<div align="center">論文の内容の要旨</div>

論文題目　　Development of a Time-Resolved Method and Electric Quadrupolar Theory for Heterodyne-Detected Vibrational Sum Frequency Generation at Air/Liquid Interfaces
（気液界面におけるヘテロダイン検出振動和周波発生のための時間分解測定法と電気四極子理論の開発）

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Introduction

Air/liquid interfaces are important in various physical and chemical processes. To study those interfaces, heterodyne-detected vibrational sum frequency generation (HD-VSFG) spectroscopy has proven to be an especially powerful tool. It allows us to selectively probe the vibrational features and the absolute orientation of molecules within the interface layer as thin as 1 nm [1]. In this study, HD-VSFG spectroscopy has been extended in both experimental and theoretical aspects.

First, HD-VSFG was extended to UV-excited time-resolved spectroscopy, allowing us to study the ultrafast dynamics of the interfacial molecules following the electronic excitation. Using this technique, hydrated electrons at the air/water interfaces were studied. A hydrated electron is made up of one electron and several water molecules that solvate the electron, and recently, the hydrated electrons at the air/water interface have attracted much attention both theoretically and experimentally. However, even the presence or absence of hydrated electrons at the interface is still controversial. In the first part of my study, I aimed to give a conclusive answer to this controversy using this novel spectroscopic technique.

Second, the theory of VSFG has been extended to account for the experimental observation of VSFG at the air/benzene interface [2]. In the ordinary theory within the dipole approximation, VSFG occurs only when the inversion symmetry is broken, and it is forbidden at the air/benzene interface due to the centrosymmetric structure of benzene molecules. In order to explain the origin of the experimentally observed VSFG, a novel mechanism involving an electric quadrupole contribution is proposed, which is in principle applicable to VSFG at various other interfaces. The details of these two studies are discussed below.

Development of UV-excited time-resolved HD-VSFG spectroscopy and the observation of hydrated electrons at the air/water interfaces

The apparatus constructed in the present study is schematically shown in Fig. 1. The narrowband visible ω_1

beam and the broadband infrared ω_2 beam are first focused into a thin crystal of quartz to generate the local oscillator which is used for the heterodyne detection. Subsequently, the generated local oscillator and the transmitted ω_1 and ω_2 beams are refocused onto the sample surface by a spherical concave mirror where VSFG of ω_1 and ω_2 takes place. The VSFG signal and the local oscillator are collinearly introduced into a polychromator, dispersed,

FIG. 1. UV-excited time-resolved HD-VSFG setup.

and detected by a CCD camera. The detected signal shows the interference between the local oscillator and the VSFG beam, which is then analyzed to give the HD-VSFG spectra. Time-resolved HD-VSFG spectra are acquired using the pump-probe method by additionally introducing the UV pump light at 267 nm. In the time-resolved measurements, a sample flow cell specially designed for this experiment is used to avoid the sample degradation by the UV pump light. This cell is capable of flowing the sample liquid while keeping the sample surface at the same height with the accuracy of ~1 μm, which is essential for the heterodyne detection.

As the sample, the air/neat water and the air/indole aqueous solution interfaces were used. For the latter sample, the bulk concentration of indole was 17 mM. At these two interfaces, electrons are prepared by the two-photon ionization of water and by the one-photon ionization of indole, respectively.

$$H_2O \xrightarrow{2h\nu,\ H_2O} H_3O^+ + OH + e^-(H_2O) \qquad indole \xrightarrow{h\nu,\ H_2O} (indole)^+ + e^-(H_2O)$$
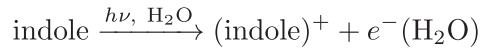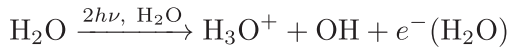
The observed time-resolved spectra in the OH stretch region at the two interfaces are shown in Fig. 2. At the air/neat water interface (Fig. 2(a)), only one transient band was observed at 3270 cm⁻¹, and it decayed within 100 ps. The spectrum and the temporal change of this transient component are shown in Fig. 3(a). On the other hand, the time-resolved spectra at the air/indole solution interface exhibited more complicated temporal changes (Fig. 2(b)). The singular value decomposition (SVD) analysis showed that one positive band at 3430 cm⁻¹ decayed quickly while the positive band at 3640 cm⁻¹ and the negative band at 3230 cm⁻¹ persisted for more than 300 ps as can be seen in Fig. 3(b) and (c).

