

## Surface Structure at Hexadecane and Halo-hexadecane Liquid/Vapor Interfaces

Okan Esenturk and Robert A. Walker\*

Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742

Received: May 11, 2004; In Final Form: June 11, 2004

Vibrational spectra in the CH stretching region have been acquired from the *n*-hexadecane, 1-chlorohexadecane, and 1-bromohexadecane liquid/vapor interfaces using broadband vibrational sum-frequency spectroscopy. Different polarization conditions of the incident and generated fields are used to assess surface structure based on functional group alignment along the surface normal ( $S_{\text{sum}}S_{\text{vis}}P_{\text{IR}}$ ) and within the plane of the surface ( $S_{\text{sum}}P_{\text{vis}}S_{\text{IR}}$ ). The *n*-hexadecane liquid/vapor interface evinces a surprising degree of conformational order, given that X-ray scattering studies imply an absence of any surface organization for alkanes above their surface freezing temperature. Replacing a terminal hydrogen of *n*-hexadecane with either a chlorine or bromine substituent significantly changes the out-of-plane surface structure, but the in-plane surface structure remains qualitatively unchanged. These effects are attributed to dipole–dipole interactions between the halogenated ends of the  $C_{16}$  alkanes and are indicative of a higher surface activity of the halogenated ends, compared to the unsubstituted ends of the molecule.

## Introduction

Alkanes might be considered the simplest type of organic molecule, because of their chemical homogeneity and weakly interacting nature. Nonetheless, alkanes have complex roles in biological systems such as lipids, surfactants, and liquid crystals, and alkanes constitute the dominant component of fuels and lubricants. Although the bulk properties of alkanes are well-described,<sup>1–6</sup> the characterization of the alkane surface structure and surface properties remains incomplete. These surface properties will control many chemical processes, such as adsorption/desorption and, ultimately, the way in which alkanes interact with an adjacent phase. The surface properties of alkane systems have been studied by various surface methods, ranging from newly developed optical techniques (i.e., sum-frequency (SF) spectroscopy) to conventional surface techniques (such as surface infrared and X-ray spectroscopy, neutron and light scattering, and ellipsometry).<sup>7–15</sup> Most of these studies seek to characterize the surface properties by varying either the experimental conditions such as temperature and pressure or by varying the chain length of the alkanes.

The surface structure of liquid alkanes is controlled by weak van der Waals interactions between adjacent solvent molecules. Here, the term surface structure refers to any net ordering of liquid molecules at the liquid/vapor interface due to intrinsic interfacial anisotropy. The surface structure—those functional groups of a solvent molecule presented to the vapor phase—is different than the long-range surface order, which is a term that refers to the relative positions and conformations of interfacial solvent molecules at the liquid/vapor boundary. This distinction becomes quite apparent when comparing the results of room-temperature X-ray scattering from the *n*-hexadecane/vapor interface to vibrational spectra acquired from the same system. X-ray scattering data from the *n*-hexadecane liquid/vapor interface show no diffraction features leading Ocko and co-workers to conclude that at room temperature, this surface

possesses no long-range order.<sup>10</sup> In contrast, vibrational spectra of the *n*-hexadecane/vapor interface show a very pronounced feature assigned to a methyl symmetric stretch. With 14 methylene groups and only 2 methyl groups, one would not anticipate such a strong methyl response *unless* there existed surface structure having a nonstatistical number of methyl groups aligned perpendicular to the interfacial plane.<sup>9</sup> This apparent discrepancy between X-ray and vibrational data simply reflects differences in the properties probed by the two techniques. Long-chain alkanes *can* possess surface structure (e.g., methyl groups oriented toward the vapor phase) without having any long-range order (e.g., beneath the terminal methyl groups, the solvent structure is randomized).

Predicting how surface structure changes with subtle alterations in a solvent's molecular structure is far from straightforward. For example, if one end of a long chain *n*-alkane were replaced with a weak dipole, one might guess that the polar ends of the solvent should be preferentially solvated due to solvation and surface free energy considerations. Preferential solvation would lead to a distinct absence of polar endgroups at the liquid/vapor interface. However, an alternative perspective presents a surface excess of polar endgroups so that dipoles can interact more freely without the steric constraints imposed by the accompanying long chains in bulk solution. These two pictures existed—solvated polar ends vs surface active polar ends—predict very different properties for a liquid/vapor interface. In the case where the polar ends are solvated, the liquid/vapor interface will be very inert and chemically similar to the surface of other liquid alkanes. The surface that has an excess of polar endgroups is much more polarizable and more likely to promote efficient adsorption of gas-phase species and, perhaps, enhances reactivity. To date, there exists little information to guide intuition predicting the surface structure of weakly associating liquids at the liquid/vapor interface.

