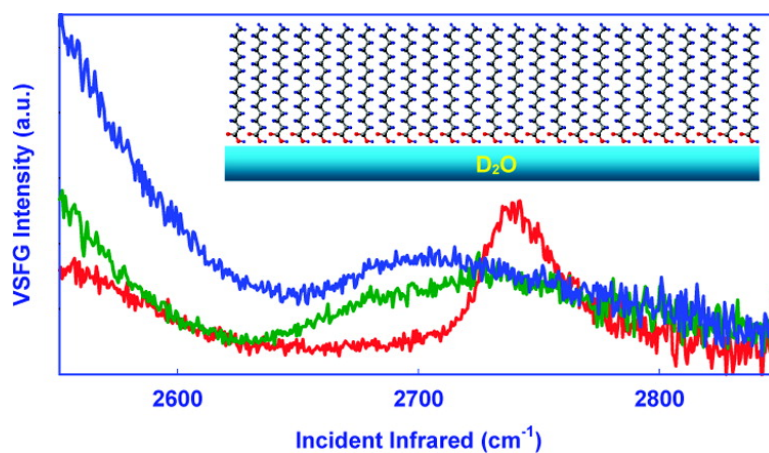


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## Dangling OD Confined in a Langmuir Monolayer

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**Abstract:** Novel structural features of water confined in lipid Langmuir monolayers are revealed. Using vibrational sum frequency generation spectroscopy at the air/D<sub>2</sub>O/monolayer interface, dangling OD bonds were investigated. Upon increasing the monolayer surface coverage, the dangling OD stretching mode showed a marked frequency red-shift as well as spectral structure. Furthermore, the dangling OD was found to exist even when a D<sub>2</sub>O surface was fully covered by the lipid molecules. This phenomenon was observed in monolayers formed with dipalmitoylphosphatidylcholine and with palmitic acid. The frequency red-shift of the dangling OD is interpreted to be due to the perturbation imposed by the lipid hydrophobic tail groups. The observed persistence of the dangling OD at full surface coverage is related to hydrophobicity-induced drying.

## Introduction

Water in confining geometries exists in many physical, chemical, and biological processes and plays critical roles in these processes.<sup>1,2</sup> Protein folding, biological membrane formation, lung surfactant function, catalysis, and heterogeneous aerosol processing are just a few examples involving confined water. A detailed understanding of confined water will not only improve our current knowledge about water itself but also lead to significant advances in our understanding of the structure and process with which confined water is associated. For instance, recent investigations have demonstrated that adding a water-mediated interaction to an established Hamiltonian can significantly improve protein structure prediction.<sup>3,4</sup> Studies on interfacial water structure of sea salt solutions have revealed that halides can be present in the interfacial water layer, a seminal finding that has a direct impact on heterogeneous reaction modeling in atmospheric aerosol chemistry.<sup>5,6</sup> In this report, we present our recent studies on a unique type of water bond, the dangling bond of surface water, confined in a two-dimensional environment, a Langmuir monolayer. D<sub>2</sub>O was utilized as a proxy for H<sub>2</sub>O.

Dangling bonds of water are observed at air/water,<sup>7</sup> air/ice,<sup>8,9</sup> and water/hydrophobic interfaces<sup>10,11</sup> and at cluster surfaces.<sup>12</sup>

They reside at the utmost surface layer and are sensitive to environmental perturbations by surface reaction and adsorption. Their existence is also characteristic of water structure observed on extended hydrophobic surfaces,<sup>10,11</sup> thus relevant to hydrophobicity-induced drying.<sup>13</sup>

A Langmuir monolayer is a monomolecular insoluble film spread onto a liquid surface.<sup>14,15</sup> It is commonly formed with amphiphilic molecules such as lipids on an aqueous surface. The amphiphilic molecule has two distinct moieties, a hydrophobic nonpolar tail and a hydrophilic polar head. The Langmuir monolayer is where hydrophobicity and hydrophilicity meet. In this study, we use vibrational sum frequency generation (VSFG) spectroscopy to investigate how dangling bonds of water (i.e., the dangling OD of D<sub>2</sub>O) respond to the presence of a Langmuir monolayer.

