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Absolute Orientation of Molecules with Competing Hydrophilic Head Groups at the Air/Water Interface Probed with Sum Frequency Generation Vibrational Spectroscopy[†]

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The constructive or destructive spectral interference between the molecular groups oriented up and down at the interface in the sum-frequency generation (SFG) spectra provides a direct measurement of the absolute orientation of these molecular groups. This simple approach can be employed to interrogate absolute molecular orientations other than using the complex absolute phase measurement in the SFG studies. We used the $-CN$ group in the *p*-cyanophenol (PCP) molecule as the internal phase standard, and we measured the phases of the SFG fields of the $-CN$ groups in the 3,5-dimethyl-4-hydroxy-benzonitrile (35DMHBN) and 2,6-dimethyl-4-hydroxy-benzonitrile (26DMHBN) at the air/water interface by measuring the SFG spectra of the aqueous surfaces of the mixtures of the PCP, 35DMHBN, and 26DMHBN solutions. The results showed that the 35DMHBN had its $-CN$ group pointing into the aqueous phase; while the 26DMHBN, similar to the PCP, had its $-CN$ group pointing away from the aqueous phase. The tilt angles of the $-CN$ group for both the 35DMHBN and 26DMHBN molecules at the air/water interface were around 25° - 45° from the interface normal. These results provided insights on the understanding of the detailed balance of the competing factors, such as solvation of the polar head groups, hydrogen bonding and hydrophobic effects, etc., on influencing the absolute molecular orientation at the air/water interface.

Key words: Sum frequency generation vibrational spectroscopy, Air/water interface, Molecule orientation, *p*-cyanophenol

I. INTRODUCTION

Knowledge of molecular orientation and alignment at surfaces and interfaces is of tremendous interest to scientists because of its relevance to understanding the detailed mechanisms of chemical reactions, molecular interactions, and phase transitions on the molecular surfaces. The orientation of the amphiphilic molecules at the aqueous interfaces is generally determined by its hydrophilic and hydrophobic (or lipophilic) groups, usually with its hydrophilic groups solvated into the aqueous phase and with the hydrophobic groups staying away from the aqueous phase [1]. Therefore, it is easy to understand the orientational structure of interfacial

molecule by identifying its hydrophilic and hydrophobic parts. However, this simple picture does not always work for complex molecules since the molecular orientation as well as conformation is the result of the detailed balance between various competing factors, such as the enthalpy and entropy of the solvation of the polar head groups, hydrogen bonding, and hydrophobic effects, etc. [1,2]. One of the simplest cases is to consider the orientation at the aqueous solution surface of a molecule with two hydrophilic groups attached at the opposite ends of a rigid phenyl ring, such as *p*-cyanophenol (PCP, $CN-C_6H_4-OH$) [3], *p*-hydroxy benzoic acid (PHBA, $HO-C_6H_4-COOH$), or *p*-nitroamine (PNA, $H_2N-C_6H_4-NO_2$), etc. One may have to scratch his head to try to figure out which end of these molecules is oriented up or down at the aqueous solution surfaces. And one of the possibilities is that they might even lie flat at the aqueous solution surface.

Polarization dependent vibrational spectroscopic techniques, such as the linear polarization modulated infrared reflection absorption spectroscopy (PM-IRRAS) and the nonlinear sum frequency generation vibrational spectroscopy (SFG-VS), have been proven

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useful techniques to derive information on the alignment and orientation of the molecular groups at interface or in thin films [4-9]. However, as an incoherent technique, PM-IRRAS can not provide information on the phase, *i.e.* the sign, of the electric field of the vibrational dipoles at the interface. Thus, it can not directly provide information on the absolute orientation of the corresponding molecular groups. On the other hand, SFG-VS, as well as the second order nonlinear second harmonic generation (SHG) spectroscopy, both of which have been proven to be the interfacial specific spectroscopic techniques [10-14], is the coherent radiation from the interfacial dipoles. Therefore, specially designed procedures with SFG-VS and SHG can be developed to directly measure the phase, *i.e.* the sign, of the electric field of the vibrational or electronic dipoles, respectively, at the interface [15-31]. Thus, the information about the absolute orientation of the corresponding molecular groups can be directly determined. Furthermore, issues and procedures in SFG-VS and SHG on accurate determination of the orientational tilt angles of molecular groups and chromophores at the interface have been developed over the years [7,9,32-37], and many successful applications have been achieved [38-44].