In this study, we have investigated the effect of end group dipoles and endgroup size on surface structure by comparing surface vibrational spectra of *n*-hexadecane (*n*- $C_{16}$ ) to those of 1-chlorohexadecane (Cl- $C_{16}$ ) and 1-bromohexadecane

\* Author to whom correspondence should be addressed. Telephone: (301) 405-8667. Fax: (301) 314-9121. E-mail address: rawalker@umd.edu.

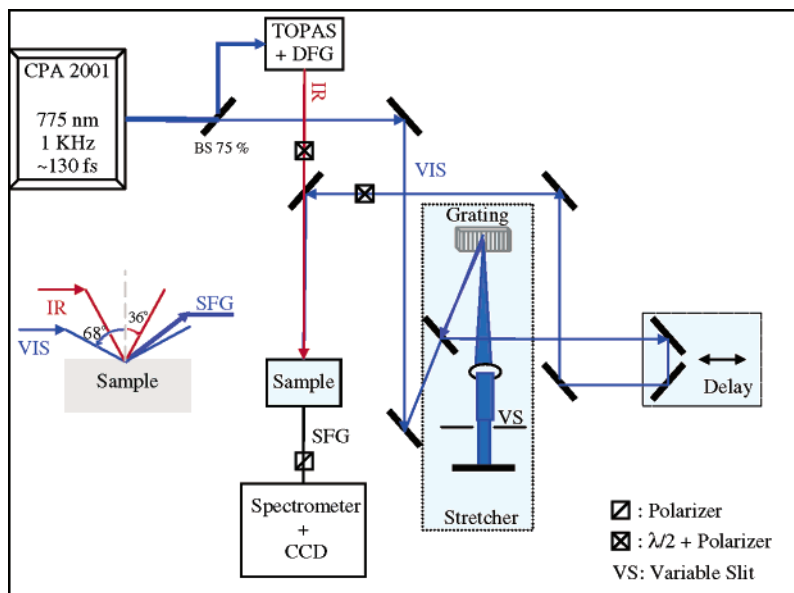


Figure 1. Schematic diagram of the optical system.

(Br-C<sub>16</sub>). Spectra were acquired using vibrational sum-frequency generation, which is a noninvasive, surface-specific technique.<sup>7–9</sup> Data show that solvent molecules prefer an orientation with one end exposed to vapor (instead of a random chain segment), and molecules have a relatively large degree of disorder along the rest of the chain. The two haloalkanes adopt surface structures that have halogen ends primarily oriented toward the vapor phase, with the other CH<sub>3</sub> end being distributed almost isotropically in the liquid. Experiments performed with *n*-C<sub>16</sub> are quantitatively consistent with previous vibrational spectra from the same system<sup>9</sup> and contrasts with X-ray scattering studies that posit an absence of surface structure at the liquid/vapor interface when the sample is above the surface freezing temperature.<sup>10</sup> Results presented below mark the first evidence of surface structure in weakly associating liquids depends sensitively on a liquid's molecular structure. These findings add molecular level insight into thermodynamic differences between the different liquids and vibrational spectra provide the first benchmarks for testing newly developed methods intended to simulate surface structure at liquid/vapor interfaces.<sup>16</sup>

## Experimental Section

The alkanes used in these studies were obtained from the Aldrich Chemical Co., with reported purities of 99+ % for *n*-hexadecane and 1-bromohexadecane and 98.6% for 1-chlorohexadecane. The major contaminants reported by the manufacturer were branched alkanes (in the *n*-C<sub>16</sub>) and halo-alkanes having different chain lengths (in the range of chain lengths of Cl-C<sub>16</sub> and Br-C<sub>16</sub>). Given that these impurities were prohibitively difficult to separate from the samples and were unlikely to show pronounced surface activity, the samples were used without further purification. The experiments were performed at room temperature (23 ± 1 °C), well above the bulk melting point of all three alkanes: *T*<sub>fus</sub> = 18 °C for *n*-C<sub>16</sub>, 14 °C for Cl-C<sub>16</sub>, and 17 °C for Br-C<sub>16</sub>.