VSFG spectroscopy was used because of its surface selectivity and sensitivity to OD bonds at the air/water interface. VSFG is a second-order nonlinear optical spectroscopy that requires lack of inversion symmetry.<sup>16</sup> To drive a sum frequency generation (SFG) process at the interface, two pulsed laser beams, one visible and the other infrared, are utilized. When the infrared pulse has its frequency tuned to match the vibrational frequency of a surface molecular species, an SFG signal enhancement occurs. Thus, VSFG provides a vibrational spectrum from the interface. VSFG is one of the very few techniques that can directly probe the air/water interface.<sup>17</sup> The detailed SFG theory

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can be found in previous studies.<sup>18–20</sup> Briefly, the SFG signal ( $I_{\text{SFG}}$ ) reflected from the interface is proportional to the absolute square of the surface second-order nonlinear susceptibility ( $\chi^{(2)}$ ), as described in eq 1,

$$I_{\text{SFG}} \propto |\chi^{(2)}|^2 \propto |\chi_{\text{NR}}^{(2)} + \sum_v \chi_v^{(2)}|^2 \quad (1)$$

where  $\chi^{(2)}$  consists of resonant terms ( $\chi_v^{(2)}$ ) and a nonresonant term ( $\chi_{\text{NR}}^{(2)}$ ). The resonant macroscopic nonlinear susceptibility,  $\chi_v^{(2)}$ , is related to  $\omega_{\text{IR}}$ , the frequency of the incident infrared beam, through eq 2,

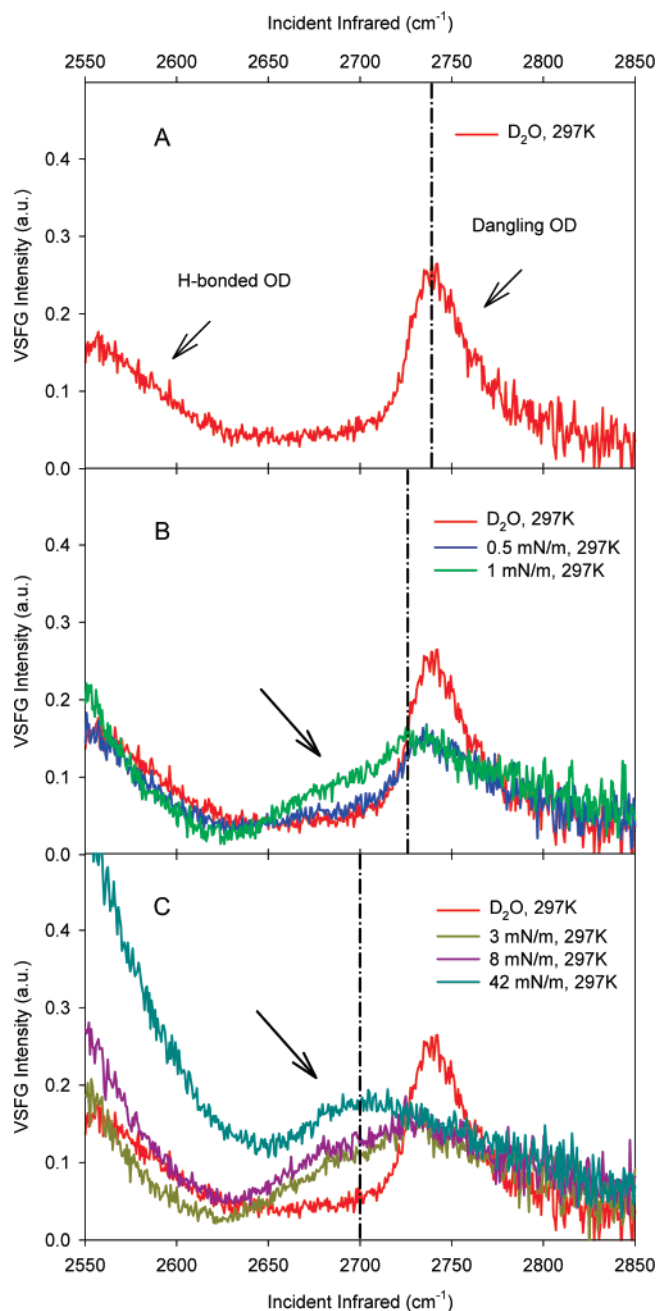
$$\chi_v^{(2)} \propto \frac{A_v}{\omega_{\text{IR}} - \omega_v + i\Gamma_v} \quad (2)$$

where  $A_v$  is the strength of the transition moment,  $\omega_v$  is the frequency of the transition moment, and  $\Gamma_v$  is the line width of the transition.

