

Ultrafast Vibrational Spectroscopy at Liquid Interfaces by Heterodyne-Detected Sum-Frequency Generation

Tahei Tahara

Molecular Spectroscopy Laboratory, RIKEN, 2-1, Hirosawa, Wako 351-0198, Japan. E-mail: tahei@riken.jp
Ultrafast Spectroscopy Research Team, RIKEN Center for Advanced Photonics (RAP), 2-1 Hirosawa, Wako 351-0198, Japan
E-mail: tahei@riken.jp

Abstract: Ultrafast dynamics at liquid interfaces are still obscure. Femtosecond time-resolved heterodyne-detected vibrational sum-frequency generation spectroscopy now enables us to investigate vibrational/photochemical dynamics at liquid interfaces with the same clarity as in solution-phase ultrafast spectroscopy.

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1. Introduction

Liquid interfaces are unique environments where a variety of important molecular processes take place. Therefore, it is highly desirable to elucidate steady-state and dynamic properties of interfaces at the molecular level. Nevertheless, our understanding of liquid interfaces is very limited, compared with the rich knowledge accumulated for molecules in solution. Vibrational sum-frequency generation (VSFG) spectroscopy is a second-order nonlinear spectroscopy that has intrinsic interface selectivity. VSFG spectroscopy has been extensively utilized for studying the steady-state properties of interfaces, and a few pioneering time-resolved works have also been reported. However, ultrafast dynamics at liquid interfaces are still obscure.

In traditional VSFG measurements, sum-frequency signals generated at interfaces are directly detected. The interfacial vibrational spectra obtained with this homodyne detection method are spectra of the absolute square of the 2nd-order nonlinear susceptibilities ($|\chi^{(2)}|^2$). This absolute square nature of the signal causes a number of problems, e.g., low sensitivity and spectral deformation due to the interference between resonant peak(s) and nonresonant background. These issues of conventional VSFG have hindered extension to time-resolved measurements.

Recently, the drawbacks of conventional VSFG has been solved by heterodyne detection, which provides information on the phase and amplitude of the sum-frequency signal [1-3]. Heterodyne-detected VSFG (HD-VSFG) provides $\text{Im}\chi^{(2)}$ spectra which can be directly compared to absorption spectra (i.e., $\text{Im}\chi^{(1)}$) in solution. In particular, broadband HD-VSFG, developed in our group [2,3], can be readily extended to femtosecond time-resolved measurements by introducing pump pulses for photoexcitation.

In this presentation, I will discuss two types of femtosecond time-resolved HD-VSFG (TR-HD-VSFG) spectroscopy which we developed: infrared-excited and ultraviolet-excited TR-HD-VSFG.

2. Infrared-excited TR-HD-VSFG and 2D-HD-VSFG to study ultrafast vibrational dynamics at liquid interfaces

Water is the most important liquid, and its unique properties originate from its ability to form hydrogen bond networks. Vibrational dynamics of bulk water have intensively been studied by ultrafast time-resolved infrared and two-dimensional infrared (2D IR) spectroscopies. We developed infrared-excited TR-HD-VSFG and investigated the ultrafast vibrational dynamics of water at interfaces by measuring time-resolved $\text{Im}\chi^{(2)}$ spectra in the OH stretch region [4-6]. In these experiments, we first excited a part of the broad OH band of water by femtosecond infrared pulses with $\sim 100 \text{ cm}^{-1}$ bandwidth. Then, we measured the pump-induced change of the $\text{Im}\chi^{(2)}$ spectra ($\Delta\text{Im}\chi^{(2)}$) by changing the delay time [4]. This infrared-excited TR-HD-VSFG have been extended to 2D spectroscopy (2D-HD-VSFG) by collecting the time-resolved $\Delta\text{Im}\chi^{(2)}$ spectra generated by different pump wavelengths [6].

