Two-Dimensional Heterodyne-Detected VSFG Spectroscopy of Water Molecules at Charged Interfaces

S. Nihonyanagi, P. C. Singh, S. Yamaguchi, T. Tahara

Molecular Spectroscopy Laboratory, RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

Abstract. Two-dimensional heterodyne-detected vibrational sum-frequency generation (2D-HD-VSFG) spectroscopy of water at interfaces has been realized for the first time. In the present study, 2D-HD-VSFG spectra were measured at a charged monolayer / isotopically diluted water interface. In contrast to the 2D-IR spectrum of bulk isotopically diluted water, the 2D-HD-VSFG of the charged interface shows a narrower bleach band in the higher frequency region immediately after the photoexcitation. The results clearly show that the dynamics of the water at the charged interface is different from that in the bulk, reflecting the different environment where water molecules are located.

1 Introduction

Dynamics of liquid water have been one of the central subjects in the field of ultrafast spectroscopy. The water dynamics in the bulk has been intensively studied by various time-resolved (TR-) spectroscopies, and the ultrafast dynamics relating to the spectral diffusion, inhomogeneity, energy transfer etc. have been observed. Especially, two-dimensional infrared (2D-IR) spectroscopy has been playing a key role because it can provides detailed information about the pump & probe frequencies dependency of the vibrational response and its temporal evolution with the change of the time delay [1]. On the other hand, the dynamics of interfacial water is much less understood compared with a wealth of knowledge about the bulk water dynamics. It is because an interface-selective spectroscopic technique is needed to probe only interfacial water molecules in the presence of bulk water behind. The 2nd-order nonlinear spectroscopy, in particular vibrational sum frequency generation (VSFG), has intrinsic interface specificity and has been widely utilized to study steady-state properties of water at various interfaces [2]. Recently, TR-VSFG measurements (i.e., pump-probe and 2D-VSFG) have been realized at aqueous interfaces [3-5]. However, conventional homodyne detection was employed in these TR-VSFG measurements, and hence only the absolute square of 2nd-order nonlinear susceptibility ($|\chi^{(2)}|^2$) was measured. This absolute square nature of the homodyne detection causes substantial spectral deformation due to the interference between resonant peak(s) and nonresonant background, which prevent us from observing the true spectral response of the interfaces even in the steady-state measurement. This problem become much more serious in TR measurements because the transient signals are much weaker and the broad bleach signals are always accompanied by the hot band appearing with the opposite sign. Since these problems are absent in complex $\chi^{(2)}$ spectra [6], it is very crucial to realize heterodyne detection in TR-VSFG

measurements to obtain time-resolved complex $\chi^{(2)}$ spectra. The time-resolved heterodyne-detected VSFG (TR-HD-VSFG)[7] [8] can directly provide the imaginary part of a pump-induced change in $\chi^{(2)}$ ($\Delta\text{Im}\chi^{(2)}$), which makes interpretation as straightforward as the case of bulk transient absorption spectra that correspond to $\Delta\text{Im}\chi^{(1)}$ ($\chi^{(1)}$; linear susceptibility). In the present paper, we extend our TR-HD-VSFG method [7] to 2D spectroscopy that is applicable to the liquid interface and report 2D-HD-VSFG spectra of water at an aqueous interface for the first time.

2 Experimental

The air/cetyltrimethylammonium bromide (CTAB) solution interface was chosen as a prototype of the positively charged aqueous interface. To remove inter- and intramolecular vibrational couplings, the isotopically diluted water (HOD-D_2O) (H_2O : HOD : D_2O =1 : 8 : 16) was used as the aqueous phase. The optical layout is shown in Figure 1. The multiplex-detection with a broad
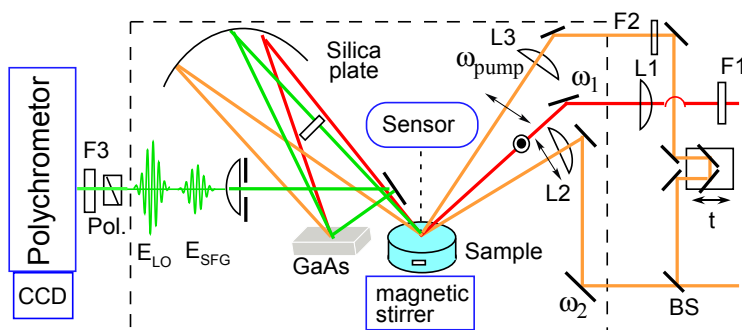

Fig.1 Optical layout of TR-HD-VSFG. F1: band pass filter centered at 795 nm, bandwidth 1.5 nm.
F2: IR band pass filter. BS: 1:4 beam splitter. L1: silica lens, L2 and L3: CaF$_2$ lens.