A striking finding is that the transient component at the air/neat water interface (Fig. 3(a)) and one of the transient components at the air/indole solution interface (Fig. 3(b)) have a similar spectral feature and an almost identical kinetics. Since the electron is the only transient species that exists in common at the two interfaces, these transient components can be assigned to the OH stretch mode of the water molecules interacting with electrons. Based on the observed transient spectra, the
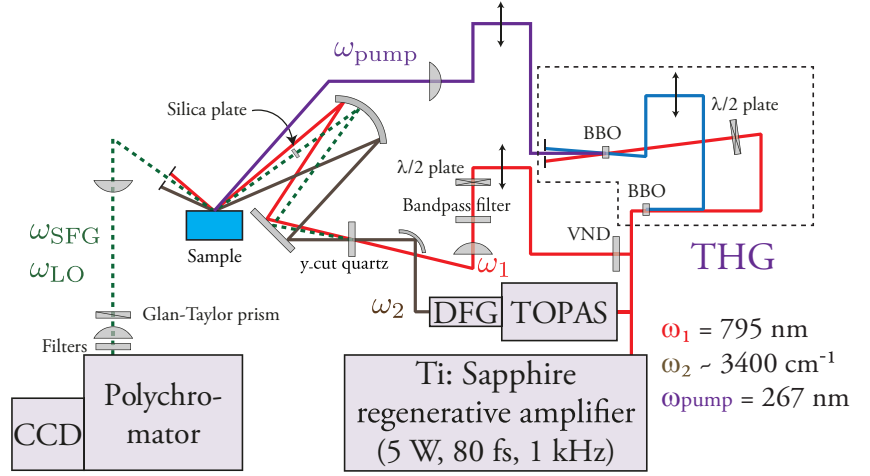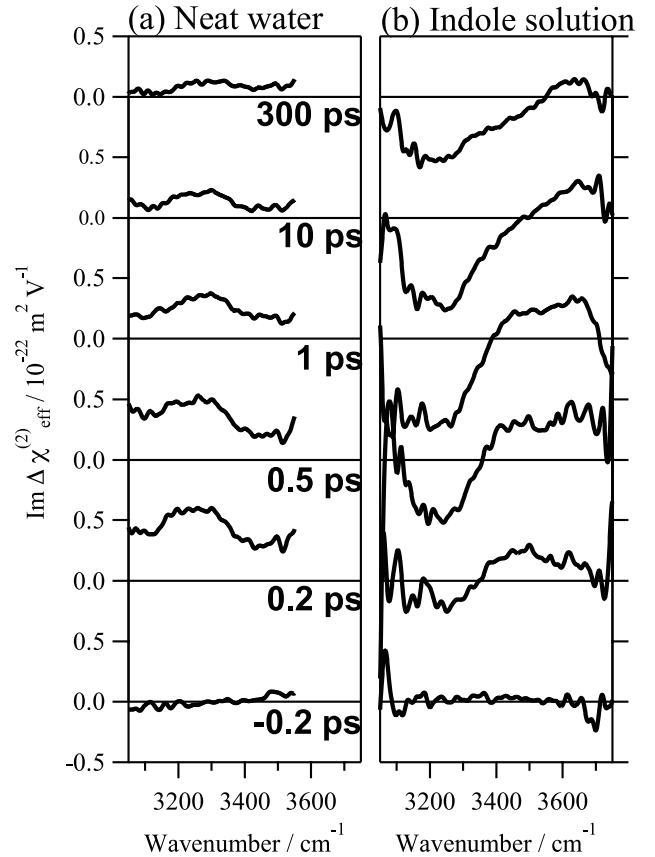

