

Surface Dipoles Induce Uniform Orientation in Contacting Polar Liquids

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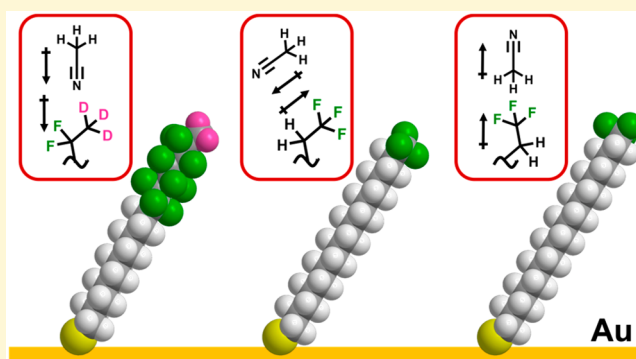


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Supporting Information

ABSTRACT: Molecular interactions at the solid–liquid interface have a profound impact on the macroscale wetting properties of surfaces. Surface-specific sum frequency generation (SFG) spectroscopy, one of a limited number of techniques having the capability to probe such interfaces, generates a surface vibrational spectrum that is sensitive to molecular structure and is used to determine the orientation of molecules at the interface. This study utilized SFG spectroscopy to study the interactions between the polar liquid acetonitrile and selectively fluorinated self-assembled monolayer (FSAM) interfaces generated by the adsorption of $\text{CF}_3(\text{CH}_2)_{17}\text{SH}$ and $\text{CD}_3(\text{CF}_2)_6(\text{CH}_2)_{10}\text{SH}$ on gold; these SAMs exhibit strong oriented molecular dipoles at their chain termini. We used SFG spectroscopy to examine the C–N and C–H stretching regions, 2000–2300 and 2800–3050 cm^{-1} , respectively, to probe the solid–liquid interface of the FSAMs in contact with acetonitrile. The appearance of positive- or negative-going peaks in the SFG spectrum of acetonitrile as a function of the variation in the terminal group of the FSAMs could be attributed, to a first-order approximation, to the orientation (CH_3 up or down) of the acetonitrile molecules with respect to changes in the direction of the FSAM dipole. Coherent molecular spectroscopy was used as a direct probe of this effect by examining the differences in the SFG spectra to determine the relative orientation of acetonitrile with respect to the underlying SAM and, therefore, provided direct evidence for the dipole-influenced wettability behavior of these unique model surfaces.



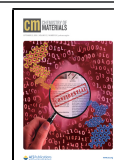
INTRODUCTION

The wetting of solid surfaces is a complex phenomenon governed by a balance of interactions between the cohesion of the liquid molecules and their adhesion at the solid interface.¹ To gain insight into the interactions that govern such macroscale properties of surfaces, studies at the nanoscale solid–liquid interface are needed. Several reviews on solid–liquid interfaces have been published^{2,3} and have shown sum frequency generation (SFG) spectroscopy to be a useful tool in selectively probing interfacial phenomena buried beneath a bulk liquid. Vibrational SFG is a nonlinear spectroscopic technique that obtains signals from the second-order process forbidden in centrosymmetric media under the electric-dipole approximation.³ By generating a vibrational spectrum at the interface between two media, where there is no inversion symmetry, SFG provides information about the order and average orientation of functional groups at the molecular scale. Importantly, SFG spectroscopy can be performed in situ, allowing for the buried solid–liquid interface to be probed in real-time and under ambient conditions.

Self-assembled monolayers (SAMs) derived from the adsorption of alkanethiols on gold provide conformationally

ordered organic thin films with a precise orientation of the terminal functional groups.^{4–6} Studies undertaken to determine SAM structure and organization when in contact with liquids have shown the composition and orientation of the terminal group strongly influences the wettability of the SAMs.^{4–7} Recently, Zenasni et al., using selectively fluorinated SAMs on gold with oppositely oriented dipoles at the chain termini, concluded that an inversion of the terminal dipole in a monolayer film can cause a reversal of the odd–even wettability effect with polar contacting liquids.⁷ Furthermore, increasing the length of the hydrocarbon chain atop the terminal dipole, effectively burying the dipole into the film, caused the contact angle value to start anew, with the fluorocarbons serving as a surrogate substrate.⁸ These findings provided unequivocal evidence for the influence of surface

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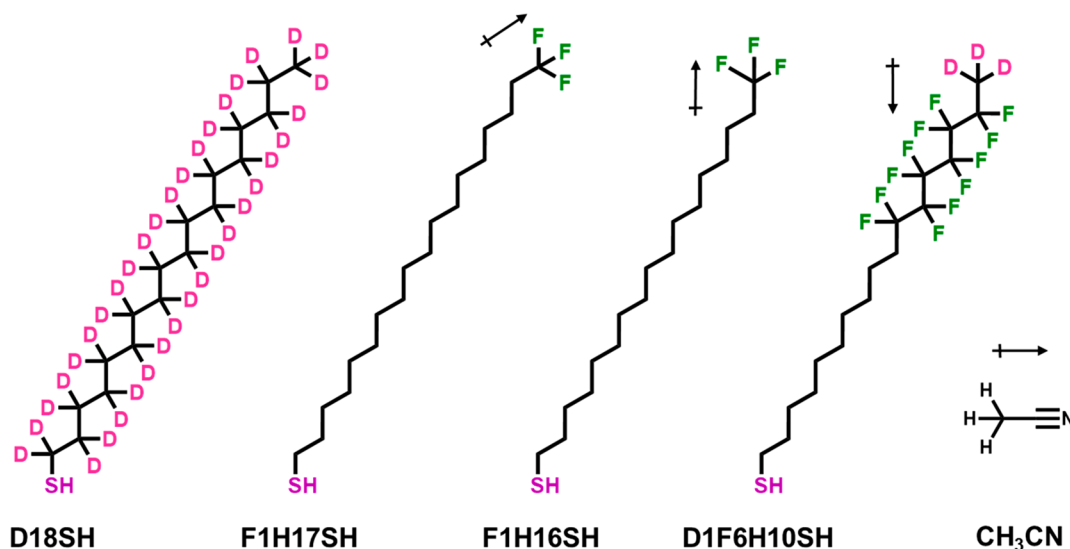


Figure 1. Molecular structures of the deuterated alkanethiol (D18SH) and the partially fluorinated alkanethiols (F1H17SH, F1H16SH, and D1F6H10SH) used to generate self-assembled monolayers on gold. For the fluorinated molecules, the terminal dipole vector is shown with the arrow pointing toward the negative pole. The structure of acetonitrile (CH_3CN) is also included.

