Chem.* **64**, 579 (2013)

[2] M. Vinaykin *et al*. *J. Phys. Chem. Lett.* **3(22)**, 3348 (2012)

[3] C. Dutta *et al*. *J. Phys. Chem. Lett.* **8(4)**, 801 (2017)

[4] A. Kundu *et al*. *J. Phys. Chem. Lett.* **7(13)**, 2597 (2016)

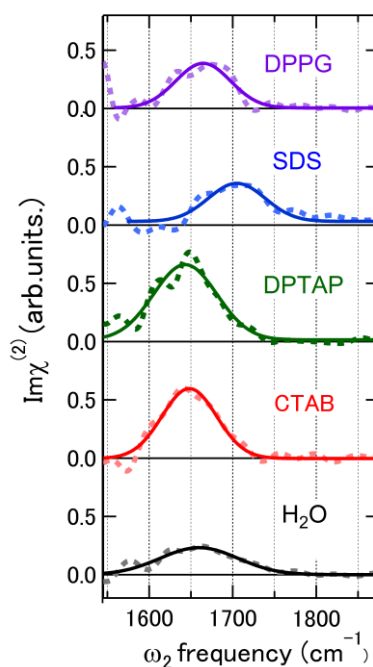[5] Y. Nagata *et al*. *J. Phys. Chem. Lett.* **4(11)**, 1872 (2013)