FIG. 2. Time-resolved HD-VSFG spectra at (a) the air/neat water and (b) the air/indole solution interfaces.
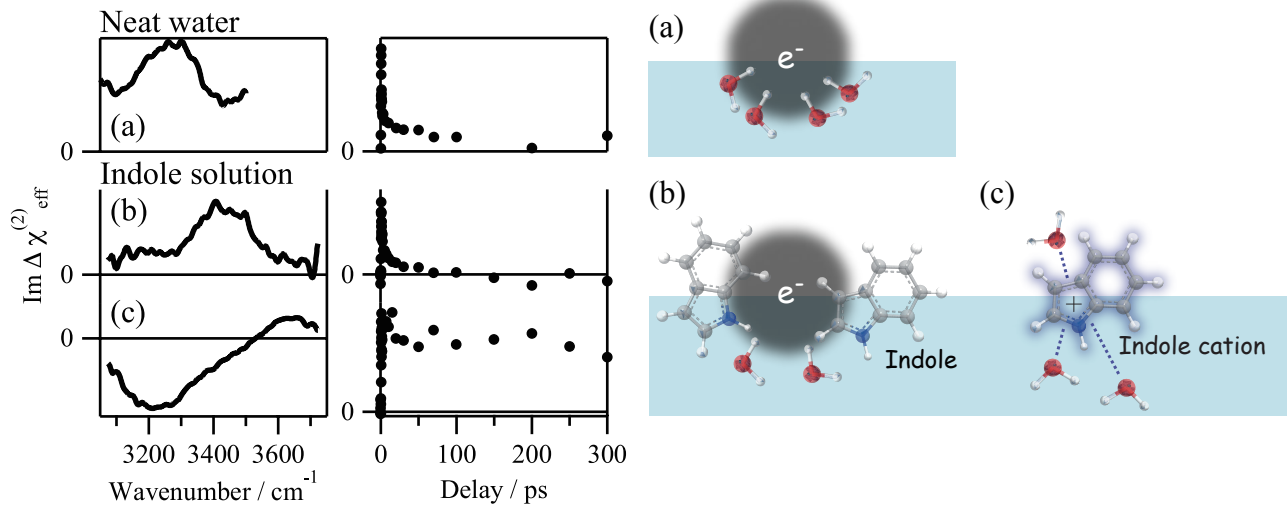
FIG. 3. Spectra and temporal changes of the transient components observed at the two interfaces. Sketches of the assigned transient species are also shown.

molecular level picture of the electron hydration can be elucidated. Since the positive transient band means that the hydrogen atom of water is pointing up towards the air, the experimental data indicates that the electron exists at the top of the water surface and is hydrated by the water molecules from below. Meanwhile, the other transient component observed at the air/indole solution interface (Fig. 3(c)) can be assigned to the OH stretch vibration of water molecules that interact with the indole cations.

The present study shows that the hydrated electrons exist at the air/water interface only temporarily, and they migrate into the bulk within 100 ps. Judging from the position and sign of the observed band, it is highly likely that the electrons are half hydrated at the air/water interface.

Electric quadrupolar theory for VSFG

Although VSFG at the air/benzene interface is forbidden under the dipole approximation because of the centrosymmetric structure of benzene, it has actually been observed experimentally [2]. In order to thoroughly examine the mechanism of VSFG at this interface, steady-state HD-VSFG spectra were recorded for all the four polarization combinations that can cause VSFG at an in-plane isotropic interface as shown in Fig. 4. In the figure, the polarization combinations are indicated by "SSP", "SPS", "PSS", and "PPP", where the three letters correspond to the polarization direction of the sum frequency, ω_1, and ω_2 beams. IR and Raman spectra of bulk liquid benzene
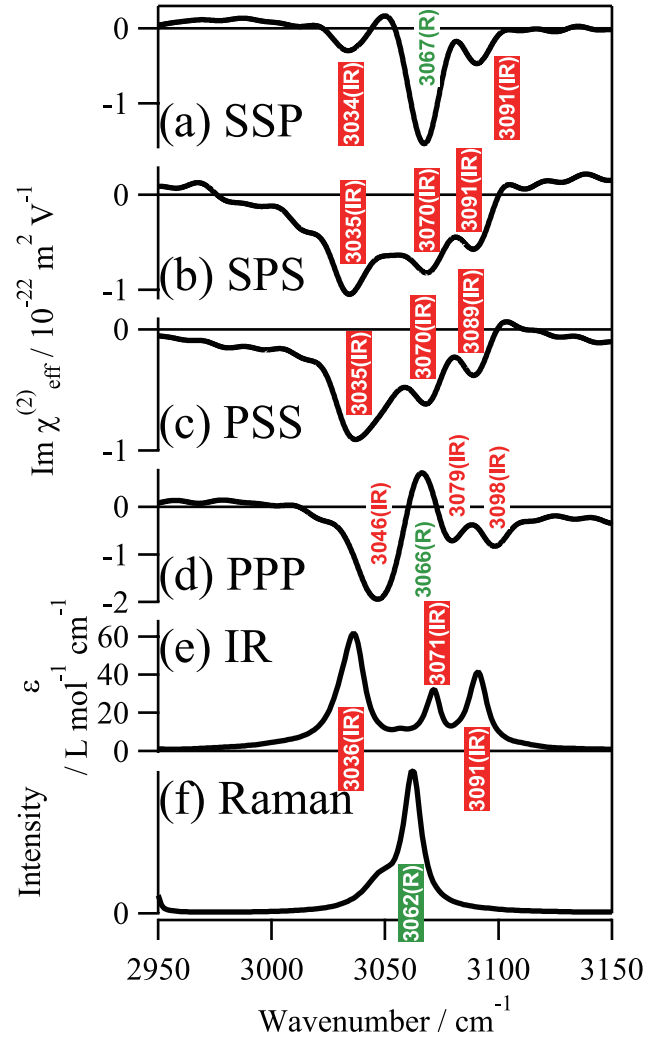