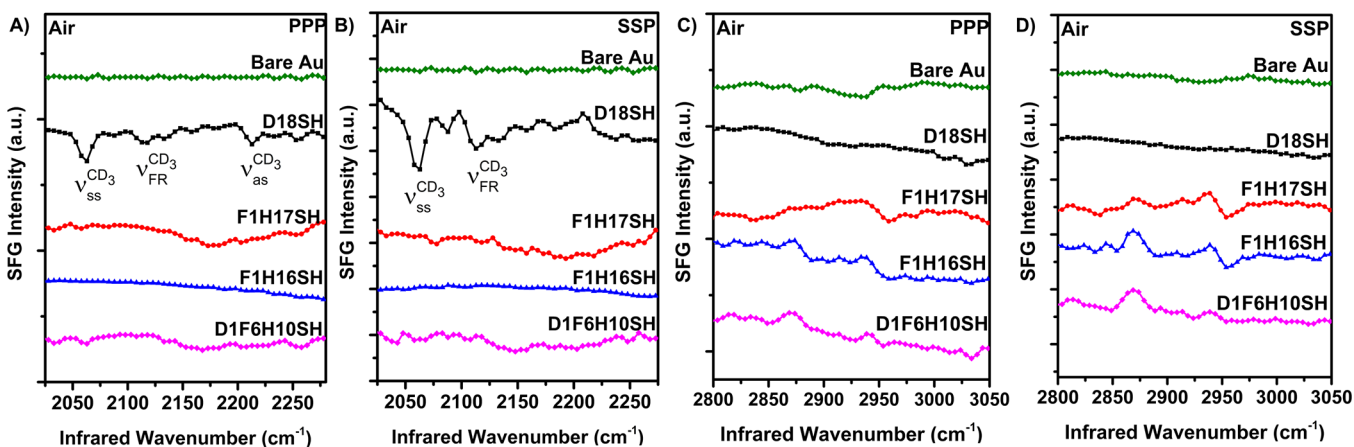


Figure 2. Solid–air SFG spectra in ppp and ssp polarization combinations for the SAMs and bare Au in the (A and B) $\text{C}\equiv\text{N}$ and (C and D) C-H stretching regions.

dipoles on the macroscopic wettability of surfaces.^{4,5,7,8} Despite the many studies analyzing the structure of fluorinated SAMs in comparison to their contact angle wettability,^{9,10} there remains insufficient information regarding the liquid structure at the SAM interface, perhaps due to the limited number of techniques with the capacity to survey buried interfaces. Only a handful of studies have shown the interaction of liquids in proximity to polar interfaces, such as the use of SFG to study the dipoles in water reorienting in the presence of charged surfactants,¹⁰ and the use of noncontact atomic force microscopy to study ethanol selectively wetting polar functional groups in a patterned surface.¹¹

Herein, this Article aims to elucidate the role of terminal dipoles on the orientation of polar liquid molecules at the SAM interface and relate these findings to their macroscopic wetting phenomena. The adsorbates used in the study, shown in Figure 1, consist of two types of partially fluorinated alkanethiols— $\text{CF}_3(\text{CH}_2)_n\text{SH}$, where $n = 17$ and 16 (F1H n SH), and $\text{CD}_3(\text{CF}_2)_6(\text{CH}_2)_{10}\text{SH}$ (D1F6H10SH)—as well as a fully deuterated alkanethiol (D18SH) to serve as a reference. To make full use of the spectroscopy and the need for clearly

separated mode frequencies, the SAMs used in this study were deuterated where necessary.

Acetonitrile (CH_3CN) was selected as the polar liquid in this investigation due to its strong molecular dipole as well as its two distinct stretching modes available to examine (i.e., $\text{C}\equiv\text{N}$ and C-H between $2000\text{--}2300\text{ cm}^{-1}$ and $2800\text{--}3050\text{ cm}^{-1}$, respectively), providing a broad range of data for the purpose of determining its orientation at the surface. Previous studies using surface-sensitive spectroscopic methods, such as SFG, have sought to determine the organization and orientation of CH_3CN at solid dielectric interfaces^{12–17} and metal electrode interfaces.^{18,19} We note also that researchers have examined the interactions of acetonitrile in contact with SAM surfaces; however, these prior studies focused exclusively on the SAM structure/organization under the liquid.^{20–23} In contrast, this study focuses on the organization of acetonitrile in contact with the terminal dipoles of partially fluorinated self-assembled monolayers on gold, with the goal of determining whether SAMs having oriented terminal dipoles can systematically influence the interfacial structure of the contacting polar liquid acetonitrile.

EXPERIMENTAL SECTION

The Supporting Information provides descriptions of the reagents, chemicals, and materials used in this research, the synthesis and characterization of **D1F6H10SH** (Figures S1–S4), the techniques used to prepare the SAMs, additional analytical data for the SAMs (Tables S1–S6 and Figures S5–S15), and a brief description of the theoretical underpinnings of the SFG orientation analysis.

RESULTS AND DISCUSSION

Ellipsometric analysis of the SAMs showed that the thicknesses of the films are consistent with those found in the literature (see Table S1).⁷ Analysis by X-ray photoelectron spectroscopy (XPS) showed that the binding energies of each element agree well with literature values for SAMs on gold, and that there was minimal or no unbound thiol present (see Figure S7).²⁴ This information, along with analysis of the conformational order of the films using surface infrared spectroscopy (Figure S8) and SFG (vide infra) are consistent with a model in which the SAMs formed densely packed, well-ordered, trans-extended chains on the gold surfaces. Further details regarding the characterization of the SAMs, including their thicknesses, compositional analysis, and structural characterization by surface infrared spectroscopy can be found in the Supporting Information.

