Ultrafast vibrational dynamics of water at a zwitterionic lipid/water interface revealed by two-dimensional heterodyne-detected vibrational sum frequency generation (2D HD-VSFG)

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Abstract: 2D HD-VSFG is applied to the study of ultrafast vibrational dynamics at a zwitterionic lipid/water interface for the first time. The 2D spectrum reveals spectral diffusion of three distinct water species existing at the interface.
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Introduction

Biological membranes play an essential role in maintaining the cellular environment properly to enable a variety of biological processes. Therefore, a molecular-level understanding of structure and dynamics of the membrane/water interface is indispensable for obtaining physicochemical understanding of biological processes.

So far, lipid monolayers on the water surface have been extensively studied as model systems of the membrane/water interface. Vibrational spectra of the OH stretch region provide abundant information about water because the OH stretch frequency is sensitive to the environment around water. Thus, surface-sensitive vibrational sum frequency generation (VSFG) spectroscopy of the OH stretch can provide rich information about interfacial water. In particular, heterodyne-detected VSFG (HD-VSFG) enables us to measure not only the amplitude of the second-order nonlinear susceptibility ($\chi^{(2)}$), but also its phase, providing $\mathrm{Im}\chi^{(2)}$ spectra which can be directly compared to the absorption spectra ($\mathrm{Im}\chi^{(1)}$) in the bulk [1].

Previously, our group reported the steady-state HD-VSFG study of a zwitterionic lipid/water interface, which is a major constituent of biological membranes [2]. The analysis of the $\mathrm{Im}\chi^{(2)}$ spectra showed that there are three distinct water species at the interface: the water in the vicinity of the negatively charged phosphate group, the water in the vicinity of the positively charged choline group, and the water existing in the hydrophobic region. In the present study, we applied two-dimensional (2D) HD-VSFG to the study of ultrafast dynamics of water at the zwitterionic lipid/water interface for the first time.

Experimental Methods

We used 1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC), shown in Figure 1(a), as a zwitterionic lipid. Water was isotopically diluted (H_2O:HOD:D_2O=1:8:16) to eliminate the effects of the intra- and intermolecular couplings. HD-VSFG measurements of a Langmuir monolayer of DPPC at the water surface were performed at a temperature of 298 K and at a surface pressure of 35 ±3 mN/m, which corresponds to the liquid condensed (LC) phase.

2D HD-VSFG is an extension of HD-VSFG to 2D spectroscopy, and it enables us to observe the time evolution of vibrationally excited states. The optical setup for 2D HD-VSFG measurements was described in detail previously [3]. Briefly, a narrow-band visible ω_1 pulse (center wavelength: 795 nm, bandwidth: 25 cm^{-1}, pulse width: 0.5 ps, S-polarized) and a broadband infrared ω_2 pulse (center wavenumber: 3350 cm^{-1}, bandwidth: 250 cm^{-1}, pulse width: 0.1 ps, P-polarized) were focused into a y-cut quartz crystal and then onto the lipid/water interface to generate sum frequency ($\omega_1+\omega_2$, S-polarized). The former SFG was used as a local oscillator (LO) and passed through a glass plate (2 mm) to be delayed with respect to the latter SFG from the sample by 3.5 ps. The spectral interferograms were recorded by using a polychromator with a charge-coupled device camera. Time-resolved HD-VSFG measurements were carried out with pump ω_{pump} pulses (bandwidth: 160 cm^{-1}, pulse width: 0.2 ps, P-polarized) at 3100 cm^{-1}, 3200 cm^{-1}, 3300 cm^{-1}, 3400 cm^{-1}, 3500 cm^{-1}, and 3600 cm^{-1}. By linearly interpolating the observed spectra, 2D vibrational spectra of the zwitterionic lipid /water interface were obtained.

Results and Discussion

Figure 1(b) shows the steady-state $\mathrm{Im}\chi^{(2)}$ spectrum (filled) and the fitting components (solid line, dotted line, and dashed line). As reported before, this spectrum was successfully decomposed into three components [2]. Components 1, 2, and 3 have been assigned to the water species associated with phosphate, choline, and the hydrophobic region of the lipid, respectively.