Direct measurement of the phase in the SFG-VS based on the coherent nature of the SFG process often requires complex experimental and data processing procedures [15,16,25,30,31]. Actually, since most of the time the absolute orientation, as well as the corresponding sign of the SFG field, of one or sometimes more than one interfacial molecular groups are known, relative phases or signs between the SFG vibrational spectral features from different molecular groups can provide detailed information on the absolute orientation of the interfacial molecular groups, as well as the conformation of the interfacial molecules [3,27,45]. These spectra features with known phases or signs actually serve as the internal standard in the phase measurement. The relative phases or signs can be obtained from SFG spectral fitting when these spectral features corresponding to the different molecular groups or vibrational modes at the same interface are overlapping or interfering with each other in the same wavelength range or spectral region [3,27,45]. If no such overlapping features or interference is available, a phase standard has to be employed to compare the phases or signs of different spectral features in different spectral regions. In such cases, a quartz crystal reference is usually used as the external phase standard in the SFG-VS and SHG phase measurements, and some extra experimental procedures have to be introduced in addition to the standard SFG or SHG measurements [9,15,16,25,30,31,36]. In the latter case, one alternative to obtain the phase or sign information of a particular interfacial molecular group is to introduce a molecule with the same molecular group and known absolute orientation to the interface to serve as the internal phase standard in the

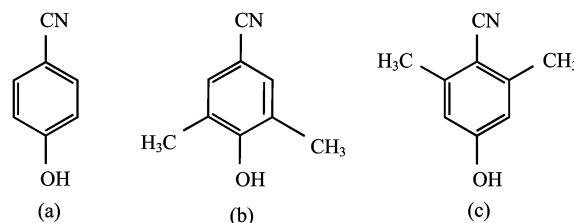


FIG. 1 Structures of three molecules. (a) *p*-cyanophenol(4-hydroxy-benzonitrile, or PCP), (b) 35DMHBN, and (c) 26DMHBN.

SFG and SHG measurement. The spectral feature of this introduced molecular group would interfere either constructively or destructively with that of the interfacial molecular group under investigation to report the phase or sign of the SFG field of this particular molecular group.

In this work, we used the $-CN$ group in the *p*-cyanophenol (PCP) molecule as the internal phase standard since its absolute orientation was known [3], and we measured the phases of the SFG fields of the $-CN$ groups in the 3,5-dimethyl-4-hydroxybenzonitrile (35DMHBN) and 2,6-dimethyl-4-hydroxybenzonitrile (26DMHBN) at the air/water interface by measuring the SFG spectra of the aqueous surfaces of the mixtures of the PCP, 35DMHBN, and 26DMHBN solutions. The structures of the three molecules are illustrated in Fig.1. The results showed that the 35DMHBN had its $-CN$ group pointing into the aqueous phase, *i.e.* with its SFG field in the opposite sign with that of the PCP; while the 26DMHBN, similar to the PCP, had its $-CN$ group pointing away from the aqueous phase, *i.e.* with its SFG field in the same sign with that of the PCP. It is interesting to find that the different positions of the two methyl groups on the phenyl ring in the 35DMHBN and 26DMHBN molecules actually resulted in the completely tipping over of the molecular orientation, which made the $-OH$ group in the 35DMHBN molecule non-solvated. These results provided insights on the competing factors, such as solvation of the polar head groups, hydrogen bonding and hydrophobic effects, etc., on influencing the absolute molecular orientation at the air/water interface.

II. BASIC THEORY OF INTERFERENCE IN SFG-VS

Sum frequency generation (SFG) is the second order nonlinear process when two photons at the frequency ω_1 and ω_2 simultaneously interact with a molecule to generate a photon with the frequency at the sum of the two frequencies, *i.e.* $\omega = \omega_1 + \omega_2$. It has been known that because of the symmetry requirement, all the even order nonlinear processes, including the second order SFG process, are surface specific and can be used as surface selective probes [46]. In the SFG vibrational spectroscopy, ω_1 is usually fixed at a visible light fre-

quency, and the SFG signal at ω is recorded at different ω_2 in the infrared frequencies. When the ω_2 is in resonance with the vibrational frequency of the interfacial molecules, the SFG signal is enhanced to give the spectroscopic response of the interfacial molecular vibrations [7,9]. The intensity of the SFG signal ($I(\omega)$) is proportional to the intensities of the incident visible and infrared light beams ($I(\omega_1)$ and $I(\omega_2)$, respectively), as well as the square of the effective susceptibility $\chi_{\text{eff}}^{(2)}$ of the interface [7,9].

$$I(\omega) \propto \left| \chi_{\text{eff}}^{(2)} \right|^2 I(\omega_1) I(\omega_2) \quad (1)$$

Here, the effective second-order susceptibility $\chi_{\text{eff}}^{(2)}$ is the scalar tensorial product of the SF, visible and infrared optical electric field vectors with the susceptibility tensors of the molecular system [7,9].

