

## ARTICLE

## Orientation and Motion of Water Molecules at Air/Water Interface

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Here we report a quantitative study of the orientational structure and motion of water molecule at the air/water interface. Analysis of Sum Frequency Generation (SFG) vibrational peak of the free O-H stretching band at  $3700\text{ cm}^{-1}$  in four experimental configurations showed that orientational motion of water molecule at air/water interface is libratory within a limited angular range. The free OH bond of the interfacial water molecule is tilted around  $33^\circ$  from the interface normal and the orientational distribution or motion width is less than  $15^\circ$ . This picture is significantly different from the previous conclusion that the interfacial water molecule orientation varies over a broad range within the ultrafast vibrational relaxation time, the only direct experimental study concluded for ultrafast and broad orientational motion of a liquid interface by Wei *et al.* (Phys. Rev. Lett. 86, 4799, (2001)) using single SFG experimental configuration.

**Key words:** Air/water interface, Water molecules, Orientation and motion

## I. INTRODUCTION

Due to lack of direct experimental measurement techniques, motion and dynamics of molecules at liquid interface are yet to be well understood [1]. In the past decade, air/water interface, as one of the most important liquid interfaces, has been intensively investigated both theoretically and experimentally [1–20]. Experimental method such as X-ray reflection can be used to get the liquid surface roughness [2, 3], but orientational structure and dynamics information at molecule level can only be obtained by Sum Frequency Generation (SFG) or Second Harmonic Generation (SHG) because of their submonolayer sensitivity and interface specificity [1]. It has been generally accepted that the interfacial water molecule has one free OH bond protruding out of the interface. However, the existence of water molecules with both OH bonds pointing to the vapor phase is still a controversial issue [6, 11–13, 18]. The dynamics of water molecule at air/water interface has been discussed theoretically in literatures [5, 7–10, 14, 16–18]. The only direct experimental study so far concluded a fast orientational motion over a broad range of  $102^\circ$  centered at the surface normal ( $\theta_M = 51^\circ$ ) within a time scale comparable or less than 0.5 ps, by Wei *et al.* from the fact of the vanishing of the SFG vibrational peak of the free OH stretching mode of the interfacial water molecule around  $\sim 3700\text{ cm}^{-1}$  in the sps polarization (denoting s- p- and s-polarized SFG output, visible input, and infrared input, respectively) [12]. This result indicated a very dynamic and disordered physical picture for the air/water interface.

Femtosecond pump-probe experimental studies have shown that orientational relaxation dynamics of water molecules in bulk water is as fast as 1 ps and also the motion of non-hydrogen bonded water molecules

is faster than hydrogen bonded water molecules [21]. Therefore, it is reasonable to predict very fast orientational motion of interfacial water molecules, which is less hydrogen bonded as bulk water molecules. However, theoretical simulation by Chandra *et al.* argued for slower dynamics for interfacial water molecules than that of bulk ones (10.5 ps *vs.* 7.1 ps) [16, 17]. Simulation by Benjamin *et al.* also suggested that the lifetime of hydrogen bond at interface between water and an organic liquid is significantly longer than that of bulk water molecules [22]. No matter what, these all suggested ultrafast orientational motion of interfacial water molecules. Most importantly, ultrafast orientational motion may have effects on vibrational spectral width, as well as the strength of vibrational resonance in different input/output polarization combinations, provided that the motion is faster than the time scale of  $1/\Gamma_q$  (the rapid motion limit) and the motion covers a broad range centered around the surface normal, as reported by Wei *et al.* [12].

Recent quantitative analysis of data in SFG vibrational spectroscopy suggested that vapor/liquid interface are generally well ordered and sometimes even with anti-parallel double-layered structures [1, 23–27]. It has been generally accepted that liquid interface with strong hydrogen bonding between molecules should be well ordered [1]. Therefore, it is surprising to comprehend the picture dictated by ultrafast orientational motion in such a broad angular range [12].

Here we show from SFG-VS measurements in four sets of experimental configurations that Wei *et al.*'s analysis [12] can only be considered valid for the particular SFG experimental configuration. We conclude that the orientational motion of water molecules at the air/water interface can only be libratory within a limited angular range around a tilting angle about  $33^\circ$ , instead of being around the interface normal. (As illustrated in Fig.1) Therefore, the air/water interface is much better ordered than previously suggested.