SFG Spectra of the Solid–Liquid Interface. To probe the interfacial interactions selectively between SAMs and the contacting probe liquid acetonitrile, we employed SFG in the C–H and C≡N stretching regions. The spectra of the solid–air interface, shown in Figure 2, provide a reference for peak positions and resonance orientations. In this study, upward-pointing resonances are defined as “peaks”, and downward-pointing resonances as “dips”. Table 1 lists the observed

Table 1. Observed Vibrational Mode Frequencies and their Assignments for the SAMs Generated from the Adsorbates in Figure 1 and for Acetonitrile^{23,25–27}

vibrational mode assignment		resonance position (cm ⁻¹)
D18SH : CD ₃ symmetric stretch	$\nu_{ss}^{CD_3}$	2060
D18SH : CD ₃ symmetric stretch split by Fermi resonance	$\nu_{FR}^{CD_3}$	2109
D18SH : CD ₃ antisymmetric stretch	$\nu_{as}^{CD_3}$	2212
CH₃CN : C≡N stretch	ν^{CN}	2245
CH₃CN : CH ₃ symmetric stretch	$\nu_{ss}^{CH_3}$	2942

vibrational mode frequencies for the molecules studied and their assignments derived from the bulk IR and Raman results shown in Figures S14 and S15 and from literature values.^{23,25–27}

Apparent from the spectra in Figures 2A and 2B is the lack of the C≡N stretch at 2245 cm⁻¹, consistent with the expected absence of acetonitrile on the **D18SH** SAM surfaces; correspondingly, Figures 2C and 2D fail to exhibit any resonances in the high-frequency C–H stretching region (2942 cm⁻¹). Instead, Figures 2A and 2B for the **D18SH** SAM show the typical deuterated methyl stretching resonances as dips in the ppp and ssp SFG spectra for the low-frequency infrared region, consistent with the exclusive presence of the deuterated SAM. Representative ppp and ssp SFG spectra in the C–H stretching region of a nondeuterated octadecanethiol (**H18SH**) monolayer on gold are shown in Figure S9 with their corresponding resonance assignments. Densely packed self-assembled monolayers on gold, such as those formed from

H18SH and the molecules used in this study, are known to be tilted ~30° from the surface normal so that their tailgroups are oriented away from the surface of gold.²⁸ It is important to note that similar to an **H18SH** monolayer and its SFG spectra, the methyl group at the terminus of the **D18SH** monolayer points away from the Au surface and produces dips in the SFG spectrum. This is an important reference point for later analysis of the orientation of the acetonitrile molecules. Figure 2 shows further that the SAMs generated from the fluorinated molecules, **F1H17SH**, **F1H16SH**, and **D1F6H10SH** exhibit small resonances in the C–H stretching region that can be attributed to the methylene group below the fluorinated segment.²³ Conveniently, the methylene resonances are far from the acetonitrile methyl stretching peak and will not be analyzed in the current study.

To establish that the resonances observed in the SFG spectra of the interface between acetonitrile and the self-assembled monolayers, heretofore labeled as the CH₃CN/SAM interface, do not arise from IR absorption by the bulk liquid, representative spectra for the simultaneously collected sample and reference SFG signals are plotted in Figure 3A. The reference spectra show no significant resonances in the regions of the C≡N and CH₃ stretches, which demonstrates that there are no IR absorptions by the bulk acetonitrile between the gold surface and the window. Figure S10 provides representative spectra of infrared absorption by bulk acetonitrile, when the layer of liquid is sufficiently thick to obscure the SFG resonance completely.

Since SFG is a second-order nonlinear spectroscopy, by definition the signal will arise only from interfaces where the centrosymmetry of a system is broken. As shown in the illustration in Figure S6, the input and output beams of the spectrometer travel through several interfaces before reaching the detector; therefore, the interface from which the SFG signal originates needs to be carefully defined.

The first interface encountered by the laser beams, the boundary between the CaF₂ window and the liquid CH₃CN, can generate SFG signal, as shown by the small resonances in the CH₃CN/CaF₂ ppp and ssp spectra in Figure 3B. Note, the data were gathered from the CH₃CN/CaF₂ interface with no sample underneath. While it is apparent from the peaks in the ssp spectra that the CH₃CN molecules gather at the boundary with the window, it is unlikely that this signal is contributing to the signal at the CH₃CN/SAM interface. As shown by the spectra in Figure 3B, the intensity of the signal from the resonances at the CH₃CN/CaF₂ interface is more than ten times lower than the signal of acetonitrile atop the **D18SH** SAM. Therefore, the signal from the CH₃CN/CaF₂ interface is too weak to contribute to the signal produced from the CH₃CN/SAM interface.

The second interface that could contribute to the signal is the acetonitrile interacting with the gold substrate. Using a bare piece of gold, the spectra at the CH₃CN/Au boundary were gathered and plotted in Figure 3B. There is a clear dip in the ppp C≡N spectrum and asymmetric line-shapes to the resonances in the ssp C≡N and both C–H spectra for the acetonitrile in contact with bare Au, in contrast to the line-shape of the spectral features of the **D18SH** SAM. This spectral feature provides evidence for a different interaction, and possibly orientation, of the acetonitrile in response to a metal surface lacking a well-ordered alkanethiol monolayer. The literature presents experimental evidence for the preferential binding of acetonitrile to Au through the nitrile

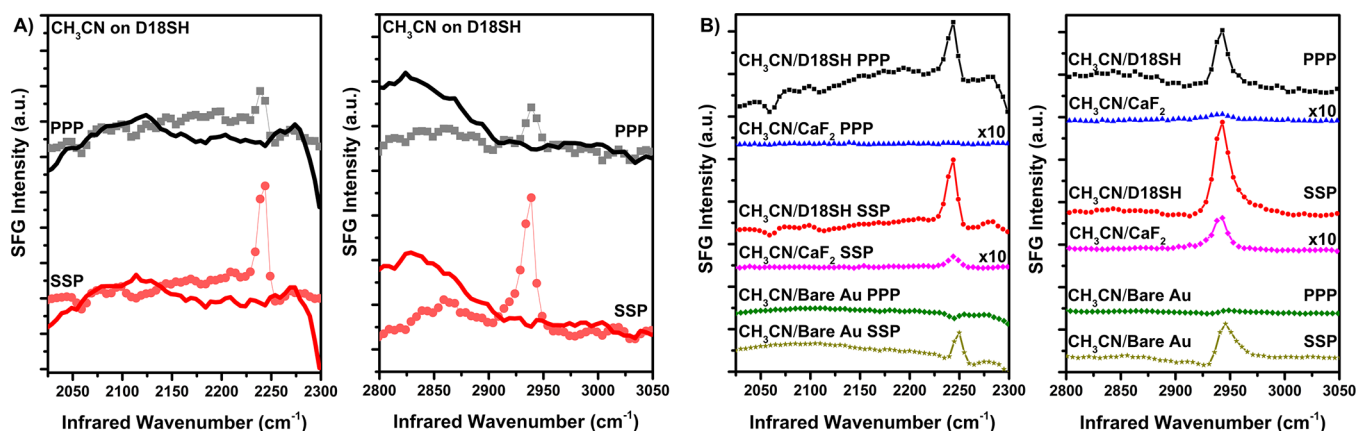


Figure 3. Solid-liquid SFG spectra in the C≡N and C-H stretching regions for ppp and ssp polarization combinations for acetonitrile in contact with (a) the D18SH monolayer on gold and (b) the CaF₂ window and bare gold. The dotted lines are the SFG spectra from the CH₃CN/sample surface, and the solid lines are the reference channel SFG spectra. The sharp decline in the reference signal as the IR frequency is scanned to 2300 cm⁻¹ is due to IR absorption by the carbon dioxide gas present in air.

