2D Heterodyne-Detected VSFG Spectroscopy of a Model Membrane Interface

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2D HD-VSFG is applied for studying a zwitterionic lipid/water interface as a model membrane interface. The transient spectra in the OH stretch region reveal the presence of "H-down" oriented water associated with a choline group in addition to "H-up" oriented water in the vicinity of a phosphate group.

The biological membrane maintains proper environments inside the cell. Molecular-level elucidation of the structure and dynamics of water at the membrane is indispensable for understanding the membrane function. Zwitterionic lipid with phosphate and choline groups is a major constituent of the biological membrane. The zwitterionic lipid/water interface has been intensively studied experimentally and theoretically as a model membrane interface [1-5]. Steady-state measurement of the interface with heterodyne-detected vibrational sum frequency generation (HD-VSFG) spectroscopy indicated that there are "H-up" and "H-down" oriented water molecules, which are attributed to water in the vicinity of the phosphate group (W_P) and the choline group (W_C), respectively [1]. However, theoretical studies of the water structure based on molecular dynamics (MD) simulation have not reached a consensus regarding the existence of the "H-down" oriented water [2-5]. The discrepancy originates from the fact that the negative OH band of the "H-down" oriented water has not directly been observed experimentally. This is because the negative band overlaps with the stronger positive OH band of the "H-up" oriented water and is therefore not apparent in the steady-state spectrum. In the present study, the zwitterionic lipid/water interface was studied from the viewpoint of dynamics using two-dimensional (2D) HD-VSFG spectroscopy.

2D HD-VSFG spectroscopy is an interfacial analog of 2D IR spectroscopy, which is utilized in bulk study, and enables us to observe the vibrational dynamics at interfaces. The optical setup for 2D HD-VSFG measurements was described in detail previously [6]. In the 2D spectra of the OH stretch region, distinct transient bands that can be attributed to the coexistence of the "H-up" and "H-down" oriented water were clearly observed. In addition, the "H-up" and "H-down" oriented water bands each show a distinct peak frequency and spectral diffusion associated with their respective OH stretch bands, which can be rationalized in terms of the intrinsic interaction with the respective head groups (the phosphate and choline groups).

References

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