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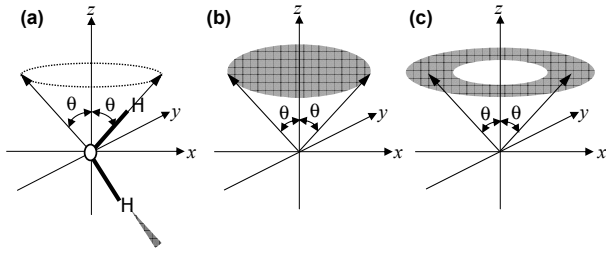


FIG. 1 Illustration of orientation and distribution of the free OH bond at the air/water interface: (a) The water molecule at the interface (parallel to the  $xy$  plane) with a free OH bond points into the air phase, and the lower H atom is hydrogen bonded in the bulk phase; (b) Orientational distribution of the free OH bond, indicated by the vectors, is within the shadowed region of the cone defined by orientational angle  $\theta$  from the interface normal  $z$ ; (c) Orientational distribution of the free OH bond is within the shadowed belt region around the cone surface plane of  $\theta$ . Quantitative analysis of the SFG-VS data in different experimental configurations and polarizations supports the physical picture in (c), while (b) is impossible.

## II. EXPERIMENTAL

The detail of the SFG-VS experiment was described elsewhere [28]. Figure 2 contains SFG spectra of the air/water interface in reflective geometry with ssp, ppp and sps polarization combinations at four sets of incident angles for the visible(Vis) and IR laser beams, namely, Config.1: Vis= 39°, IR= 55°; Config.2: Vis= 45°, IR=55°; Config.3: Vis= 48°, IR= 57°; Config.4: Vis= 63°, IR= 55°. The spectral intensity was normalized to Z-cut quartz [28, 29].

## III. RESULTS AND DISCUSSION

It is clear that there is strong dependence of ppp and sps spectra on the incident angles, especially on the visible beam. The sps spectra in Config.4 exhibits clearly much larger intensity at  $\sim 3700\text{ cm}^{-1}$  than those of the other three configurations. Even though the sps intensity is generally much smaller than that of ssp and ppp polarizations, the sps intensity is well above the experimental noise level, and the experiments were repeated more than a dozen times. It is important to see that the spectra in Config.2 resembles closely the data obtained by Wei *et al.* with Vis= 45°, IR=57° [12]. It is clear that the polarization dependence of these SFG spectra is drastically different from the recent theoretical time correlation function (TCF) description of the polarization dependence of the SFG spectra of the water/vapor interface, even though the TCF approach can provide a resemblant ssp spectra [19]. Such correlation between experimental measurement and theoretical interpretation is certainly far from satisfactory, and further improvement in the theoretical description is certainly warranted.

The ssp spectra of all four experimental configurations overlap with each other well within experimental