Figure 1(c) shows 2D HD-VSFG spectrum at 0.0 ps delay. In this spectrum, the following three bands are observed: a positive peak (denoted as A) on the low frequency side, a negative peak (B) in the center, and a positive peak (C) on the high frequency side. The peaks A and B are assignable to the hot band (v=1→v=2 transition) and bleaching of the v=0→v=1 transition of the OH stretch, respectively. The appearance of peak C is evidence that the single positive band in the steady-state spectrum is actually a superposition of negative and positive bands. Otherwise, the positive peak can never appear in the 2D spectrum in the high frequency side. We consider that peak C appears due to the following mechanism: with irradiation of the ω_{pump} pulses, spectral holes are simultaneously created in the positive component 1 and negative component 2 at the wavenumber of the pump pulse. Then, the center of mass of the bleaching of each component starts shifting toward its inherent peak frequency by spectral diffusion, so that a negative feature appears around the peak of the positive component 1, while a positive feature appears around the peak of the negative component 2. Therefore, the positive sign of peak C indicates that a negative component (i.e., the OH stretch band due to water associated with choline) is buried in the positive OH stretch band in the $\mathrm{Im}\chi^{(2)}$ spectrum. Peak C disappeared in 300 fs, as a result of energy transfer and/or interconversion among the three water species. The present 2D HD-VSFG experiments revealed ultrafast vibrational dynamics of distinct water species existing at a zwitterionic lipid/water interface.

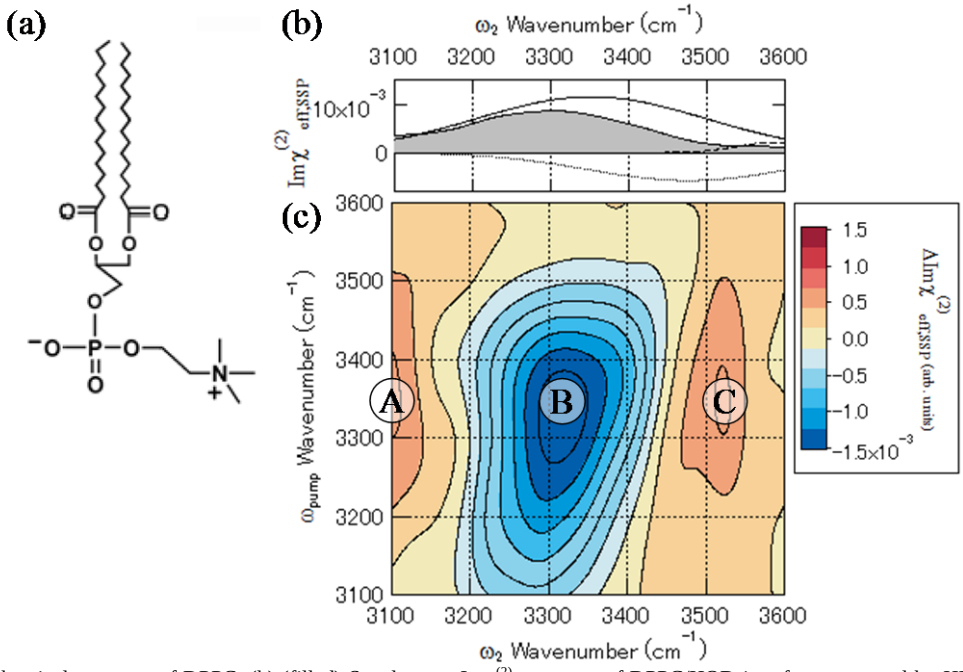

Figure 1. (a) Chemical structure of DPPC. (b) (filled) Steady-state $\mathrm{Im}\chi^{(2)}$ spectrum of DPPC/HOD interface measured by HD-VSFG. The steady-state spectrum was fitted with three Gaussians: (solid line) component 1 (dotted line) component 2 (dashed line) component 3. (c) 2D HD-VSFG spectrum of the DPPC/HOD interface at 0.0 ps delay.

References

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