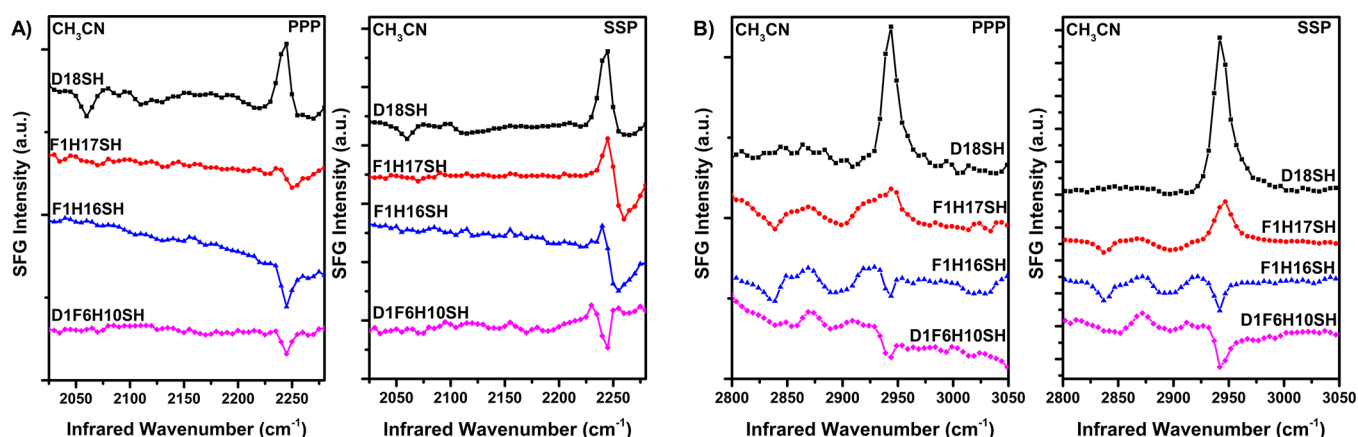


Figure 4. Solid-liquid SFG spectra in ppp and ssp polarization combinations for the acetonitrile in contact with the SAMs in the (A) C≡N and (B) C-H stretching regions.

group, suggesting that the methyl group should be pointed away from the bare Au surface.^{18,29,30} Baldelli et al. noted that the methyl symmetric stretching frequency red-shifts due to mode softening if the group interacts with a metal surface.¹⁸ The resonances in Figure 3B are not shifted, pointing to a lack of interaction between the methyl group of the liquid and the metal surface. Therefore, because of the lack of frequency shifts in the C-H spectra and the asymmetric shape of the resonances implying that there could be multiple types of interactions at the surface, the nitrile group might plausibly be pointing toward the Au surface in the absence of an intervening organic monolayer. A relatively broad distribution of interaction geometries is likely here; however, the analysis is beyond the scope of this study.

The solid-liquid interface SFG spectra of acetonitrile in contact with the SAMs are plotted in Figure 4. The acetonitrile vibrational bands, the C≡N stretch at ~2250 cm⁻¹ and the CH₃ symmetric stretch at 2940 cm⁻¹, are evident in each frequency region of the spectra, with the orientations of the resonance (peaks vs dips) differing between the surfaces. Despite the strong antisymmetric methyl stretching band shown by the bulk acetonitrile at 3010 cm⁻¹ in Figure S10, the same resonance is absent from the SFG spectra in Figure 4B. The ssp and ppp spectra for the D18SH SAM interacting with CH₃CN (see Figure 4A) show dips for the methyl resonances,

$\nu_{ss}^{CD_3}$ at 2060 cm⁻¹ and $\nu_{FR}^{CD_3}$ at 2109 cm⁻¹, originating from the CD₃ group, which is pointing away from the surface. This spectral feature is used as an internal reference to guide our interpretation of the consequently upward-pointing peaks of the C≡N and CH₃ vibrational bands of the acetonitrile exhibited at 2250 and 2940 cm⁻¹, respectively. Taking van der Waals forces as the main driving force for the interaction between D18SH and the liquid, the attraction of the CH₃ of the acetonitrile to the CD₃ of the SAM should lead to the methyl group of acetonitrile pointing downward toward the Au surface.

Experimental evidence from previous studies suggests favorable methyl-to-methyl interactions between hydrocarbon SAMs and acetonitrile.^{14,23,31,32} Previously, Ward et al. analyzed the behavior of various surfactants adsorbed onto D18SH SAMs on Au surfaces and noted that the surfactants preferred to orient with the methyl terminal group of the surfactants pointing toward the CD₃ termini of the D18SH surface.^{31,32} In a study by Ong et al., dispersive interactions between the polar liquid and the hydrocarbon monolayer were noted in the SFG spectra of octadecanethiol in contact with CD₃CN.²⁰ Considering previous literature examples, if the CD₃ of our D18SH SAM is oriented away from the surface and produces a dip in the spectrum, then the CH₃ of the acetonitrile, pointed toward the surface, should produce an

Table 2. Expected versus Observed Resonance Orientations for the Acetonitrile Methyl and Nitrile Stretching Modes in the ppp and ssp SFG Spectra

surface	expected peak orientation ^a	$\nu_{\text{CH}_3}^{\text{CH}_3}$ resonance orientation		$\nu_{\text{CN}}^{\text{CN}}$ resonance orientation	
		observed, ppp	observed, ssp	observed, ppp	observed, ssp
bare Au	↓	↑	↑	↓	↑
D18SH	↑	↑	↑	↑	↑
F1H17SH	↑	↑	↑	↓	↑
F1H16SH	↓	↓	↓	↓	↓
D1F6H10SH	↓	↓	↓	↓	↓

^aExpected SFG resonance orientations are for both the CH₃ and C≡N modes and are derived following intuition regarding van der Waals forces and permanent dipole–induced dipole interactions that can plausibly influence the acetonitrile interactions with the surfaces.

oppositely oriented, upward-pointing peak.^{23,31} Concurrently, the favorable dispersive interactions between the methyl groups will lead the C≡N group to point away from the surface and produce a peak. Following this model and intuition regarding permanent dipole–induced dipole interactions (i.e., Debye forces), the expected resonance orientations as well as the observed orientations for the acetonitrile on bare Au and the D18SH SAM are listed in the first two rows of Table 2.