## Results and Discussion

The VSFG spectrum of the pure (neat) D<sub>2</sub>O surface in the dangling OD stretching region is shown in Figure 1A. The dangling OD stretching peak is located at 2735 cm<sup>-1</sup>. The left-hand portion of the VSFG spectrum is from the hydrogen-bonded OD stretch. Water forms a three-dimensional hydrogen-bonding network in the bulk, while at the interface, a fraction of the surface water molecules have only one of their two hydrogens hydrogen-bonded to an adjacent water molecule.<sup>7</sup> The non-hydrogen-bonded OH is the dangling OH (free OH), and its OH stretching mode arises at 3700 cm<sup>-1</sup> in the VSFG spectrum of H<sub>2</sub>O.<sup>7</sup> For D<sub>2</sub>O, the isotope effect shifts the frequency to 2735 cm<sup>-1</sup>. In this study, we explore the situation when a Langmuir monolayer covers the D<sub>2</sub>O surface. What happens to the dangling OD? The first subject of investigation is the chain-perdeuterated dipalmitoylphosphatidylcholine (*d62*-DPPC) Langmuir monolayer. The chain-perdeuterated DPPC was used to avoid spectral overlap in the 2600–2800 cm<sup>-1</sup> region.

Figure 1B,C shows a series of VSFG spectra in the dangling OD region obtained under different DPPC surface coverages. Here surface pressure is used to indicate surface coverage. Surface pressure is the difference between the surface tension of water and the surface tension of the monolayer. Thus, higher surface pressure corresponds to higher DPPC surface coverage. It is clear from Figure 1B,C that the presence of DPPC causes dramatic spectral changes of the dangling OD band. When DPPC adsorbs at the air/D<sub>2</sub>O interface, its hydrophilic head hydrates by forming hydrogen bonds with interfacial waters. This hydration process is expected to consume dangling ODs. As shown in Figure 1B, at 0.5 mN/m, the dangling OD indeed decreases its intensity, while its frequency remains constant (refer to the blue curve). Following this trend, one might expect the dangling OD band to eventually vanish if the DPPC surface coverage is increased. However, the 1 mN/m spectrum (green curve) in Figure 1B demonstrates that the interfacial dangling OD has a far more complicated behavior than one might expect.



**Figure 1.** *ssp* VSFG spectra of the D<sub>2</sub>O surfaces in the dangling OD stretching region at 297 K: (A) air/D<sub>2</sub>O surface; (B,C) air/D<sub>2</sub>O/*d62*-DPPC monolayer surfaces under different surface coverages (the air/D<sub>2</sub>O surface spectrum, the red curve, is re-shown for comparison). “au” means arbitrary units.

By further increasing DPPC surface coverage to 1 mN/m (Figure 1B), the dangling OD peak does not further decrease its intensity; rather, it red-shifts to ~2720 cm<sup>-1</sup>. In addition, a shoulder grows between 2650 and 2710 cm<sup>-1</sup>. With further increasing surface pressure (3, 8, and 42 mN/m; Figure 1C), this shoulder continues to grow into a broad peak centered at ~2700 cm<sup>-1</sup> at a surface pressure of 42 mN/m. At 42 mN/m, the D<sub>2</sub>O surface is covered by the DPPC molecules at the maximum surface number density. Yet, we still observe the dangling OD peak. These structural features have not been previously observed.

To understand the spectral variations shown in Figure 1, three fundamental questions are addressed. What is the cause of the

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frequency red-shift? How is the spectral structure (i.e., asymmetric band broadening) explained? How can the dangling OD stretch exist when the D<sub>2</sub>O surface is fully covered by DPPC?