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

where $\hat{\mathbf{e}}(\omega_i)$ and $\mathbf{L}(\omega_i)$ are the unit electric field vectors for frequency ω_i and the Fresnel factor for frequency ω_i , respectively. The susceptibility tensor $\chi_{ijk}^{(2)}$ contains all the information of the molecular interface, including the density, the molecular orientation, and orientational distribution, as well as the molecular polarizability, which contains the information of the spectroscopic response, of the interfacial molecules [7,9,47].

$$\begin{aligned} \chi_{ijk}^{(2)} &= \chi_{\text{NR}}^{(2)} + \chi_{\text{R}}^{(2)} \\ &= \chi_{\text{NR}}^{(2)} + \sum_q \frac{A_{q,ijk}}{\omega_2 - \omega_q + i\Gamma_q} \end{aligned} \quad (3)$$

where $\chi_{\text{NR}}^{(2)}$ and $\chi_{\text{R}}^{(2)}$ denote the terms for the non-resonant and the resonant contributions, respectively. $A_{q,ijk}$, ω_q , and Γ_q represent the sum frequency strength factor tensor, resonant frequency, and damping constant of the q th molecular vibrational mode, respectively. For dielectric interfaces, such as liquid interfaces, the non-resonant term $\chi_{\text{NR}}^{(2)}$ is usually small and real, in many cases can be negligible comparing with the resonant terms. For metal surface, $\chi_{\text{NR}}^{(2)}$ is usually complex and is comparable to or even larger than the resonant terms.

The information of the density, the orientation, and the orientational distribution is contained in the term $A_{q,ijk}$. Since $A_{q,ijk}$ is a third rank pseudoscalar tensor, the sign of the $A_{q,ijk}$ shall change when the average orientation of the corresponding interfacial molecular group is changed from pointing up to the upper phase to pointing down into the lower phase [46]. This is the very basis for the above-mentioned method by introduction of a molecular group with known orientation at the particular interface to serve as the internal reference for the sign of the SF field. According to the Eq.(3),

when the absolute value of the total $\chi_{ijk}^{(2)}$ become significantly small after introducing the reference molecular group, one can conclude that the molecular group under investigation points to the opposite direction from the interface in comparison to the reference group, and vice versa. For example, such destructive interference due to oppositely oriented surface dipoles was identified for the air/methanol and air/acetone aqueous solution surfaces [38,39].

III. EXPERIMENTS

The details of the laser system were described previously [48-50]. Briefly, the 10 Hz and 23 ps SFG spectrometer laser system (Ekspla) is in a co-propagating configuration. The efficiency of the detection system has been improved for the weak SFG signal of the air/water interface. A high-gain low-noise photomultiplier (Hamamatsu, R585) and a two channel boxcar average system (Stanford research systems) are integrated into the Ekspla detection system. The voltage of R585 was 1.3 kV in the measurement for the air/aqueous solution interface and 900 V for the Z-cut quartz surface. The wavelength of the visible beam is fixed at 532 nm and the full range of the IR tunability is 1000-4000 cm^{-1} . The incident angle of visible beam and IR beam is $45^\circ \pm 1^\circ$ and $55^\circ \pm 1^\circ$ respectively. Each scan of SFG spectrum was with a 5 cm^{-1} increment and was averaged over 300 laser pulses per point. Each spectrum was repeated for at least several times. The energy of the visible beam is typically less than 300 μJ and that of the IR beam is less than 200 μJ around 2100 and 2300 cm^{-1} . The measured spectra is firstly normalized to the energy of the incident laser beams, and then normalized to the SFG signal of Z-cut quartz (also normalized by the energy of the incident lasers), the details of the procedure of normalization can be found in Refs.[47,51,52].