A similar analysis regarding the orientation of the acetonitrile liquid molecules atop the fluorinated surfaces can be made. The upward-pointing peak in the C–H spectra of the CH₃CN/F1H17SH interface shown in Figure 4B is consistent with a model in which the acetonitrile adopts a similar orientation on this SAM as it does on the D18SH SAM. Furthermore, due to the nature of the upward-pointing oriented dipole at the termini of the F1H17SH SAM (see Figure 1) and the nature of the attraction between the dipole of the SAM and that of acetonitrile (i.e., head-to-tail alignment), the methyl group of the acetonitrile is expected to point toward the F1H17SH SAM surface. This proposed model is consistent with the observed C–H spectra and ssp C≡N spectrum, but qualitatively inconsistent with the ppp C≡N spectrum. To understand the origin of the dip in the ppp C≡N spectrum of the CH₃CN/F1H17SH interface, the nonlinear susceptibility factors, $\chi_{\text{eff,ppp}}^{(2)}$, that govern the orientation of the resonances in SFG spectra must be taken into consideration:

$$I_{\text{ppp}} \propto |\chi_{\text{eff,ppp}}^{(2)}|^2 \propto |-\chi_{\text{xxx}}^{(2)} + \chi_{\text{zzz}}^{(2)}|^2 \quad (1)$$

where the ratio of the two susceptibilities, $\chi_{\text{xxx}}^{(2)}$ and $\chi_{\text{zzz}}^{(2)}$, can be defined to determine their independent contribution to the effective susceptibility and finally the intensity shown in the SFG spectrum. The ratio between $\chi_{\text{xxx}}^{(2)}$ and $\chi_{\text{zzz}}^{(2)}$ is dependent on the value of the hyperpolarizability ratio, R , which is determined from the Raman depolarization ratio for acetonitrile, and the orientation of the molecule with respect to the surface normal, as shown in a previous report by Saito et al.³³ In the case of the C≡N stretch, if $R = 0.48$,¹⁵ the ratio $\frac{\chi_{\text{zzz}}^{(2)}}{\chi_{\text{xxx}}^{(2)}}$

vacillates between about 0.6 and 2.9 (as shown in Figure S11), implying that for most molecular orientations, the effective $\chi_{\text{zzz}}^{(2)}$ will be greater than the effective $\chi_{\text{xxx}}^{(2)}$. Since the components in eq 1 are opposite in sign, both the relative magnitude of the component and its corresponding Fresnel factors will contribute to the susceptibility. The spectra follow the relationships:

$$I_{\text{ppp,CH}} \propto |-(0.51 - 0.83i)\chi_{\text{xxx}}^{(2)} + (0.67 + 1.68i)\chi_{\text{zzz}}^{(2)}|^2 \quad (2)$$

$$I_{\text{ppp,CN}} \propto |-(0.51 - 0.88i)\chi_{\text{xxx}}^{(2)} + (0.63 + 1.62i)\chi_{\text{zzz}}^{(2)}|^2 \quad (3)$$

which show that the Fresnel factors in both regions of the infrared are greater for the $\chi_{\text{zzz}}^{(2)}$ component than for the $\chi_{\text{xxx}}^{(2)}$; therefore, the $\chi_{\text{zzz}}^{(2)}$ will have a greater contribution to the final intensity of the peak in the ppp SFG spectrum than the $\chi_{\text{xxx}}^{(2)}$, regardless of molecular orientation. The SFG spectra show that the ssp polarization combination, and therefore, $\chi_{\text{xxx}}^{(2)}$ produces a peak for the CH₃ stretch and must have a “positive” value; consequently, the lower intensity in the ppp can be attributed to an overall “negative” $\chi_{\text{zzz}}^{(2)}$ contribution. In terms of the CH₃CN/F1H17SH ppp C≡N spectrum in Figure 4A, this information indicates that the dip in the ppp is due to the opposite sign and larger magnitude of the $\chi_{\text{zzz}}^{(2)}$ component of the effective susceptibility and its corresponding Fresnel factors. Therefore, the model suggested by the CH₃CN/D18SH data is still in line with the experimental results of the CH₃CN/F1H17SH interface, and the resonance orientations in the ssp spectra can be considered a good basis for determining the relative orientation of the liquid in contact with the SAM.

The F1H16SH SAM possesses one less carbon atom than the F1H17SH SAM, which leads to a tilt of the terminal dipole away from the surface normal. This tilt allows the dipoles of the acetonitrile molecules to interact and align differently on the F1H16SH SAM than the head-to-tail manner described for the F1H17SH SAM, where the terminal dipole is oriented roughly normal to the surface. Because the analysis with the susceptibilities sheds light into the fact that the ssp spectra hold the key to the orientation of the liquid molecules, the results point to a model in which the CH₃CN/F1H16SH surface might have antiparallel-oriented dipoles, allowing for the liquid molecules to orient at a more tilted angle on the F1H16SH SAM than on the F1H17SH SAM.

Notably, the F1H16SH SAM possesses the same total number of carbon atoms as the D1F6H10SH SAM but an oppositely oriented terminal dipole, yet shares similar characteristics with the spectra of the CH₃CN/D1F6H10SH interface. Specifically, the C–H ssp spectrum in Figure 4B for the F1H16SH SAM shows a clear dip signifying that the CH₃ is pointing away from the surface as with the inverted dipole D1F6H10SH SAM. The ssp C≡N spectrum for the F1H16SH SAM has an asymmetric-shaped peak with a negative amplitude, which indicates that the nitrile group points toward the SAM surface.

The interpretation for the CH₃CN/D1F6H10SH interface is simplified due to the appearance of only dips in the spectra in Figure 4, opposite to that of the CH₃CN/D18SH spectra, indicating that the interaction at the CH₃CN/D1F6H10SH

interface must be opposite to that at the $\text{CH}_3\text{CN}/\text{D18SH}$ interface; consequently, the methyl group of the acetonitrile molecules must be pointing away from the **D1F6H10SH** surface. This assumption agrees well with the model of head-to-tail alignment of the dipole vectors of the liquid and the SAM, due to the existence of the “inverted” dipole of the **D1F6H10SH** monolayer (see **Figure 1**).