The frequency red-shift no doubt indicates a perturbation imposed by DPPC molecules on the dangling OD. The environmental perturbation can be indirect or direct. An indirect perturbation would arise from perturbation through the hydrogen-bonded OD that then intramolecularly couples to the dangling OD. The intramolecular coupling can red-shift the dangling OD stretch. This may occur if DPPC can strengthen the hydrogen-bonding network through head group hydration. Direct perturbation would be due to the direct interaction between the DPPC molecule and the dangling OD. This effect is intermolecular.

Previous vibrational studies on water provide a resource for elucidating whether an indirect or direct perturbation is the dominating factor to cause the observed frequency red-shift. A free H<sub>2</sub>O monomer has two stretching bands in its vibrational spectrum, the asymmetric stretch (HOH-*as*) and the symmetric stretch (HOH-*ss*). When one OH becomes hydrogen-bonded while the other remains free, the HOH-*as* and HOH-*ss* no longer exist due to a decoupling. Two new bands appear. The hydrogen-bonded OH stretch will appear in the low-frequency region, below 3500 cm<sup>-1</sup> (below 2600 cm<sup>-1</sup> for D<sub>2</sub>O), while the dangling OH stretch appears at ~3700 cm<sup>-1</sup>.<sup>12</sup> Though decoupled, the dangling OH stretch can still be affected by the hydrogen-bonded OH since the decoupling is not absolutely complete.<sup>21,22</sup> Therefore, there is a possibility that the frequency red-shift observed in Figure 1 is due to the hydrogen-bonding network variation induced by the DPPC hydration, instead of a direct intermolecular interaction between DPPC and the dangling OD bond. However, in the studies of benzene-(H<sub>2</sub>O)<sub>*n*</sub> clusters (*n* = 2–7) performed by Pribble et al. using resonant ion-dip infrared spectroscopy,<sup>12</sup> when the cluster size varied from 2 to 7, the hydrogen-bonded OH stretching modes changed significantly, but the free OH stretch was found virtually unchanged, with 3722 cm<sup>-1</sup> for (H<sub>2</sub>O)<sub>2</sub>, 3716 cm<sup>-1</sup> for (H<sub>2</sub>O)<sub>3</sub>, and 3713 cm<sup>-1</sup> for (H<sub>2</sub>O)<sub>7</sub>. This study suggests that the coupling between the two OHs is not strong. A recent quantum-chemical calculation on water clusters with size varying from (H<sub>2</sub>O)<sub>6</sub> to (H<sub>2</sub>O)<sub>30</sub> demonstrated that the dangling OH stretch is negligibly affected by the hydrogen-bonding network, once again supporting that the coupling between the two ODs in the dangling water is weak.<sup>23</sup> However, these are cluster studies, and one might argue that the bonding environment is very different relative to the surface of bulk water. Yet, a VSFG study on the surface of water and ice showed that the free OH stretch is located at the same location, 3700 cm<sup>-1</sup>, even though the water and ice hydrogen-bonded OH stretching mode frequencies and intensities differ significantly.<sup>9</sup> The strengthening of the hydrogen-bonded surface water molecules in ice would have red-shifted the free OH peak as compared with that of liquid water if the coupling of the two OHs were strong. Yet, this is not the case. A VSFG study on aqueous acid surfaces showed that even adding acid (HCl, HBr, HI) significantly perturbs the hydrogen-bonded network of surface water; yet, the free OH stretch position remains unchanged at 3700 cm<sup>-1</sup>.<sup>24</sup> Furthermore, a

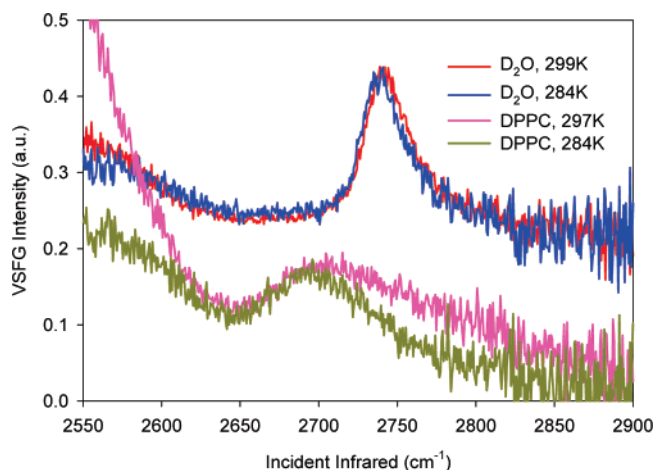
VSFG study on H<sub>2</sub>O and HOD at CCl<sub>4</sub>/water interfaces showed that H<sub>2</sub>O and HOD gave similar free OH stretching frequencies, 3669 cm<sup>-1</sup> for H<sub>2</sub>O and 3667 cm<sup>-1</sup> for HOD.<sup>11</sup> Clearly, coupling between the two ODs is not the dominant cause for the more than 15 cm<sup>-1</sup> and up to 35 cm<sup>-1</sup> red-shifts observed for the dangling OD bonds in Figure 1. Therefore, an indirect perturbation is ruled out.