3,5-dimethyl-4-hydroxy-benzonitrile (Acros Organics, purity>97%), *p*-cyanophenol (Acros Organics, purity>99%), and 2,6-dimethyl-4-hydroxy-benzonitrile (Maybridge, purity>97%) were used without further purification. The aqueous solution was made with ultrapure water from standard Millipore treatment (18.2 M Ω -cm), and the solution was sonicated for more than three hours in order to ensure full dissolution.

The aqueous solution was housed in a round Teflon beaker (diameter=5 cm) for SFG measurement. All measurements were carried out at controlled room temperature ($22.0 \pm 1.0^\circ\text{C}$) and humidity (40%). The whole experimental setup on the optical table was covered in a plastic housing to reduce the air flow. No detectable evaporation effect was observed in each scan of SFG spectrum. This was checked with consecutive scans in both directions.

IV. RESULTS AND DISCUSSION

We were interested in understanding the molecular orientation of the 35DMHBN and 26DMHBN at the air/water interface mainly because it is interesting to see how different molecular groups or different factors can influence the orientation of molecules at the water surfaces. As one can see from their structures in Fig.1, the difference between the 35DMHBN and 26DMHBN is whether the two $-\text{CH}_3$ groups are on the $-\text{OH}$ group side (for 35DMHBN) or on the $-\text{CN}$ group side (for 26DMHBN). Both the $-\text{CN}$ and $-\text{OH}$ groups are hydrophilic. This difference with the $-\text{CH}_3$ groups may affect the orientation of two molecules at the interface.

Even though the dipole moment of the $-\text{CN}$ group is more than twice of that for the $-\text{OH}$ group [53], the *p*-cyanophenol (PCP), whose structure is shown in Fig.1, at the air/water interface has its $-\text{OH}$ group immersed into the aqueous phase and its $-\text{CN}$ pointed away from the aqueous phase [3]. This is mainly because the $-\text{OH}$ group can form hydrogen bond with the water molecules in the aqueous phase and such orientation with the $-\text{OH}$ pointing 'down' at the interface is energetically favorable.

In a recent study, Richmond and co-workers investigated the SFG spectra of the $-\text{CN}$ groups of the *p*-cyanophenol(PCP) and *m*-cyanophenol(MCP) molecules at aqueous solution interfaces [3]. From the significantly different interference patterns between the $-\text{CN}$ SFG field and the SFG field of the non-resonant background, believed to be the contribution from the interfacial water molecules, they found that the $-\text{CN}$ SFG fields for the PCP and MCP bore opposite signs. Based on these data, they concluded that the PCP molecules at the aqueous solution surfaces had their $-\text{CN}$ group pointing out from the interface with a tilt angle around 65° to 80° from the interface normal; while the MCP molecules had their $-\text{CN}$ groups pointing into the aqueous phase with a tilt angle around 96° to 106° from the interface normal.

Figure 2 shows the SFG spectra of the $-\text{CN}$ group at the air/water interfaces of 3 mmol/L 35DMHBN and 3 mmol/L 26DMHBN aqueous solutions taken in three different polarization combinations, namely, ssp, ppp, and sps polarization combinations. Here, s denotes the polarization perpendicular to the incident plane, and p denotes polarization within the incident plane. The index ssp denotes that the polarizations for the SF, visible, and infrared optical fields are in the s, s, and p polarizations, respectively; and so on for the ppp and sps polarization combinations [7,9].

As shown in Fig.2, the peak position for 35DMHBN is slightly blue shifted and the peak itself is also slightly broader than that of the 26DMHBN. Fitting of the spectra in Fig.2 with Eq.(3) gives $\omega_q=2231.8\pm 0.2\text{ cm}^{-1}$, $\Gamma_q=9.6\pm 0.2\text{ cm}^{-1}$ for 35DMHBN and $\omega_q=2225.1\pm 0.2\text{ cm}^{-1}$, $\Gamma_q=8.3\pm 0.2\text{ cm}^{-1}$. The intensity ratio between the ssp, ppp, and sps polarization combinations