Figure 1A shows the 2D HD-VSFG spectra in the OH stretch region obtained from a positively-charged surfactant/water interface [5]. We used isotopically diluted water to suppress the intra/intermolecular vibrational couplings, and the OH stretch band under this experimental condition predominantly arises from HOD species. The 2D HD-VSFG spectrum immediately after photoexcitation is diagonally elongated, clearly demonstrating

inhomogeneity in the interfacial water. This elongation almost disappears at 300 fs, owing to spectral diffusion. This measurement clearly revealed hole-burning and the subsequent spectral diffusion of interfacial water for the first time. We also carried out 2D HD-VSFG measurements of the OH stretch region at the air/water (H_2O) interface as well as at a lipid/water interface. At the air/water interface, we observed off-diagonal cross peaks among the three OH bands that are observed in the steady-state $\text{Im}\chi^{(2)}$ spectra, indicating that the relevant OH oscillators are vibrationally coupled [6].

3. Ultraviolet-excited TR-HD-VSFG to study ultrafast photochemical dynamics at liquid interfaces

For investigating the dynamics of chemical processes at the interface, we developed ultraviolet-excited TR-HD-VSFG, in which we initiate the photochemical process by electronic excitation of the molecules and observe the resulting dynamics by HD-VSFG. We used this new method to study hydrated electrons at the water interface. Hydrated electrons are the most fundamental anion species, consisting only of electrons and surrounding water molecules, and they have been extensively studied in the bulk aqueous solutions. At the interface, however, even their existence is still controversial.

Figure 1B shows time-resolved $\Delta\text{Im}\chi^{(2)}$ spectra at the air/indole aqueous solution interface obtained with ultraviolet excitation at 265 nm. With photoexcitation, indole molecules are photoionized, and electrons are generated. The time-resolved $\Delta\text{Im}\chi^{(2)}$ spectrum immediately after photoexcitation shows a transient signal with one negative peak around 3200 cm^{-1} and one positive peak around 3500 cm^{-1} . The spectra exhibit substantial temporal change, and a positive feature around 3400 cm^{-1} vanishes in a few hundred femtoseconds. SVD analysis showed that the time-resolved $\Delta\text{Im}\chi^{(2)}$ spectra consist of two components. We assigned them to water near the indole cation and that interacting electrons at the interface. We also carried out TR-HD-VSFG experiments at the air/water interface where the electrons are generated by multi-photon ionization of water. The results of these experiments revealed the dynamics and unique solvation environment of the excess electrons at the aqueous interface [7].

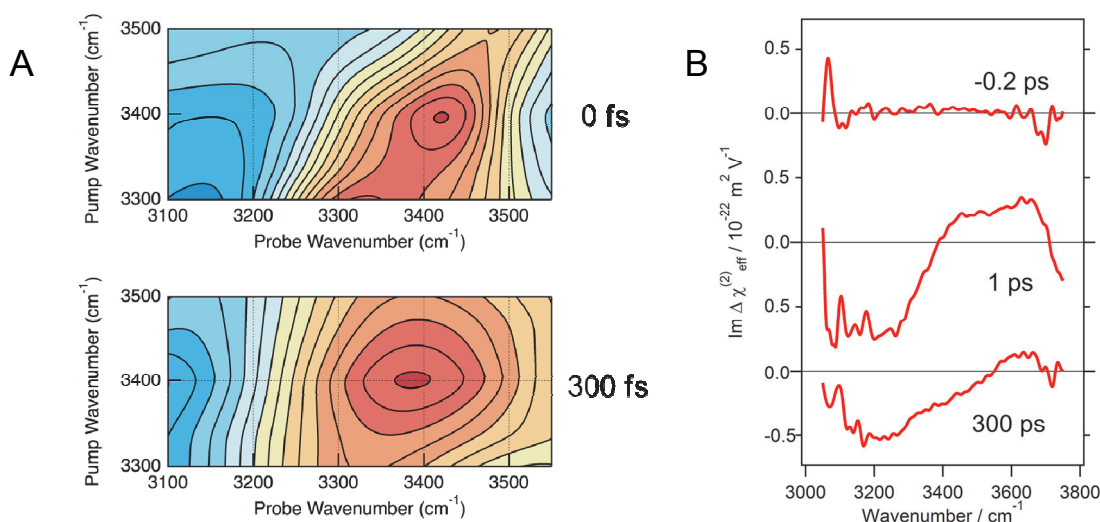


Fig. 1. (A) 2D-HD-VSFG (infrared excited TR-HD-VSFG) spectra of a positively charged water interfaces. (B) ultraviolet-excited TR-HD-VSFG spectra at the air/indole aqueous solution interface.

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