With respect to the direct perturbation, *d62*-DPPC has several moieties that can be involved, including the methylenes in the tail groups and the C–O, C=O, PO<sub>4</sub><sup>-</sup>, and N(CH<sub>3</sub>)<sub>3</sub><sup>+</sup> in the head group. If the dangling OD directly interacts with the oxygen from the C=O, the C–O, or the PO<sub>4</sub><sup>-</sup>, a hydrogen bond will form and the OD stretch will red-shift to below 2600 cm<sup>-1</sup> into the hydrogen-bonded region. The VSFG spectra in Figure 1 show only a 15–35 cm<sup>-1</sup> shift. Thus, an OD–O interaction is easily ruled out. The choline portion of the head group (N(CH<sub>3</sub>)<sub>3</sub><sup>+</sup>) will not form a hydrogen bond with water. It is also unlikely that the positive charge will interact with the oxygen of the dangling OD because this oxygen prefers bonding with another deuterium from another D<sub>2</sub>O through a hydrogen bond. Therefore, quite clearly, the most likely moieties of DPPC that can be involved in a direct perturbation are the CD<sub>2</sub> groups in the hydrocarbon tails. A previous computer simulation on a dilignoceroylphosphatidylcholine monolayer in the condensed phase and an FTIR study on dimyristoylphosphatidylcholine in gel and liquid-crystalline phases support that water penetrates into the hydrophobic tail region.<sup>25,26</sup> Thus, a direct interaction between the dangling OD and the tail group is spatially feasible. CD<sub>2</sub> is relatively nonpolar, and water is polar. Previous studies by Rowland et al. have shown that the interaction between water and a nonpolar molecule is strong enough to cause the dangling OH (or OD) stretch to have a relatively large frequency red-shift in its vibrational spectrum.<sup>8</sup> These researchers performed infrared studies on an ice surface and found that adsorption of H<sub>2</sub>, Ar, N<sub>2</sub>, and CH<sub>4</sub> red-shifts the dangling OD stretch by as much as ~30 cm<sup>-1</sup> (in the case of D<sub>2</sub>O–CH<sub>4</sub>). Scatena et al. investigated the dangling OH stretch at the H<sub>2</sub>O/CCl<sub>4</sub> and H<sub>2</sub>O/hexane interfaces with VSFG spectroscopy.<sup>11</sup> It was found that the dangling OH stretch at 3700 cm<sup>-1</sup> observed at the air/H<sub>2</sub>O interface red-shifts to 3669 cm<sup>-1</sup> when water is in contact with the nonpolar CCl<sub>4</sub> or hexane solvents at liquid/liquid interfaces. These previous results are consistent with the assertion that the observed frequency red-shift is due to a direct perturbation imposed by the hydrocarbon tail on the dangling OD.