band femtosecond IR-probe pulse provides $\text{Im}\chi^{(2)}$ spectra in the entire OH stretch region with a high signal to noise ratio. For 2D-HD-VSFG measurements, 80 % of IR light (ω_2) is split by a beam splitter (BS). The bandwidth of this IR is narrowed by a bandpass filter (F2: centered at 3300 cm^{-1}, 3400 cm^{-1} or 3500 cm^{-1}) down to ca. 100 cm^{-1}, and it was used as the pump IR light (ω_{pump}). The ω_{pump} pulse first excited the OH stretch vibration of water, and the subsequent ω_1 and ω_2 pulses generated sum-frequency (ω_{SFG}) pulse at the interface after a certain delay time. The electric field of the ω_{SFG} light was measured through the interference with the local oscillator (LO) [6]. The $\Delta\text{Im}\chi^{(2)}$ spectra obtained at different ω_{pump} were interpolated and combined to produce 2D plots. The instrumental response function measured as a three pulse cross-correlation was ca. 180 fs, allowing us to investigate the ultrafast dynamics of the interfacial water.

3 Results and Discussion

Figure 2 shows the 2D-HD-VSFG spectrum of the charged HOD-D_2O interface obtained at a delay time (a) t = 0, (b) 0.1 and (c) 0.2 ps. In these 2D spectra, an upper positive band appears in the $\omega_2 >$ 3250 cm^{-1} region and lower negative band appears in the $\omega_2 <$ 3250 cm^{-1} region. At the positively charged interface, the steady-state $\text{Im}\chi^{(2)}$ spectrum shows a broad OH band having a negative sign, reflecting the net H-down orientation of water molecules at the interface. Therefore, the positive signal in the 2D spectra corresponds to the bleaching of the negative ground-state OH band while the negative signal corresponds to the transient band attributed to the v=1→2 hot band. In these 2D-HD-VSFG spectra, the bleach band and the hot band can be unambiguously identified with their opposite sign. This is a sharp contrast to the homodyne TR-VSFG spectra where the bleach and hot band
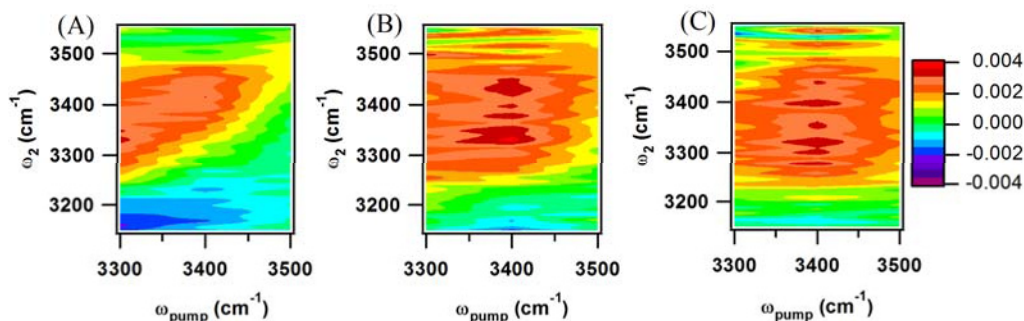
Fig.2 2D-HD-VSFG spectra of CTAB/HOD-D_2O (H_2O : HOD : D_2O = 1 : 8 : 16) interface at (A) t=0 ps, (B) 0.2 ps and (C) 0.4 ps.

appear as one broad band due to the square nature. This clearly demonstrates the necessity of the heterodyne detection to measure the true spectral response in time-resolved measurements.

The 2D-HD-VSFG spectrum at 0 ps (Figure 2A) clearly manifests frequency dependent line broadening for the spectral hole burnt by the pump pulse: With ω_{pump} at 3300 cm^{-1}, the bandwidth of the spectral hole along the ω_2 axis is as broad as 150 cm^{-1} whereas it is only 70 cm^{-1} with ω_{pump} at 3500 cm^{-1}. At 0.2 ps (Figure 2B), the spectral hole for ω_{pump} at 3300 cm^{-1} is broadened to 200 cm^{-1}, indicating that the spectral diffusion is almost over at this delay time. For ω_{pump} at 3500 cm^{-1}, on the other hand, the bandwidth is still 130 cm^{-1} at 0.2 ps, and thus the spectral diffusion is still ongoing. The 2D-HD-VSFG spectrum at 0.4 ps (Figure 2C) does not show any frequency dependent line broadening, which means that the spectral diffusion is completed for all ω_{pump}. The present 2D-HD-VSFG data clearly show that the spectral diffusion of the OH stretch at this charged interface is *slower* at higher ω_{pump}. This makes a striking contrast to the result of 2D-IR studies which showed that the spectral diffusion of the OH stretch band is *faster* at higher ω_{pump} in the bulk [1]. Based on MD simulations, it has been proposed that non hydrogen bond (NHB) water molecules, which give rise to the high frequency OH band, are intrinsically unstable in the bulk and their existence is only momentary, making the spectral diffusion faster [1]. The trend of the spectral diffusion observed for the charged HOD-D_2O interface suggests the presence of a long-lived, weakly hydrogen bonded water at the interface.

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