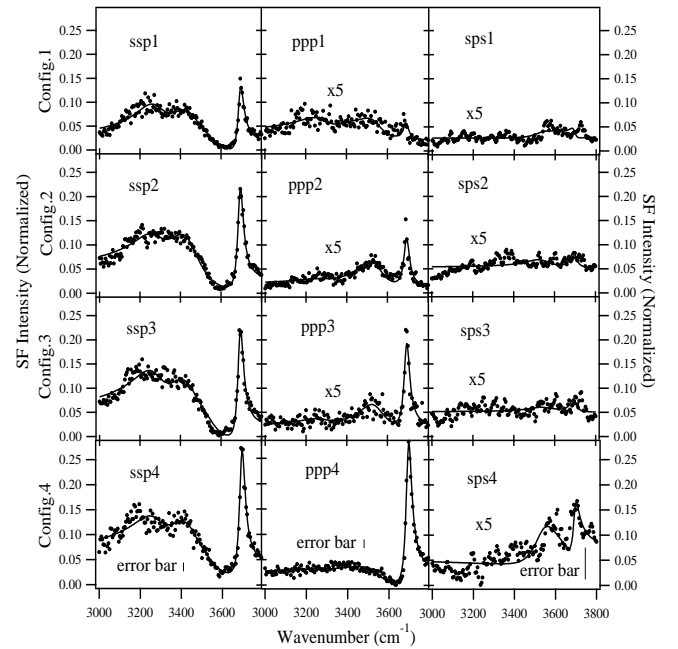


FIG. 2 SFG spectra of air/water interface in different polarization combination and experimental configurations. All spectra are normalized to the same scale. The conversion factor from the intensity read from the figure to  $|\chi_{\text{eff}}^{(2)}|^2$  is to time by  $(24.1\text{sec}^2\beta)^{-1} \times 10^{-40}\text{V}^4/\text{m}^2$ , where  $\beta$  is the angle between the SF signal beam and the interface normal for different experimental configurations. The solid lines are globally fitted curves with Lorentzian line shape function. The significant non-zero sps spectra in Config.4 proves that the ultrafast broad motion of the free O-H bond is not possible at the air/water interface. Note the different error bars for graphs in different scales.

error when normalized to the  $\sim 3700\text{ cm}^{-1}$  peak intensity. The difference of their absolute intensities can be quantitatively accounted from the Fresnel coefficients with different incident angles. These facts indicate that SFG data with different incident angles are from interfacial layers without detectable bulk contributions [30].

Quantitative polarization and orientational analysis in different experimental configurations can provide detailed information on structure, conformation and dynamics of molecules at liquid interfaces [12, 31–36]. The polarization dependent SFG intensity is [31]:

$$I(\omega) = \frac{8\pi^3\omega^2\sec^2\beta}{c^3n_1(\omega)n_1(\omega_1)n_1(\omega_2)} \left| \chi_{\text{eff}}^{(2)} \right|^2 I(\omega_1)I(\omega_2) \quad (1)$$

with

$$\chi_{\text{eff}}^{(2)} = [\hat{e}(\omega) \cdot \mathbf{L}(\omega)] \cdot \chi_{ijk}^{(2)} : [\mathbf{L}(\omega_1) \cdot \hat{e}(\omega_1)][\mathbf{L}(\omega_2) \cdot \hat{e}(\omega_2)] \quad (2)$$

in which  $n_i(\omega_i)$  is the refractive index of phase  $i$  at frequency  $\omega_i$ ;  $\beta$  is the angle of the outgoing SFG signal beam;  $I$  is the intensity of the laser beam or the SFG signal.  $\chi_{\text{eff}}^{(2)}$  is the effective second order susceptibility;  $\chi_{ijk}^{(2)}$  is the macroscopic susceptibility tensor elements, determined by the macroscopic and molecular symmetry [33–35];  $\mathbf{L}(\omega_i)$  the local field factor tensor, and  $\hat{e}(\omega_i)$

the unit vector of the corresponding optical field, which is responsible for the experimental configuration dependence.

As Wei *et al.* had demonstrated [12], when orientational motion average is considered, if the orientational motion is faster than the vibrational relaxation time scale  $1/\Gamma_q$  of the  $q$ th mode, slow motion average of the orientation motion is no longer valid. The slow motion limit gives,

$$\chi_{ijk}^{(2)} = N_s \sum_q \sum_{\lambda\mu\nu} \frac{a_{q,\lambda\mu\nu}}{\omega_2 - \omega_q + i\Gamma_q} \langle D_{i\lambda} D_{j\mu} D_{k\nu} \rangle \quad (3)$$

And the fast motion limit gives,

$$\chi_{ijk}^{(2)} = N_s \sum_q \sum_{\lambda\mu\nu} \frac{a_{q,\lambda\mu\nu}}{\omega_2 - \omega_q + i\Gamma_q} \langle D_{i\lambda} D_{j\mu} \rangle \langle D_{k\nu} \rangle \quad (4)$$

in which  $N_s$  is the surface density of molecules;  $a_{q,\lambda\mu\nu}$  and  $\omega_q$  and  $\Gamma_q$  are the amplitude, resonant frequency and damping constant of the  $q$ th molecular vibrational mode, respectively; and  $D_{l\xi}(t) = \hat{l} \cdot \hat{\xi}(t)$  is the time-dependent direction cosine matrix with  $l=i,j,k$  for laboratory coordinates and  $\xi=\lambda,\mu,\nu$  for molecular coordinates.

