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Elucidating water structure at the hydrophobic/water interface by heterodyne detected vibrational sum frequency generation (HD-VSFG) spectroscopy

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[Abstract] Hydrophobicity is an important property in chemistry and biology. However, the microscopic understanding of the hydrophobic interface is insufficient. We employed HD-VSFG spectroscopy to obtain a relevant molecular picture of the hydrophobic interface. A thin film of a hydrophobic polymer (cytop, a fluorinated organic polymer) was prepared on a silica substrate, and this hydrophobic polymer/water interface was monitored with HD-VSFG spectroscopy. It was found that the spectra of cytop/water interface show strong pH dependence. The spectra showed that interfacial water is oriented with pointing its hydrogen toward the hydrophobic interface (H-up) at basic pHs whereas the orientation is inverted (H-down) at acidic pHs. The origins of the observed orientation of interfacial water are discussed.

[Introduction] Hydrophobic/water interfaces are very commonly found interfaces in chemistry and biology. These interfaces are believed to play important roles in protein folding, enzymatic activity, micellar structure formation, etc. However, the molecular level understanding of hydrophobic/water interfaces is insufficient due to the limited number of studies and the lack of experimental techniques which can provide molecular level information of the interface. In this context, VSFG spectroscopy is a powerful experimental technique which can provide detail structural information of an interface because of its inherent selectivity for the interface. Moreover, its phase-sensitive variant, HD-VSFG spectroscopy provides the information of $\text{Im } \chi^{(2)}$ with its sign [1]. $\text{Im } \chi^{(2)}$ spectrum has absorptive line shape, therefore, directly provides the information of vibrational resonance of the interfacial molecules without any spectral distortion. In addition, the sign of $\text{Im } \chi^{(2)}$ contains precise information of up-down orientation of the interfacial molecules. Previously, Shen group used phase-sensitive sum-frequency vibrational spectroscopy to study hydrophobic octadecyltrichlorosilane (OTS) monolayer (prepared on silica substrate)/water interface at different pHs [2]. They concluded that hydrophobic OTS/water interface is dominated by OH^- adsorption at neutral and basic pHs. However, it has been reported by other groups [3,4] that the pH dependence of the SFG/second harmonic generation (SHG) spectra of OTS modified silica/water interface mainly arises due to the protonation/deprotonation equilibria of the unreacted silanol groups of silica surface at different pHs. To elucidate the true molecular picture of hydrophobic/water interface, we plan to study hydrophobic cytop (Fig.1a) polymer film (thickness > 20 nm)/water interface, where cytop film will be prepared on a silica substrate. We expect that hydrophobic polymer film blocks water/ion penetration through the film to the substrate better than OTS monolayer. Here, we report water structure at the hydrophobic cytop/water interfaces at different pHs with 10 mM ionic strengths using HD-VSFG spectroscopy.

[Methods] A thin film of cytop polymer was prepared on a silica substrate using spin coating method and probed by HD-VSFG spectroscopy in a buried configuration in contact with

water (Fig.1b). The detail of the HD-VSFG apparatus has been described elsewhere [5]. The $\chi^{(2)}$ spectra of the buried interface were normalized by that of the silica/gold interface. The complex phases of the spectra were obtained by multiplying a constant phase factor to the silica/gold normalized spectra. The phase factor was chosen in such a way that the $\text{Im } \chi^{(2)}$ in the ‘free O-H’ stretch frequency region ($\sim 3700 \text{ cm}^{-1}$) appear as positive and at off-resonance frequency region ($\sim 3800 \text{ cm}^{-1}$) as zero. This is because we can assume that, at the hydrophobic/water interface, water molecules have ‘free O-H’ pointing upwards to the hydrophobic surface and that there is no vibrational resonance in the frequency region of $> \sim 3800 \text{ cm}^{-1}$.

[Results and Discussion] Fig.1c shows $\text{Im } \chi^{(2)}$ spectra of cytop/water interfaces at various pHs in the OH stretch frequency region. It is very clear from the figure that $\text{Im } \chi^{(2)}$ spectra of the cytop/water interfaces show strong pH dependence. At basic pHs, the spectra show a positive band while at acidic pHs, they give a negative band in the hydrogen-bonded OH stretch frequency region. These results suggest that the hydrogen-bonded OH of water molecules are net upward oriented (H-up) at basic pHs whereas they are net downward oriented (H-down) at acidic pHs. The spectrum of cytop/neat water (pH=5.6, red trace) shows positive $\text{Im } \chi^{(2)}$ in the $3000\text{-}3300 \text{ cm}^{-1}$ region, indicating H-up, hydrogen bonded OH of water. However, the positive band disappears completely in addition of 10 mM salt (see dark yellow trace), implying that these H-up water molecules are attributable to the water molecules which are oriented due to the presence of a surface electric field. The electric field can be generated due to the two reasons: 1) adsorption of OH^- ions at the interface, 2) surface charge of silica substrate which creates an electric field through the cytop film. Fig.1c also shows that at basic pHs (pH= 8.3, 10.7, and 12.2), the amplitude of positive $\text{Im } \chi^{(2)}$ increases with increase of the pH value of the solution. This likely suggests that with the increase in pH, OH^- adsorption at the interfaces increases, which increases negative charges at the interface making more number of water molecules in the electric double layer in H-up configuration. However, we

cannot ignore the possibility of the substrate effect. If water and ions penetrate through the cytop film, at higher pH, more SiO^- will be generated at the silica surface, which can also orient more number of water molecules in the electric double layer in H-up configuration. At acidic pHs, water molecules are H-down oriented either due to the H^+ adsorption, or it can be the nature of the hydrophobic/water interface itself. The spectra show negative $\text{Im } \chi^{(2)}$ below 3200 cm^{-1} , which is probably the signature of H^+ adsorption as suggested by a group [6].

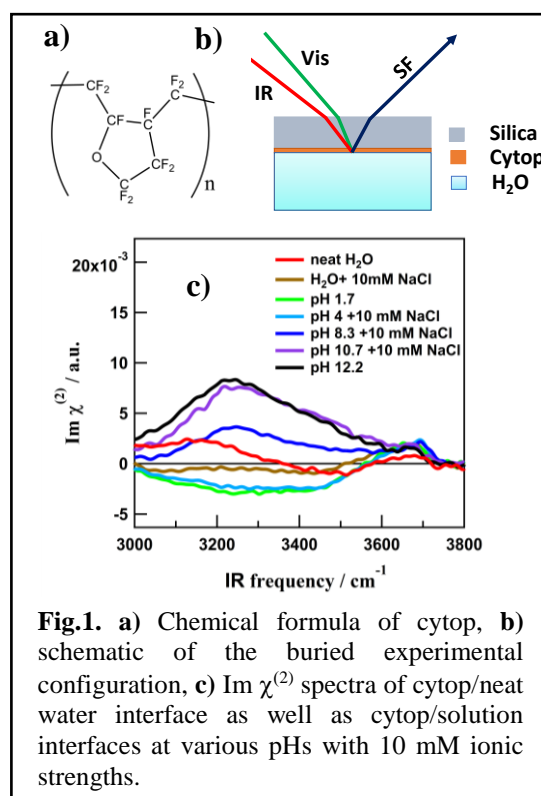


Fig.1. a) Chemical formula of cytop, b) schematic of the buried experimental configuration, c) $\text{Im } \chi^{(2)}$ spectra of cytop/neat water interface as well as cytop/solution interfaces at various pHs with 10 mM ionic strengths.

[References]

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