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Study of the Water Bending Mode at the Air/Water Interface by Heterodyne-Detected Vibrational Sum Frequency Generation

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Introduction

The air/water interface is important for many processes occurring in the atmosphere. To understand these processes, it is important to know the structure and dynamics of water at the air/water interface. Water structure at the air/water interface has been studied extensively by measuring the OH stretch vibration of water at the air/water interface.[1] Since the OH stretch frequency is close to the frequency of the overtone of the HOH bend, it is important to study the HOH bend in order to understand the vibrational energy relaxation pathway of the OH stretch. Vibrational spectra of the bending mode of H_2O at the air/ H_2O interface was obtained previously by conventional VSFG[2,3] and theoretical calculation.[3] Here we report for the first time an experimentally obtained heterodyne-detected vibrational sum frequency generation spectrum (HD-VSFG) of the air/water interface in the bend region.

Experimental

In our HD-VSFG setup, a narrow-band ω_1 pulse (795 nm) and a broad-band ω_2 pulse (1500 cm^{-1} ~ 1900 cm^{-1}) were focused onto the sample interface. When the ω_1 and ω_2 pulses were temporally and spatially overlapped, the SF ($\omega_1 + \omega_2$) was generated at the sample interface. The ω_1, ω_2, and SF pulses were again focused by a concave mirror onto a GaAs(110) surface to generate SF once more which acts as local oscillator (LO). The SF from the sample passes through a 2 mm thick silica plate located in between the sample and the concave mirror, which delays the SF pulse relative to the ω_1 and ω_2 pulses. This delay resulted in the time difference between the SF from the sample and that from GaAs. The two SF beams are introduced together into a polychromator and then detected by charge coupled device (CCD).

Results and Discussion

The $|\chi^{(2)}|^2$ spectra of the air/water interface in the water bend region were compared in the Figure 1a. Blue line in Figure 1a is our $|\chi^{(2)}|^2$ spectrum of the air/water interface in the bend region calculated from the complex $\chi^{(2)}$ spectrum. Black and green curves were taken from papers by Nagata et al.[3] and Vinaykin et al.[2], respectively, which were obtained by conventional VSFG measurements. The overall shape of our $|\chi^{(2)}|^2$ spectrum resembles the $|\chi^{(2)}|^2$ spectra reported by them.

Figure 1b shows the HD-VSFG spectrum of H_2O at the air/H_2O interface. The Im[$\chi^{(2)}$] spectrum of H_2O in the bend region has an resonance absorption peak at ~1660 cm^{-1} and the Re[$\chi^{(2)}$] spectrum shows a dispersive band shape with the nonresonant back ground. The peak frequency in the Im[$\chi^{(2)}$] spectrum is ~30 cm^{-1} lower than that obtained by conventional VSFG measurement. The resonant amplitude is smaller than the nonresonant background in the bend region and hence the $|\chi^{(2)}|^2$ spectrum is significantly distorted by the nonresonant background.

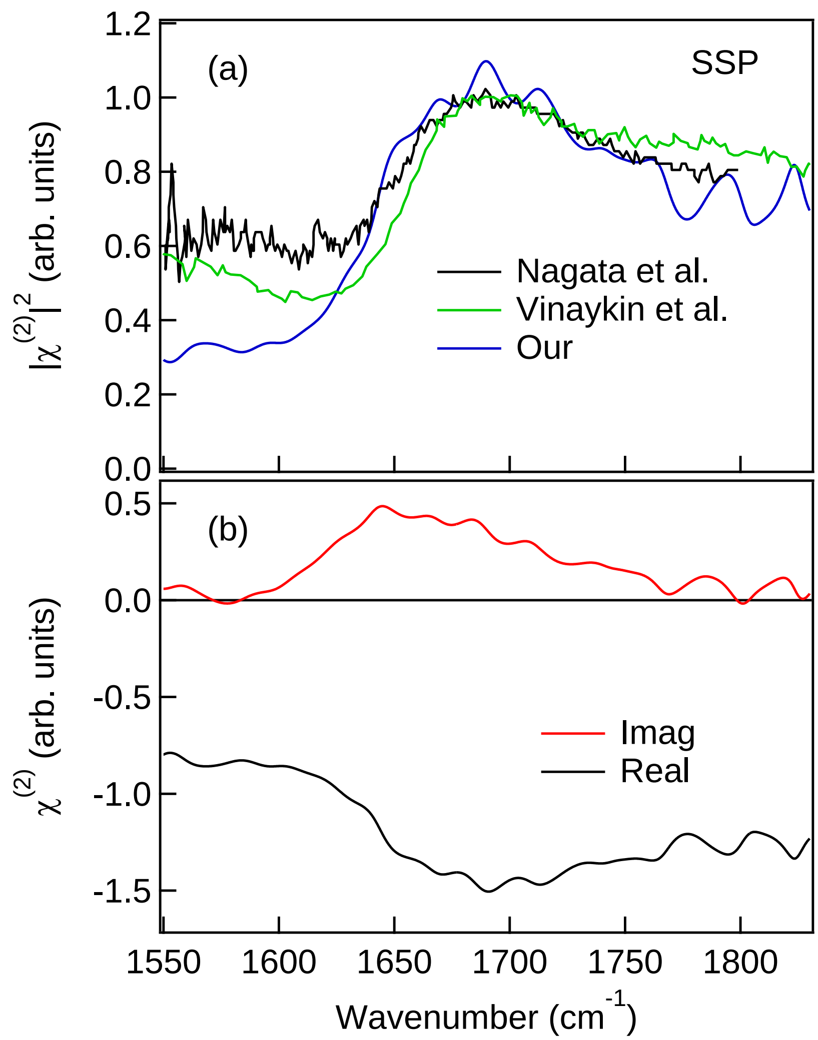

Figure 1. (a) Conventional VSFG spectra of H_2O at the air/H_2O interface. **(b)** HD-VSFG spectra of H_2O at the air/H_2O interface. Red and black lines represent the Im[$\chi^{(2)}$] and Re[$\chi^{(2)}$] spectra, respectively.

Nagata et al. reported that the calculated Im[$\chi^{(2)}$] spectrum of the bend mode at the air/ H_2O interface has a negative peak at ~1650 cm^{-1} and a positive peak at ~1730 cm^{-1}. The Im[$\chi^{(2)}$] spectrum reported here is different from their calculated Im[$\chi^{(2)}$] spectrum. Our Im[$\chi^{(2)}$] spectrum shows only one positive peak at ~1660 cm^{-1}. However, we note that, in our experimental configuration, correction of the complex reflection coefficient of the ω_2 pulse at the air/water interface is necessary. This correction is underway.

References

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