Wei *et al.* used the step orientational distribution function in Eq(5), as well as other distribution functions, such as Gaussian, centered at the surface normal, and concluded for a fast motion of the interfacial free OH bond in a range of  $\theta_M = 51^\circ$  from the data obtained with Vis=  $45^\circ$ , IR= $57^\circ$  [12]. If without the fast orientational motion average, the ppp and sps intensities should be comparable, given the ssp intensity is about 10 times of that for ppp in their SFG data.

$$\begin{aligned} f(\theta) &= \cos t & \text{for } 0 \leq \theta \leq \theta_M \\ f(\theta) &= 0 & \text{for } \theta \geq \theta_M \end{aligned} \quad (5)$$

However, such treatment can not explain the much stronger sps intensity around  $\sim 3700 \text{ cm}^{-1}$  in Config.4, even though it can seemingly explain data in Config.1,2, and 3. Using the same parameters, distribution function and calculation procedures as Wei *et al.*, we simulated the ssp, ppp, and sps intensities with both slow motion and fast motion averages. Figure 3 shows the results for Config.2 and Config.4. Our calculation of Config.2 gives the same results as that by Wei *et al.* [12]. We noticed in the calculation that the fast orientational motion centered at interfacial normal shall make all SFG intensity in sps spectra vanish for all experimental configurations, independent of the range of the motion. This is clearly in contradiction to the data from Config.4. As Wei *et al.* concluded, the slow motion limit certainly can not explain the relative intensity of the  $3700 \text{ cm}^{-1}$  peak for the ssp, ppp polarizations. Therefore, alternative description of the motion and orientation has to be invoked.

Now we consider the case when  $f(\theta)$  is a Gaussian function around  $\theta_0 \neq 0$  instead of the interfacial normal, i.e.  $\theta_0 = 0$ .

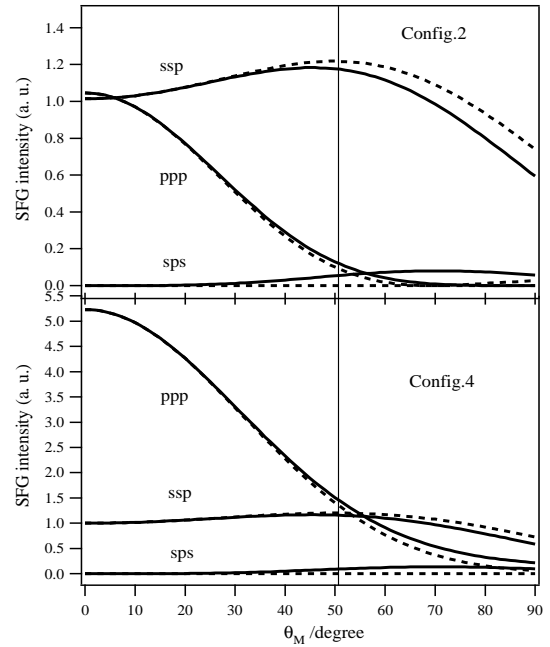


FIG. 3 SFG intensity of the free OH bond simulated with both slow motion limit (solid curves) and fast motion limit (dotted curves) following the procedure and parameters as Wei *et al.* [12]. In order to compare values in different configuration, the factor of  $\sec^2 \beta$  is included in the calculation, and all intensities are normalized to the ssp intensity in Config.4 when  $\theta_M = 0^\circ$ . The vertical line indicates  $\theta_M = 51^\circ$  given by Wei *et al.*

$$f(\theta) = \frac{1}{\sqrt{2\pi}\sigma^2} e^{-(\theta-\theta_0)^2/2\sigma^2} \quad (6)$$

Figure 4 shows simulation of Config.2 and Config.4 assuming a rotationally isotropic interface with  $\sigma = 0$ , using the same set of parameters as Wei *et al.* [12], and the average procedures [12, 24–26, 33–35, 37]. For data in all four configurations in Fig.2, a consistent  $\theta_0 = 33^\circ$  can be calculated from polarization and orientation analysis of all spectra in Figure 2 [28]. This result is in good agreement with the  $< 38^\circ$  tilt angle reported by Du *et al.* [6]. Figure 4 also indicates that the ssp intensity of the  $3700 \text{ cm}^{-1}$  is not sensitive to orientational changes and incident angle changes. However, intensity of this peak become very big in the ppp polarization with Config.4, Such sensitivity of the ppp spectra is extremely important for orientation sensitive measurement of the free O-H bond at the air/water interfaces [32, 36].