It is important to note that the dips observed in the **F1H16SH** and **D1F6H10SH** spectra in **Figure 4** provide additional evidence that the $\text{CH}_3\text{CN}/\text{CaF}_2$ signal has no impact on the $\text{CH}_3\text{CN}/\text{SAM}$ signal. If the FSAM data were influenced by the acetonitrile at the window, only positively pointing peaks would be expected in the spectra. Because the CH_3CN resonances in the solid–liquid spectra flip in orientation with a change in the SAM underneath, the peaks/dips observed in the spectra belong to the molecules aligning at the interface with the SAMs, not the window.

Orientation Analysis of Acetonitrile Molecules.

Orientation analysis was performed on the SFG spectra of the acetonitrile molecules at the solid–liquid interface to offer details regarding the structure of the liquid at the surface. Previous literature examples described below have used different models to fit the $\text{C}\equiv\text{N}$ spectra; importantly, the model used needs to be specified because it can affect the final analysis of the data. Hatch et al. fit their acetonitrile $\text{C}\equiv\text{N}$ spectra to two resonances, one at $\sim 2254\text{ cm}^{-1}$, which was attributed to the acetonitrile molecules weakly adsorbed to the substrate (ZrO_2), and the second at $\sim 2250\text{ cm}^{-1}$, which was attributed to polar intermolecular interactions between acetonitrile molecules.¹³ Baldelli et al., following a similar model by fitting their spectra to two peaks, a $\text{C}\equiv\text{N}$ resonance at 2245 cm^{-1} , corresponding to the acetonitrile adsorbed to Pt, and an SFG-active combination band at 2290 cm^{-1} .¹⁸ The resonance at 2250 cm^{-1} was attributed to the acetonitrile peak in solution.

Another feature to note involves shifts in the frequency of the CH_3 peak of acetonitrile between the ssp and ppp polarization combinations, which Ding et al. have suggested that the spectra be fit assuming the peak is composed of two Lorentzian features of opposite sign; the features corresponded to a redistribution of intensity between the two features under different polarization conditions—due to the ability of liquid acetonitrile to reorganize into different environments, leading to different peak frequencies.¹⁴ The C–H spectra shown in **Figure 4B** exhibited no shift in the frequency between the ssp and ppp combinations. Furthermore, the $\text{C}\equiv\text{N}$ spectrum of the reference system, $\text{CH}_3\text{CN}/\text{D18SH}$, exhibits no obvious polar interactions between the liquid and the SAM. Therefore, in light of the previous reports and the observations made from this study, the peaks/dips in the C–H spectra in **Figure 4B** were fit to one resonance at 2942 cm^{-1} , while the $\text{C}\equiv\text{N}$ resonance in **Figure 4A** appearing in the $\text{CH}_3\text{CN}/\text{D18SH}$ interface was fit to one frequency at 2244 cm^{-1} . On the other hand, due to the suspected dipole–dipole interactions at the $\text{CH}_3\text{CN}/\text{FSAM}$ interfaces and the asymmetric shape of the $\text{C}\equiv\text{N}$ resonances, the $\text{C}\equiv\text{N}$ spectra were fit to two resonances, one at 2244 cm^{-1} , corresponding to the interaction between the acetonitrile and the SAM, and another at 2250 cm^{-1} , corresponding to dipole–dipole interactions between the liquid molecules. The fitted data, shown in **Figure S13**, were then used to deduce the orientation of each functional group, defined by the tilt angle, θ , of the C-axis with respect to the surface normal, using the intensity ratio, $I_{\text{ssp}}/I_{\text{ppp}}$ between

the symmetric stretching vibration in the ssp and ppp SFG spectra of the acetonitrile in contact with the different SAMs. Further details on the fitting procedure and the equations used to determine the intensity ratio are provided in the **Supporting Information**. The ratios were corrected using a scaling factor to account for the reflectivities at each interface through the cell. The final values of the intensity ratios and the average orientation angles are listed in **Table S2** and the intensity ratios for both of the chromophores in acetonitrile are plotted in **Figure 5**.

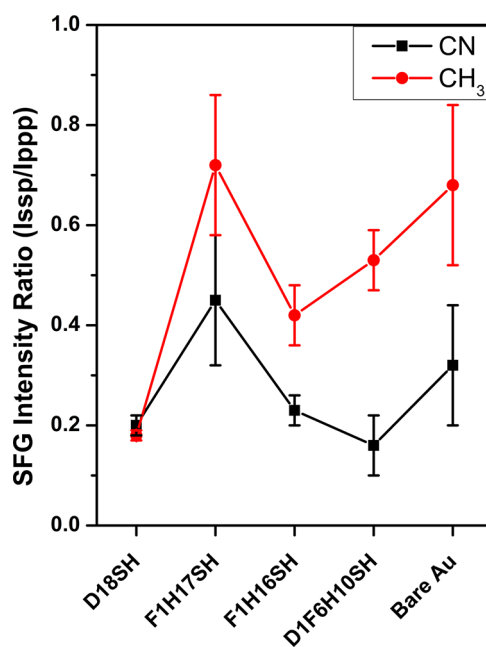


Figure 5. Resonance intensity ratios for acetonitrile in contact with SAMs and bare gold.

Acetonitrile belongs to the C_{3v} point group, where the $\text{C}\equiv\text{N}$ and CH_3 groups have a local symmetry of $\text{C}_{\infty v}$ and C_{3v} , respectively. Apparent from **Figure 5**, the intensity ratios of the CH_3 and $\text{C}\equiv\text{N}$ resonances for acetonitrile follow a similar pattern, as expected for a molecule where the local modes share a common $\text{C}_{\infty v}$ symmetry axis. The average tilt angles, assuming a narrow distribution of orientations, as well as the tilt angles derived from the Gaussian distribution of orientations with different widths, were determined using the simulated intensity ratio curves shown in **Figure S12**. The intensity ratios derived from the data fits of the $\text{CH}_3\text{CN}/\text{D18SH}$ interface are shown in comparison to the simulation in **Figure S12** to provide an example of the method used to determine the functional group orientations. The errors in the intensity ratios were used to determine the range of tilt angles for each functional group and are depicted by the asymmetric error bars in **Figure 6**, which shows the final results from the orientation analysis assuming a narrow distribution in the calculated orientations.