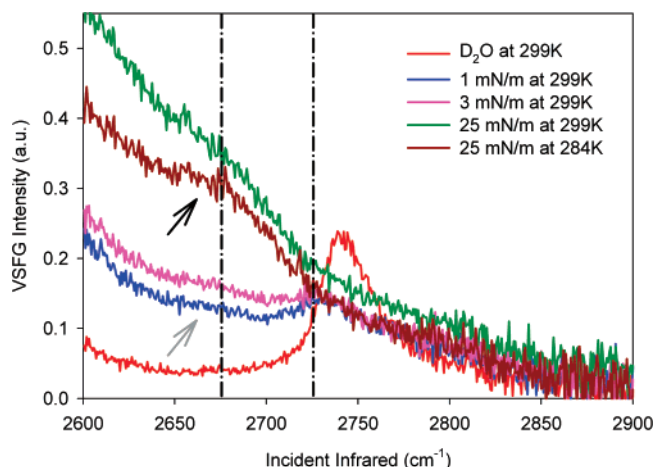
The interaction between water and CD<sub>2</sub> groups is van der Waals by nature. When a polar molecule interacts with a nonpolar molecule, the dispersion force (induced-dipole–induced-dipole) and the induction force (dipole–induced-dipole interaction) contribute to the total van der Waals interaction energy, though the dispersion force usually plays the dominant role.<sup>27</sup> For example, for the CH<sub>4</sub>–H<sub>2</sub>O complex, the dispersion force contributes 87% of the total van der Waals energy and the induction force contributes the rest.<sup>27</sup> The attraction between a hydrocarbon tail and water is considered to be stronger than the attraction between hydrocarbon tails.<sup>28</sup>

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**Figure 2.** *ssp* VSFG spectra of the air/D<sub>2</sub>O and the air/D<sub>2</sub>O/*d*62-DPPC monolayer surfaces in the dangling OD stretching region in a temperature-dependent study (the 284 K spectra of D<sub>2</sub>O and DPPC are scaled by a factor of 1.8 for comparison; the two D<sub>2</sub>O spectra are vertically offset by 0.2 unit).



**Figure 3.** *ssp* VSFG spectra of the D<sub>2</sub>O surfaces in the dangling OD stretching region at 299 and 284 K. Red curve, air/D<sub>2</sub>O surface; other curves, air/D<sub>2</sub>O/*d*31-PA monolayer surfaces under different surface coverages.

Van der Waals interactions, induction and dispersion forces, are temperature-independent.<sup>27</sup> Therefore, the perturbed dangling OD frequency should be insensitive to temperature. Indeed, lowering the temperature of a *d*62-DPPC monolayer on D<sub>2</sub>O does not significantly perturb the dangling OD frequency, as shown in Figure 2, though the high-frequency tail of the hydrogen-bonded region affects the shape of the dangling OD slightly. As a comparison, when the temperature of neat D<sub>2</sub>O is lowered to 284 K, the dangling OD peak is almost identical to the room-temperature dangling OD spectrum, also shown in Figure 2. The low-temperature VSFG comparison study in Figure 2 further confirms that the red-shifted OD peaks are correctly assigned to the perturbed dangling OD bonds.

Since the observed frequency red-shift is interpreted to be due to the perturbation imposed by the hydrocarbon tail group, the phenomenon observed in Figure 1 should be applicable to other types of lipids with quite different head groups. Figure 3 shows the results obtained from a chain-perdeuterated palmitic acid (*d*31-PA) Langmuir monolayer. When the monolayer is compressed to 1 mN/m surface pressure, the dangling OD stretch red-shifts from 2735 to 2720 cm<sup>-1</sup>. Meanwhile, a shoulder (denoted by the gray arrow) grows at ~2660 cm<sup>-1</sup>. Further

compressing the monolayer to 3 mN/m, the shoulder further grows. Compressing the monolayer all the way to the maximum surface coverage (at 25 mN/m), the shoulder (top spectrum) still exists, though it becomes less obvious due to the underlying tail from the hydrogen-bonded OD stretch. Therefore, a low-temperature VSFG study was performed. As shown in Figure 3, by lowering the D<sub>2</sub>O temperature from 299 to 284 K, the hydrogen-bonded OD stretch contribution in this region is greatly lowered and the shoulder, still remaining at 2660 cm<sup>-1</sup> (denoted by the black arrow), becomes more obvious.

DPPC and PA have the same alkyl tail group but have completely different head groups. The fact that they both can cause the frequency red-shift of the dangling OD, as shown in Figures 1–3, confirms that the red-shift of the dangling OD stretch is due to a direct perturbation by the lipid chain.