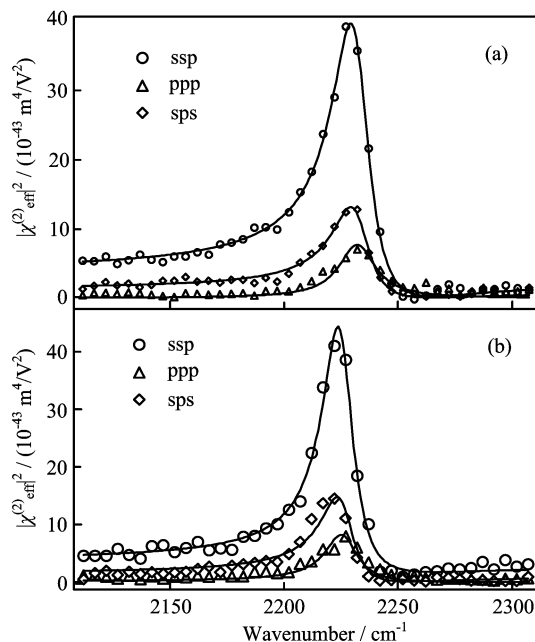


FIG. 2 ssp, ppp, and sps SFG spectra of the nitrile ($-\text{CN}$) group at the surface of 3 mmol/L aqueous solutions of (a) 35DMHBN and (b) 26DMHBN. It is noticeable that the $-\text{CN}$ spectra of the 35DMHBN are apparently broader than those of the 26DMHBN, and the peak position of the $-\text{CN}$ spectra of the 35DMHBN are a few cm^{-1} blue shifted compared with that of the 26DMHBN, even though the two sets of spectra appeared to be very similar.

can be used to derive the tilt angle of the $-\text{CN}$ groups [3,7,9]. Since these intensity ratios for the 35DMHBN and 26DMHBN are very close to each other, the tilt angles obtained from the SFG data for these two molecules are also similar. By following the same procedure and using the same Raman depolarization ratio for the $-\text{CN}$ groups as in Ref.[3], the tilt angle of the $-\text{CN}$ groups for the 35DMHBN and 26DMHBN was determined as about 25° - 45° from the interfacial normal. However, without knowing the absolute or relative phases of the SFG fields, one can not determine whether the $-\text{CN}$ groups pointed "up" or "down" from the interface plane [15].

Unlike the case for PCP and MCP [3], the shapes of the $-\text{CN}$ spectra for the 35DMHBN and 26DMHBN molecules were similar to each other in all three polarization combinations. This latter fact seemed to imply that the $-\text{CN}$ groups of the interfacial 35DMHBN molecules oriented in the same direction as the $-\text{CN}$ groups of the interfacial 26DMHBN molecules, if following the same arguments as for the case of PCP and MCP [3]. Intuitively, since it is known that the PCP molecule has its $-\text{OH}$ group pointing into the aqueous phase [3], it is reasonable to assume that the $-\text{OH}$ group of the 26DMHBN molecule, which has two more hydrophobic $-\text{CH}_3$ groups on each side of the $-\text{CN}$ group to make this end of the molecule apparently more hy-