However, because acetonitrile is in liquid form, a narrow distribution of orientations is not a perfect model for the interactions at the interface. The true nature of the arrangement of acetonitrile molecules at the interface is a distribution of possible orientations (i.e., the acetonitrile molecules could have their functional groups pointing in the same direction, but at different degrees of tilt from the surface

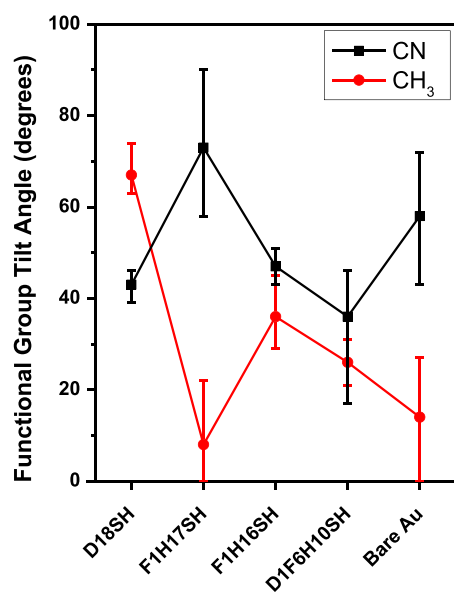


Figure 6. Average orientations and their asymmetric errors for the C≡N and CH₃ groups of CH₃CN atop the SAMs and bare gold calculated using a $\sigma = 0$ distribution of orientations.

normal). It is also possible that adjacent acetonitrile molecules are oriented with their functional groups pointing in opposite directions so that some molecules will have the CH₃ group pointing away from the surface and others will have the CH₃ group pointing toward the surface. Both arrangements will influence the intensities of the resonances in the SFG spectra; if the distribution of orientations is high, the intensity of the resonances decreases. On the other hand, a smaller distribution in the orientation, in which the acetonitrile molecules at the SAM interface are tilted at the same angle and oriented with the functional groups pointing in the same direction, will enhance the detected SFG signal. This phenomenon is illustrated by the apparent discrepancy in the tilt angles of the functional groups as shown in Figure 6. The overall C_{3v} symmetry of acetonitrile forces the C-axes of each functional group into a collinear geometry, and therefore, should give consistent functional group tilt angles with respect to the surface normal. It is apparent from Figure 6 that the tilt angles calculated for the CH₃ and C≡N groups in acetonitrile at the D18SH interface were inconsistent with each other, indicating that the simulated orientation curve failed to follow the experiment. The same inconsistency in functional group tilt angles was noted for CH₃CN at the F1H17SH surface.

To preserve the internal C₃ axis of the acetonitrile molecule and keep consistency in its tilt angles, the following unknown parameters were varied in the simulated curve: the hyperpolarizability ratio, R , typically derived from Raman depolarization data, and the refractive index value, n , of the light fields going through the SAM. The details of these tests are given in the Supporting Information, and the results demonstrate the limits of the orientation analysis from SFG when the true hyperpolarizabilities of the molecules in a solid–liquid system are unknown. It is possible that undetermined correction factors must be applied to account for the change in the local fields at metal surfaces to allow for a better fit between the experiment and the theoretical curve. Thus, due to the complex nature of the factors involved in the interactions at interfaces, the analysis provided here is reliable only for

constructing a general model of the system that should not be regarded as quantitative. Additional studies revealing the true hyperpolarizabilities of the system are needed to enable a more quantitative analysis. Figure 5 shows no obvious trend in the intensity ratios of the data, meaning that for the current simulation, no matter how the R value is manipulated, the average orientation values of the CH₃CN chromophores atop the SAMs can plausibly be inconsistent. Given that, Figure 6 shows that the CH₃CN tilt angles at the F1H16SH and D1F6H10SH interfaces were consistent and can be used as evidence that the orientations derived from SFG must be directly due to the oriented dipoles at the SAM surfaces. A summary of the SFG-derived acetonitrile orientations on the various SAMs is illustrated in Figure 7.

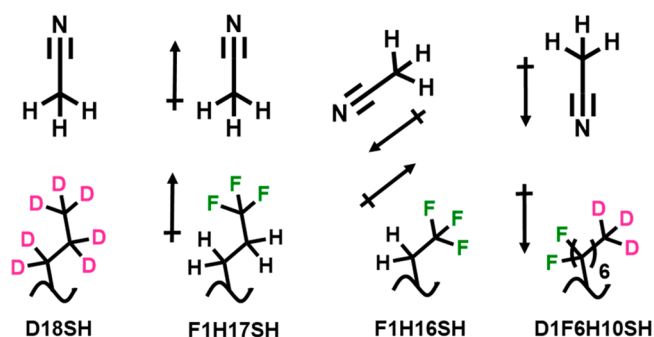


Figure 7. Illustration of the SFG-deduced acetonitrile orientations as a function of the SAM terminal group at the liquid–solid interface. The dipole vector is shown with the arrow pointing toward the negative pole.

Comparison of Wettability Data to SFG Orientation Analysis. Qualitative observations from the SFG orientation analysis can be compared to previous wettability data to provide information about how the liquid structure at the interface influences the advancing contact angles observed for acetonitrile atop each of these SAMs. The contact angles reported by Zenasni et al. for the FSAMs are listed in Table 3.⁷

Table 3. Advancing Contact Angles of Acetonitrile on the SAMs Used in this Study^a

SAM	advancing contact angle for CH ₃ CN
D18SH	68°
F1H17SH	48°
F1H16SH	53°
D1F6H10SH	46°

^aContact angles were reproducible to $\pm 1^\circ$ for each of the samples tested.⁷

The data show that the least wettable surface (i.e., highest contact angle) is the hydrocarbon surface with a 68° advancing contact angle. The large amplitude of the SFG intensity of the peaks for the CH₃CN/D18SH interface could point to a high degree of organization in the liquid molecules at the interface. The weaker Debye (permanent dipole–induced dipole) interaction between polar acetonitrile and the nonpolar hydrocarbon surface, compared to the stronger Keesom forces (permanent dipole–dipole) between the liquid molecules,¹³ likely causes the liquid to optimize the intermolecular forces at play by forming an ordered layer at the interface. While repulsion between the dipoles of the liquid molecules arranged

parallel to each other is expected, adjacent molecules can tilt to approach a lower-energy head-to-tail configuration.³⁴ Another possibility involves the liquid adopting a multilayered system to reduce the overall interaction energy, for which the upper layers leading into the bulk would be centrosymmetric and, therefore, invisible to the SFG. Hatch et al. suggested that acetonitrile forms head-to-tail dimers at the solid–liquid interface with zirconia.¹³ Ding et al. provided insight into the literature surrounding CH₃CN orientation at dielectric surfaces in conjunction with their study to provide evidence for a well-ordered layer tethered through hydrogen bonding at a silica surface with progressively less ordered layers extending into the bulk of the liquid.¹⁴ Although the systems in this study exhibit no classical hydrogen bonding,⁴ Keesom interactions between the liquid molecules could cause them to adopt a similar multilayered arrangement near the surface.

