

## 2P063

### Time-Resolved Heterodyne-Detected Vibrational Sum Frequency (TR-HD-VSFG) Study of Interfacial Water Molecules

(Molecular Spectroscopy Laboratory, RIKEN) oPrashant Chandra Singh, Satoshi Nihonyanagi, Shoichi Yamaguchi, Tahei Tahara

#### Introduction

The chemistry at soft interfaces has not been studied much due to lack of suitable experimental methods. Recently, several powerful new nonlinear spectroscopic techniques such as heterodyne-detected electronic sum-frequency generation (HD-ESFG)<sup>1</sup> and heterodyne-detected vibrational sum frequency generation (HD-VSFG)<sup>2</sup> have been developed in our group, which have enabled us to study interfacial molecules extensively. Though these new techniques provide a lot of molecular level understanding at the interfaces, the information is limited only to steady state. Dynamics study in bulk has provided deep understanding of various phenomena. Therefore, it is highly desired to develop a technique which can provide dynamics of interfacial molecule. In order to achieve this, we have developed a new technique, Time-Resolved Heterodyne-Detected Vibrational Sum Frequency Generation Spectroscopy (TR-HD-VSFG) to explore the dynamics of the interfacial molecules.

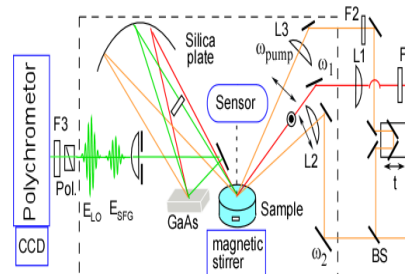
#### Experiamental Setup

Figure1 shows the optical configuration for the TR-HD-VSFG setup. A narrow band visible ( $\omega_1$ ) beam and broadband IR ( $\omega_2$ ) are used for HD-VSFG probe. The steady state spectra are normalized to the quartz spectrum. For the pump-probe measurements, ca. 80 % of IR energy is split from the  $\omega_2$  beam and is used as a pump IR. The pump IR passes through a band

pass filter to narrow the bandwidth down to ca.  $100\text{ cm}^{-1}$  ( $\omega_{\text{pump}}$ ). The modest narrowing of the bandwidth enables us to avoid a significant broadening of the pulse duration. The power of  $\omega_1$ ,  $\omega_2$  and  $\omega_{\text{pump}}$  beams are 9, 3, 2.5  $\mu\text{J}/\text{pulse}$ , respectively. The  $\omega_1$ ,  $\omega_2$  and  $\omega_{\text{pump}}$  beams are focused by calcium fluoride lenses with focal length of 200, 50 and 75 mm, respectively. The sum frequency (SF),  $\omega_1$ ,  $\omega_2$  and  $\omega_{\text{pump}}$  beams are *s*-, *s*-, *p*- and *p*- polarized, respectively, (*sspp* polarization combination). The instrument response function is ca. 170 fs, which was measured as the  $\chi^{(3)}$  cross-correlation of the three pulses ( $\omega_1 + \omega_2 + \omega_p$ ).

#### Results and Discussion

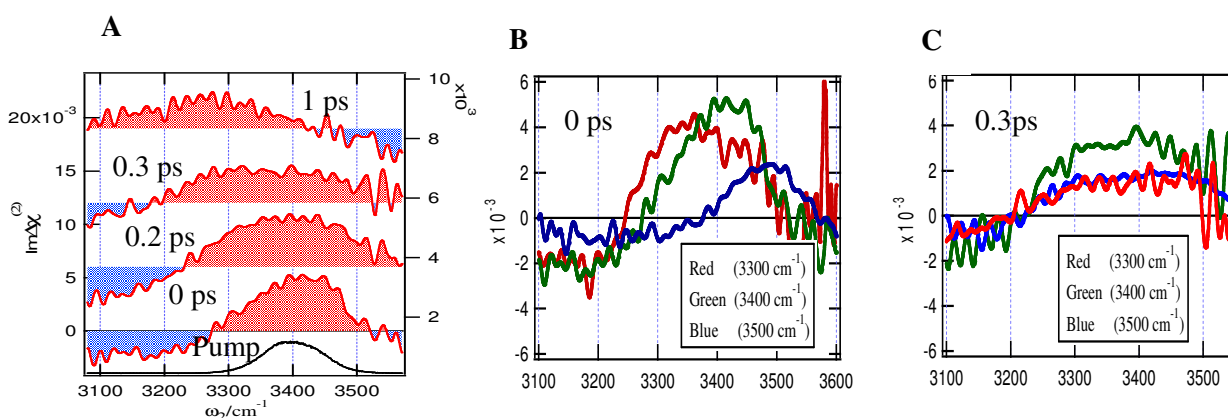
Figure 2A shows the  $\Delta\text{Im}\chi^{(2)}$  spectra of the air/aqueous-CTAB



**Figure1:** The optical Scheme of the TR-HD-VSFG setup.

(cetyltrimethylammonium bromide) solutions interface at various delay times for the isotopically diluted water excited at  $3400\text{ cm}^{-1}$ . A narrow spectral hole-burning is clearly observed at the frequency of the excitation pulse along with negative  $\nu_{1-2}$  hot band. The hole and hot band spectrally diffuse rapidly after the excitation and become almost flat at  $0.4\text{ ps}$ . At later times, the higher frequency sides of the spectra become negative while the lower frequency side turns to increase. This change is attributed to the thermalization process of the system, which causes a blue shift of the water spectrum due to the higher local temperature after the vibrational relaxation. Figure 2B shows the  $\Delta\text{Im}\chi^{(2)}$  spectra of the interfacial isotopic diluted excited for the  $3300$ ,  $3400$  and  $3500\text{ cm}^{-1}$  respectively at  $0\text{ ps}$  delay. It can be clearly seen that the observed hole position changes with the excitation, which shows the inhomogeneous nature of the interfacial water. It is very clear from Figure 2C that after  $0.3\text{ ps}$  diffusion process for sub-ensembles excited at  $3300$ ,  $3400$  and  $3500\text{ cm}^{-1}$  is over.

Hot band and spectral diffusion have been observed first time for interfacial molecules, which demonstrates the prospect of this technique. By using the novelty of this technique, inherent properties of different sub-ensembles of isotopic diluted water at interface has been explored.



**Figure 2** (A) TR-HD-VSFG spectra of the air/CTAB HOD interfaces at the pump delays of 0, 0.2, 0.3 and 1 ps, respectively for  $3400\text{ cm}^{-1}$  excitation. Black line shows the pump spectrum while red and blue colour indicate the positive value and the negative value for  $\text{Im}\Delta\chi^{(2)}$  respectively. (B) TR-HD-VSFG spectra of the air/CTAB HOD interfaces at the pump delays of 0 for  $3300$ ,  $3400$  and  $3500\text{ cm}^{-1}$  excitation. (C) TR-HD-VSFG spectra of the air/CTAB HOD interfaces at the pump delays of  $0.3\text{ ps}$  for  $3300$ ,  $3400$  and  $3500\text{ cm}^{-1}$  excitation.

## References

1. S. Yamaguchi, T. Tahara J. Chem. Phys. **129**, 101102 (2008).
2. S. Nihonyanagi, S. Yamaguchi, and T. Tahara J. Am. Chem. Soc. **132**, 6867 (2010).