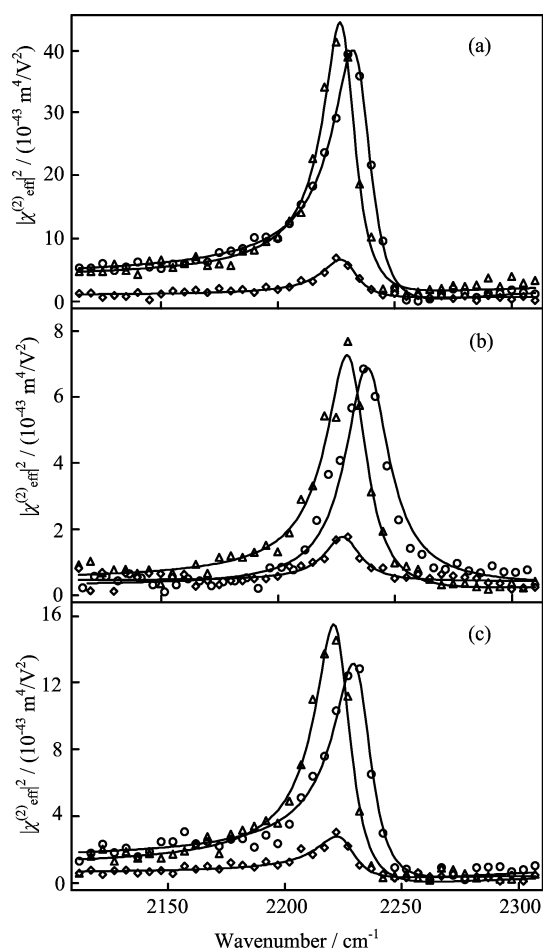


FIG. 3 Comparison of the SFG spectra of the $-\text{CN}$ group at the surfaces of the 3 mmol/L 35DMHBN (\circ), 3 mmol/L 26DMHBN (Δ), and the mixture of 1.5 mmol/L 35DMHBN and 1.5 mmol/L 26DMHBN (\diamond) (total concentration 3 mmol/L) solutions in three polarization combinations (a) ssp, (b) ppp, and (c) sps. It is apparent that in all three polarization combinations, the $-\text{CN}$ spectral intensity is greatly reduced for the mixture solution, indicating that the $-\text{CN}$ group for the 35DMHBN and 26DMHBN molecules oriented to opposite directions.

drophobic, must point down into the aqueous phase. If all these are true, then the 35DMHBN should also have its $-\text{OH}$ group point into the aqueous phase, since its $-\text{CN}$ group appeared to point to the same direction as the $-\text{CN}$ group of the 26DMHBN molecule. However, more experimental evidences suggested that this is not true.

To illustrate this, the $-\text{CN}$ group SFG spectra from the surface of the equal concentration mixture of 35DMHBN and 26DMHBN aqueous solutions were measured and presented in the Fig.3. If the $-\text{CN}$ groups of the 35DMHBN and 26DMHBN molecules oriented to the same direction, the SFG spectra intensity from the mixture solution surface is expected to remain unchanged. However, the data in Fig.3 proved it to be

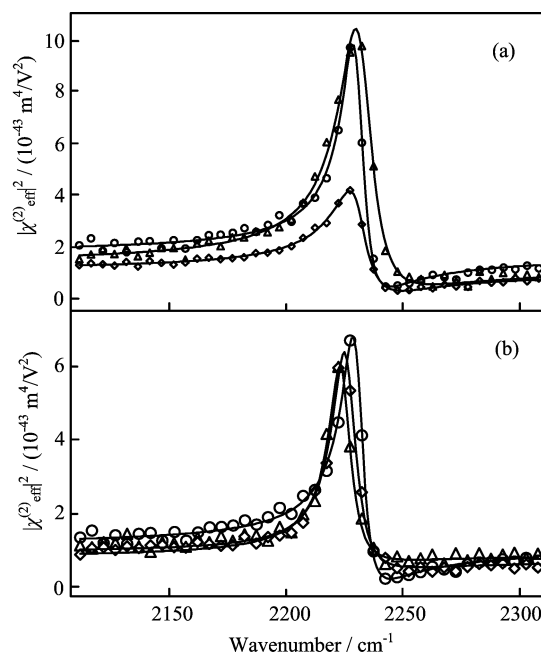


FIG. 4 Comparison of the $-\text{CN}$ group SFG spectra in the ssp polarization combinations for the aqueous surface of (a) 60 mmol/L PCP (\circ), 1.5 mmol/L 35DMHBN (Δ), and mixture of 30 mmol/L PCP and 0.75 mmol/L 35DMHBN solutions (\diamond); (b) 50 mmol/L PCP (\circ), 1.1 mmol/L 26DMHBN (Δ), and mixture of 25 mmol/L PCP and 0.55 mmol/L 26DMHBN solutions (\diamond). It is apparent that the $-\text{CN}$ group SFG intensity from the surface of the PCP/35DMHBN mixture was significantly reduced; while that of the PCP/26DMHBN mixture remained almost unchanged. These suggested that the $-\text{CN}$ group of the interfacial 35DMHBN molecule oriented in the opposite direction as that of the interfacial PCP or 26DMHBN molecule.

otherwise. In all three polarization combinations, the SFG spectral intensity from the mixture solution surface appeared to be significantly smaller than that of the individual 35DMHBN or 26DMHBN aqueous solutions. Such destructive interference pattern in SFG spectra clearly indicates that the $-\text{CN}$ groups for the 35DMHBN and 26DMHBN molecules oriented to opposite directions from the interface plane.