Our calculation showed that when  $\sigma = 0$ , fast motion and slow motion treatment converge. Further simulations show that in order to satisfy the intensities around the  $3700 \text{ cm}^{-1}$  peak in all four sets of data,  $\sigma$  can not exceed  $15^\circ$  and  $\theta_0$  changes from  $33^\circ$  to  $30^\circ$  as  $\sigma$  increases. Within such a relatively small range of  $\sigma$ , simulation results for fast and slow motions become almost indistinguishable. Step function of  $f(\theta)$  centered at  $\theta_0$  both give the same general conclusion. This clearly indicates

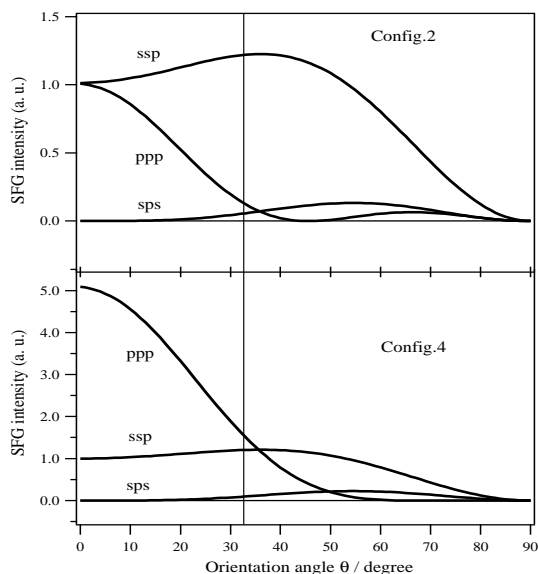


FIG. 4 Simulated SFG intensity of the free OH bonds at different tilt angle  $\theta_0$  with  $\sigma = 0^\circ$ . All curves are normalized to the ssp intensity in Config.4 with  $\theta = 0^\circ$ . The vertical line indicates the orientation which quantitatively explains the observed SFG data. Please note the difference of the scales for the two configurations.

that the assumption of  $f(\theta)$  centered at interfacial normal is out of the question.

Libration dynamics of the hydrogen bond in liquid water can be as fast as 0.1 ps [15, 38]. Therefore, from the observed SFG data our general conclusion is that such extremely fast libration dynamics of the tilted free OH bond at the air/water interface is only possible for orientational motion within a relatively narrow range. This new physical picture is illustrated in Fig.1c. Even though the orientational distribution is within the whole shadowed belt region centered at  $\theta$ , the orientational motion of each water molecule at the air/water interface is within a relatively narrow range from its equilibrium position.

In the SFG literatures on air/water interface, data were usually presented for the ssp polarization, except for very few cases [12, 27]. Polarization analysis were only performed by Wei *et al.* Our simulation showed strong dependence for the ppp intensity of the free OH bond spectra on the visible incident angle, especially when around  $\text{Vis} = 45^\circ$ . In this range, one or two degree change of the visible incident angle can cause significant percentage change of the ppp intensity, as can be indicated from data in Config. 2 and 3. Wei *et al.*'s SFG experiment was performed with  $\text{Vis} = 45^\circ$ . It happened to be that their analysis with ultrafast motion in a broad range of orientation centered around interface normal could just explain this set of data. Therefore, they did not consider other possible physical pictures [39]. Besides, Richmond *et al.* suggested two possible qualitative explanations for the lack of sps intensity of the free OH stretching mode in the SFG data [40].