The spectral structure revealed in Figures 1 and 3 demonstrates the complexity of the perturbation environment that the dangling ODs experience at the interface. An asymmetric band broadening generally suggests that there are overlapping vibrational modes under the spectral contour. Thus, the presence of a shoulder in Figures 1 and 3 implies that there is more than one type of dangling OD at the interface. For DPPC, two component peaks, 2700 and 2720 cm<sup>-1</sup>, can be deconvolved in the 1, 3, and 8 mN/m spectra in Figure 1 (see also Supporting Information Figure S3A–C). The 42 mN/m spectrum can be fitted with just one component at 2700 cm<sup>-1</sup> (Figure S3D). The two components correspond to the dangling ODs affected by perturbations of different strengths, 2700 cm<sup>-1</sup> to a stronger perturbation and 2720 cm<sup>-1</sup> to a weaker perturbation. It is difficult to explicitly assign the two components at the molecular level only on the basis of the VSFG data. Yet, a tentative assignment is hypothesized. Dangling ODs at close proximity to DPPC are being perturbed the most and thus correspond to the component at 2700 cm<sup>-1</sup>. This type of OD exists regardless of surface coverage. Dangling ODs that are farther away from DPPC can also be perturbed by the tail if the tail can disfigure to interact with the ODs. This occurs at low surface coverage (e.g., 1, 3, and 8 mN/m). This type of OD gives rise to the 2720 cm<sup>-1</sup> component. At 42 mN/m, DPPC is in an all-trans configuration, and the 2720 cm<sup>-1</sup> component diminishes. For PA, two component peaks, 2720 and 2660 cm<sup>-1</sup>, can also be deconvolved in the 1 and 3 mN/m spectra in Figure 3 (see also Figure S4A,B). Similar to DPPC, the 25 mN/m spectrum can be fit with one component peak at 2660 cm<sup>-1</sup> (Figure S4C,D). Further shifting of the dangling OD to lower frequency (i.e., to 2660 cm<sup>-1</sup>) implies a stronger perturbation.

It is scientifically intriguing that when the D<sub>2</sub>O surface is fully covered by *d*62-DPPC or *d*31-PA, the dangling OD continues to persist. This phenomenon is considered to arise from hydrophobicity-induced drying. When water is in contact with an extended hydrophobic surface (radius larger than 1 nm, as predicted by Lum, Chandler, and Weeks),<sup>29</sup> water tends to move away from the hydrophobic surface to keep the surface dry. This is called a hydrophobicity-induced drying transition. To keep the surface dry (or dewetted) in the vicinity of the hydrophobic surface, water will not be able to maintain its four-coordination hydrogen-bonding configuration, but it must sacrifice one of its hydrogen bonds by forming a dangling OH

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bond pointing toward the hydrophobic surface. This transition is viewed as an analog to the vapor/water transition. The interfacial layer therefore is similar to the vapor/water interface, possessing dangling OH bonds.<sup>30</sup> The hydrophobicity-induced drying transition has long been envisioned by Stillinger.<sup>31</sup> Supporting evidence is provided by studies using a variety of methods, such as theoretical analysis,<sup>29</sup> X-ray reflectivity,<sup>32</sup> force measurement,<sup>33,34</sup> and neutron reflectivity.<sup>35</sup> The dangling water bond is a unique structural feature arising from the drying transition. Previous VSFG studies on water/hydrophobic surfaces provided direct spectroscopic evidence about the existence of the dangling OH bond of water.<sup>10,11</sup> In a Langmuir monolayer, the long hydrocarbon tail surface of DPPC or PA is large enough (if viewed along its axis) to be considered as an extended hydrophobic surface. According to the hydrophobicity-induced drying transition hypothesis, the dangling OD should exist in

the vicinity of this hydrophobic region. This is what is observed. Therefore, the existence of a dangling OD even under full monolayer coverage is a natural phenomenon arising from the hydrophobic tail that then induces drying.

### Conclusions

In conclusion, perturbed dangling OD bonds from interfacial deuterated water exist at the surface of Langmuir monolayers. The perturbation on the dangling OD is attributed to van der Waals interactions between the hydrocarbon chain and the dangling OD bonds. Owing its relevance to hydrophobicity-induced drying, the perturbed dangling bond of water is expected to exist in other types of hydrophobic assemblies, such as micelles, vesicles, and biological membranes.

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**Supporting Information Available:** Experimental section, VSFG spectral normalization, VSFG spectral curve-fitting, a surface number density discussion, and relevant references. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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