FIG. 4. (a-d) HD-VSFG spectra of the air/benzene interface for each polarization combination, together with the (e) IR and (f) Raman spectra of bulk liquid benzene. The band whose frequency is shown with (without) the filled rectangle is assigned to bulk (interfacial) molecules, and "R" and "IR" represent Raman and IR active modes, respectively.
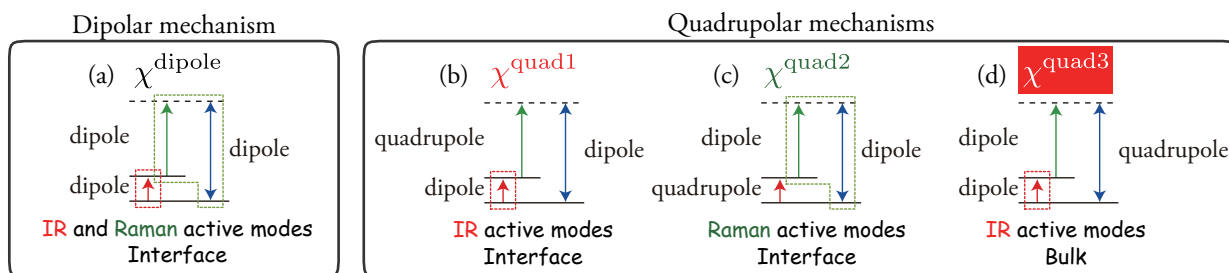
FIG. 5. Energy diagrams for the ordinary dipolar mechanism (a) and for the quadrupolar mechanisms (b-d). The vibrational mode selectivity and the interface selectivity of each diagram are also indicated.

were also measured for comparison.

First, the assignment of the bands was made based on the vibrational frequency. Some of the bands showed the frequency identical to that observed in the IR spectrum of bulk liquid (indicated by the filled rectangles in Fig. 4(a-d)). The vibrational frequency is very sensitive to the local environment around the molecule, and in fact, the frequency of the gas-phase benzene is as much as 10 cm^{-1} higher than that of the liquid-phase benzene, even though the molecular structure is practically unchanged. Hence, the exact match of the frequency indicates that the species giving rise to those bands are assignable to the bulk molecules. Meanwhile, the other bands had the vibrational frequency that is higher than in the liquid phase and lower than in the gas phase. These intermediate frequencies indicate that these bands can be assigned to the vibrational modes of benzene at the interfacial region.

The mechanism of VSFG at the air/benzene interface can then be discussed based on this vibrational assignment. Since only the interfacial molecules contribute to VSFG under the dipole approximation, the observation of the bulk molecules cannot be explained within the ordinary dipolar mechanism (Fig. 5(a)). Hence, it is natural to consider a higher order contribution, i.e. the electric quadrupole contribution [3]. The diagrams for VSFG with a quadrupole contribution are shown in Figs. 5(b-d). In these diagrams, one of the three transitions in the VSFG process is given by a quadrupole transition, while the others are given by dipole transitions. Due to the quadrupole transition, the vibrational mode selectivity and the interface selectivity are different from the dipolar mechanism. Based on these diagrams, the selection rule for each polarization combination (SSP, SPS, PSS, and PPP) can be derived. It was found that the experimental observation is fully consistent with the derived quadrupolar selection rule, and this result shows that VSFG at the air/benzene interface is indeed due to the quadrupolar mechanism.

To check the generality of this mechanism, the same HD-VSFG experiment was conducted at the air/cyclohexane interface, which is another interface comprised only of centrosymmetric molecules. The observed spectra were again consistent with the quadrupolar selection rule. These results show that the present quadrupolar mechanism has generality, and it may potentially contribute to VSFG at various other interfaces.

Conclusion

The interface selective HD-VSFG spectroscopy was extended in two aspects. First, UV-excited time-resolved HD-VSFG spectroscopy was developed to observe the ultrafast dynamics at air/liquid interfaces. Using this technique, hydrated electrons were successfully observed at the air/water interfaces. Second, the quadrupolar theory for VSFG was developed, and was used to account for VSFG at the air/benzene and air/cyclohexane interfaces.

References

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