One might expect that changing the incident angle of the infrared beam in the SFG experiment can also be useful for polarization and orientation. As we

have shown recently [33–35, 37], the polarization dependence depends on the ratios between different second order nonlinear polarizability tensors, which depend more significantly on the ratios between the Raman polarization derivative tensors than on those of the dipole moment derivatives. More importantly, even though changing the infrared incident angle may alter the total SFG intensity, polarization analysis with spectra in ssp and ppp polarizations is essentially independent from the incident angle of the infrared beam in the co-propagation experimental configuration, i.e. the visible and IR beams both in the same quadrant in the laboratory coordinates system [33–35, 37].

Polarization analysis can further determine the symmetry property of SFG spectral features [33–35]. Analysis indicates that both the sharp peak at  $\sim 3700 \text{ cm}^{-1}$  and the broad peak at  $\sim 3550 \text{ cm}^{-1}$  belong to  $C_{\infty v}$  symmetry; while both the hydrogen bonded broad peak  $\sim 3250 \text{ cm}^{-1}$  and  $\sim 3450 \text{ cm}^{-1}$  belong to symmetric type of the  $C_{2v}$  symmetry. Analysis also indicates that the existence of interfacial water molecules with two free OH bonds is not supported in SFG data [28]. If such interfacial water molecule indeed exist, it shall have  $C_{2v}$  symmetry, which should have shown clear ssp spectral intensity around  $3650 \text{ cm}^{-1}$  or much stronger ppp spectral intensity at the asymmetric stretching mode position of  $3750 \text{ cm}^{-1}$  in at least one of the four sets of SFG data [11, 18]. However, no such evidences are found in any of the SFG spectrum in Fig.2.

Thus,  $\sim 3550 \text{ cm}^{-1}$  peak with  $C_{\infty v}$  symmetry, which is apparent in the ppp polarization of Config.2 and Config.3, can be assigned to the hydrogen bonded OH of the interfacial water molecule with a free OH bond. This is further supported with the fact that  $3550 \text{ cm}^{-1}$  is also the frequency of the hydrogen bonded OH in water dimer [41]. Orientational analysis of its peak intensities in different experimental configurations indicates that this OH bond oriented with an angle around  $\sim 140^\circ$  from the interface normal. Indeed, with the free OH pointing to the vapor phase around  $35^\circ$ , the hydrogen bonded OH of the same molecule pointing into the liquid phase has to assume an orientation around  $\sim 140^\circ$ . This is consistent with the conclusion that the dipole vector of the interfacial water molecule is close to parallel to the interface [5, 9, 10, 18, 42]. The detail of this analysis shall be presented elsewhere.

Having SFG spectra in different polarizations and experimental configurations can also help on discerning ambiguous SFG spectral features [33–35]. For example, an ambiguous peak about  $3750 \text{ cm}^{-1}$  was recently invoked to fit the ssp SFG spectra of the air/water interface [43]. This peak was clearly not presented in Wei *et al.*'s spectra [12]. It is even clearer that there is no evidence for such a peak around  $3750 \text{ cm}^{-1}$  when one inspects carefully the four sets of ssp and ppp spectra, while the spectral intensity at  $3700 \text{ cm}^{-1}$  varied by almost two orders of magnitude in the ppp polarization. Therefore, we used four peaks, instead of five peaks [12, 43], for the fits of all spectra in Fig.2. A global fitting procedure was used for spectra in different polarizations, and the fitting parameters were stable [28]. Of

course, this conclusion can not be used to question the existence of the spectral peak around  $3750\text{ cm}^{-1}$  in the ssp polarization for the air/aqueous sodium halide solutions interfaces, which apparently became bigger with increasing bulk electrolyte concentration [43].

#### IV. CONCLUSION

In summary, quantitative analysis of the SFG spectra in different polarizations and experimental configurations for the air/water interface showed that the orientational motion of the interfacial water molecule is libratory, as fast as 0.1 ps it might be [15, 38], only within a limited angular range of less than  $15^\circ$  with the tilt angle around  $30^\circ$ . Therefore, the air/water interface is quite well-ordered. This picture is significantly different from the previous conclusion that the interfacial water molecule orientation varies over a broad range within the vibrational relaxation time, by Wei *et al.* using single SFG experimental configuration [12]. This progress provided a direct and detailed physical picture of the orientation and motion for the air/water interface.

#### V. ACKNOWLEDGMENT

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