To confirm this, the SFG spectra in the ssp polarization combination of the PCP/35DMHBN and PCP/26DMHBN mixture solution surfaces were also measured, as presented in Fig.4. Even though the SFG spectral intensity for the PCP/35DMHBN mixture solution surface was not as small as that of the 35DMHBN/26DMHBN mixture solution surface, as shown in Fig.3, it is clear that the interference between the PCP and 35DMHBN is destructive (upper panel); while the PCP and 26DMHBN is constructive (lower panel). This result is consistent with the destructive interference observed for the 35DMHBN/26DMHBN mixture solution surface as shown in Fig.3. Therefore, one can conclude unambiguously that the 35DMHBN

molecule oriented to the opposite direction from the interface plane in comparison to the orientations of the PCP and 26DMHBN molecules.

The orientation of the 35DMHBN means that the presence of the two $-\text{CH}_3$ groups on each side of the $-\text{OH}$ group in the 35DMHBN molecule does make this end of the molecule more hydrophobic, and tips the molecule upside down at the air/water interface. The presence of the two $-\text{CH}_3$ groups may also prevent the formation of effective hydrogen bonding network between the $-\text{OH}$ group and the water molecules in the aqueous phase. This can certainly change the balance of the energetics for the interfacial 35DMHBN molecule, which ultimately controls the orientation of the molecule at the interface. The fact that the 35DMHBN and 26DMHBN molecules orient in opposite directions at the air/water interface suggests that it is crucial to quantitatively understand the balance between the competing factors, such as solvation of the polar head groups, hydrogen bonding, and hydrophobic effects, etc., on influencing the absolute molecular orientation at the air/water interface, as well as other interfaces.

The fact that the 35DMHBN and 26DMHBN molecules orient in opposite directions at the air/water interface can also be used to understand the fact that the SFG spectra for the $-\text{CN}$ group is broader and blue shifted for the 35DMHBN those for the 26DMHBN, as shown in Fig.2. It was known that the water solvated $-\text{CN}$ groups were usually with broader infrared spectral features and are usually blue shifted compared with the $-\text{CN}$ groups in the less hydrophilic solvents or environment [54]. For the 35DMHBN molecules at the air/water interface, their $-\text{CN}$ groups point directly into the aqueous phase and are solvated by the water molecules; while for the 26DMHBN molecules, their $-\text{CN}$ groups are up in the air and not solvated by the water molecules, *i.e.* in a more hydrophobic environment. Therefore, one may naturally wonder what shall be the hydrogen bonding structure of the 35DMHBN and 26DMHBN solution surfaces. It would also be interesting to look at the non-solvated $-\text{OH}$ groups of the 35DMHBN molecules at the air/water interface. SFG measurements to study the $-\text{OH}$ and water spectra at these interfaces have been conducted in our laboratory. The results shall be reported elsewhere.

Moreover, the results reported here indicated that it is feasible to introduce chemical groups as internal phase standard in the SFG spectral measurement to obtain the information on the absolute as well as the relative signs of the SF fields at the interface. Since the SFG spectra of the $-\text{CN}$ groups of the surface of the 35DMHBN and 26DMHBN aqueous solutions share the similar interference pattern with the non resonant background term and they turned out to be oriented in opposite directions, the interference pattern with the non-resonant background may not be used as a common criterion to obtain the phase information in the

SFG-VS studies [3].

V. CONCLUSION

In this work, the absolute orientations of the 3,5-dimethyl-4-hydroxy-benzonitrile and 2,6-dimethyl-4-hydroxy-benzonitrile molecules at the air/water interface were measured with sum frequency generation vibrational spectroscopy. Other than employing the experimentally complex procedures for measuring the phase of the SFG fields, the simple approach by measuring the common SFG spectral of the mixture solutions of different molecules was used. We found that the $-\text{CN}$ groups of the 35DMHBN and 26DMHBN molecules at the air/water interface oriented with a tilt angle around 25° - 45° from the interfacial normal. We also found that the 35DMHBN molecules at the air/water interface oriented with their $-\text{CN}$ group pointing "down" into the aqueous phase; while the 26DMHBN molecules oriented with their $-\text{CN}$ group pointing "up" into the air phase. These results proved that in the SFG surface studies, it is not only feasible but also very useful to introduce molecular groups as internal phase reference, which can spectroscopically interfere with the molecular groups at a given interface. It is a simple and nevertheless effective way to obtain the information on the orientation and alignment of the molecular groups at the molecular interfaces or thin films. These results also provided insights on the detailed balance of the competing factors, such as solvation of the polar head groups, hydrogen bonding and hydrophobic effects, etc., on influencing the absolute molecular orientation at the air/water interface.

VI. ACKNOWLEDGMENTS

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