The amplitudes of the SFG resonance intensities for the acetonitrile molecules atop the three fluorinated surfaces are lower than those of the CH₃CN/D18SH system. Strong interactions between adjacent CH₃CN molecules arranged above the D18SH interface could lead to a narrow distribution of oriented molecules, which would rationalize the higher SFG intensity of the CH₃CN modes at the CH₃CN/D18SH interface in comparison to the CH₃CN/FSAM interface. Strong interactions between the liquid and the FSAM surfaces could increase the distribution of orientations at the interface and lower the SFG intensity of the CH₃CN modes. Combining the findings from the reorientation of the polar acetonitrile molecules in relation to the dipole-terminated FSAM surfaces and the fact that fluorinated monolayers are more loosely packed than a fully hydrocarbon monolayer,⁷ the lower SFG intensity of the vibrational modes at the CH₃CN/FSAM interface can be attributed, at least in part, to a larger distribution of molecular orientations as CH₃CN molecules intercalate into the FSAMs.

This model is consistent with the contact angle values of acetonitrile on the FSAMs, which decrease by more than 10° compared to the values on a hydrocarbon SAM, as shown in Table 3. This interpretation of the SFG results is also consistent with a previous report,⁴ which concluded that the surprising and significantly enhanced wettability of terminally fluorinated SAMs by polar liquids arises from the strong dipole–dipole interactions between the dipole-terminated SAMs and polar contacting liquid. Nevertheless, conclusions made from the comparison between macroscopic wettability in terms of contact angles and the microscopic information from SFG must be considered with caution. The solid–liquid interactions at the interface are only one piece of a puzzle that must be joined with other data, such as surface energy of the solid–air interface and the liquid–liquid interactions that make up the surface tension at the liquid–air interface to form a complete representation of the factors that affect the wettability of a surface.

CONCLUSIONS

Interactions at the nanoscale solid–liquid interface can have a large impact on the macroscale wetting properties of thin films. As one of a limited number of techniques that can probe such interfaces, SFG spectroscopy was employed to study the interactions between a common contacting liquid and model fluorinated surfaces generated using custom-tailored SAMs on gold. The elemental composition of the monolayers as well as the conformational order of the monolayers, confirmed with

surface infrared spectroscopy and SFG, showed that the SAMs formed densely packed, well-ordered, trans-extended chains on the gold surfaces. The SAMs used in this study served to investigate how polar liquids, such as acetonitrile, orient when exposed to various functional groups at the SAM terminus and specifically in response to terminal dipoles. Because sum frequency signal generation is allowed only from non-centrosymmetric media, this spectroscopic technique supplied vibrational spectra of the solid–liquid interface where acetonitrile contacts the SAMs. To determine the origin of the peaks versus dips in the SFG spectra, contributions to the SFG signal from the CaF₂/CH₃CN and CH₃CN/Au interfaces had to be ruled out, as well as IR absorption by the bulk liquid layer of acetonitrile. SFG spectra in both the C–H and C≡N stretching regions showed the CH₃CN peaks pointing up or down depending on the underlying SAM composition and terminal group orientation. The methyl group at the terminus of the D18SH monolayer points away from the Au surface and produces dips in the corresponding SFG spectrum. This internal reference reveals that the upward-pointing peaks of the vibrational bands of acetonitrile are consistent with a model in which the CH₃ group of acetonitrile points toward the Au surface, while the C≡N group points away from the Au surface. The observed SFG spectra for the CH₃CN/F1H17SH interface show that the methyl group of acetonitrile points toward the F1H17SH SAM surface with the dipoles in a head-to-tail configuration; however, a broad distribution of interaction geometries is likely in the fluorinated surfaces. The C–H SFG spectra for the F1H16SH SAM show a clear dip, which signifies that the CH₃ group of acetonitrile points away from the surface. The C≡N spectrum for the F1H16SH SAM has an asymmetric-shaped peak with a negative amplitude, which indicates that the nitrile group of acetonitrile points toward the SAM surface, with the CH₃CN/F1H16SH surface possibly having oriented dipoles that are antiparallel. Due to the appearance of only dips in the SFG spectra for CH₃CN/D1F6H10SH interface, which is opposite to that of the CH₃CN/D18SH spectra, the interaction is also opposite, indicating that the methyl group of the acetonitrile molecules points away from the D1F6H10SH surface, while the C≡N group points toward the FSAM. In particular, the solid–liquid SFG spectra provided here show the influence of surface dipoles on the orientation of polar contacting liquids. The results corroborate previous reports identifying the source of the interaction between the polar contacting liquids and the partially fluorinated self-assembled monolayers as a permanent dipole–dipole (i.e., Keesom force) interaction.⁷ Because the liquid can intercalate into the FSAMs, a large distribution of molecular orientations for the CH₃CN molecules is possible, causing the simulated orientation curves to fail to align with the experimental observations. Consequently, the orientation angle analysis from the SFG spectra was largely inconclusive. Although several parameters were varied in efforts to bring the simulated curves closer to the experimental data, the results demonstrated that SFG orientation analysis is limited when the true hyperpolarizabilities of the molecules in a solid–liquid system are unknown. Further studies are necessary for quantitative results to be obtained. Studies such as those detailed here lay the groundwork for determining not only the direction of the terminal dipole of a SAM, but also its energy of interaction with contacting liquids, and ultimately a molecular-scale understanding of its wettability behavior.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.chemmater.0c02471>.

Materials, methods, synthetic procedures, characterization data (^1H , ^2H , ^{19}F , ^{13}C NMR spectra; mass spectrometry) for **D1F6H10SH**, additional analytical data for the SAMs (ellipsometry, SFG, XPS, IR), and descriptions of the experimental and theoretical methods for analyzing the SAMs and the interfacial orientation of acetonitrile in contact with the SAMs (PDF)

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Notes

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