A detailed description of vibrational SF generation has appeared in numerous sources.<sup>7–9</sup> Briefly, SF generation is a nonlinear optical process that occurs when two high-intensity optical fields with frequency  $\omega_{\text{ir}}$  and  $\omega_{\text{vis}}$  overlap at the liquid/vapor interface to generate a third frequency  $\omega_{\text{sf}}$ , which is equal in energy to the sum of  $\omega_{\text{ir}}$  and  $\omega_{\text{vis}}$ . The intensity of the SF

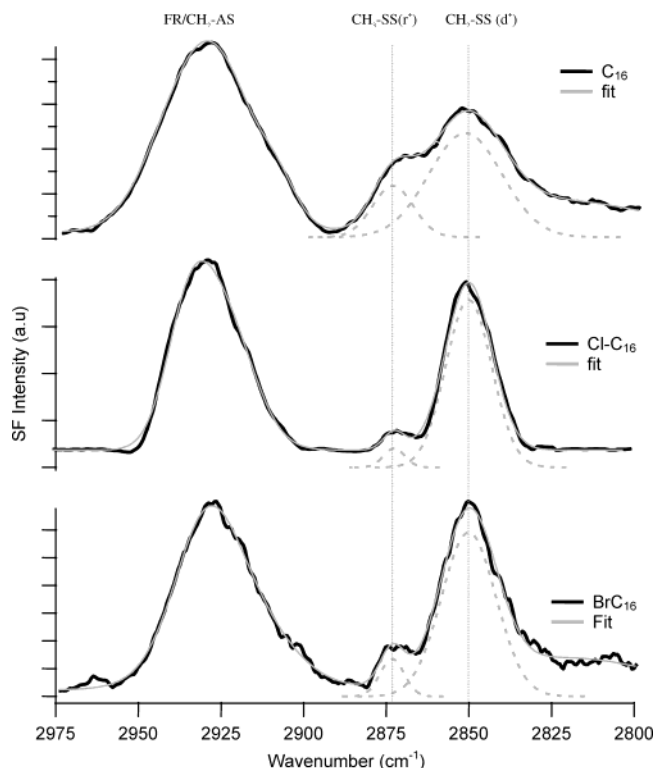
response ( $I_{\text{sf}}$ ) is proportional to the square of second-order nonlinear susceptibility tensor ( $\chi^{(2)}$ ) and the intensities of the infrared ( $I_{\text{ir}}$ ) and visible ( $I_{\text{vis}}$ ) beams:

$$I_{\text{sf}} \propto |\chi^{(2)}|^2 I_{\text{ir}} I_{\text{vis}} = |\chi_{\text{NR}}^{(2)} + \chi_{\text{R}}^{(2)}|^2 I_{\text{ir}} I_{\text{vis}} = |\chi_{\text{NR}}^{(2)} + \sum_q \frac{A_q}{\omega_{\text{ir}} - \omega_q + i\Gamma}|^2 I_{\text{ir}} I_{\text{vis}}$$

where  $\chi_{\text{NR}}^{(2)}$ ,  $\chi_{\text{R}}^{(2)}$ ,  $A_q$ ,  $\omega_q$ , and  $\Gamma$  are the nonresonant and resonant susceptibility, amplitude, vibrational center frequency, and line width for a given mode  $q$ , respectively. Previous studies of similar systems showed that the nonresonant contribution is negligible for alkane systems.<sup>9</sup> Consequently, evaluation of the spectra shown below does not include this term.

Although the  $\chi^{(2)}$  tensor has 27 elements, because of rotational invariance at the interface, there are only three independent components:  $\chi_{\text{yyz}}^{(2)}$ ,  $\chi_{\text{yzy}}^{(2)}$ , and  $\chi_{\text{zzz}}^{(2)}$ . Different polarization combinations sample different elements of the  $\chi^{(2)}$  tensor. SF spectra in this work were collected using an  $S_{\text{sf}}S_{\text{vis}}P_{\text{ir}}$  polarization combination to sample those vibrational modes that had the net transition moment aligned along the surface normal ( $\chi_{\text{yyz}}^{(2)}$ ) and an  $S_{\text{sf}}P_{\text{vis}}S_{\text{ir}}$  polarization combination to probe the modes that have their infrared (IR) transition moments aligned parallel to the surface plane ( $\chi_{\text{yzy}}^{(2)}$ ).

The IR–Vis sum-frequency spectrometer is based on the broadband technique pioneered by Stephenson and co-workers.<sup>7</sup> A schematic view of the broadband IR–visible SF spectrometer and sample stage is given in Figure 1. The visible light (at 775 nm) is generated by a regeneratively amplified Ti:sapphire laser (CPA 2001, Clark MXR) having a pulse width of 130 fs and a repetition rate of 1 kHz. The visible beam is split such that most of the energy is used to seed and pump an infrared optical parametric amplifier (TOPAS, Light Conversion) with a difference-frequency (DF) assembly. The TOPAS provides tunable mid-infrared light from 2.4 μm to 11 μm after DF mixing of signal and idler beams. The generated IR beam at ~3.5 μm (2850 cm<sup>-1</sup>) has an energy of ~6 μJ and a fwhm bandwidth of ~100 cm<sup>-1</sup>. The IR polarization is controlled by a silicon reflective polarizer and a CdGaS<sub>4</sub> phase plate. A home-built stretcher with a variable slit and 1800 g/mm grating enables

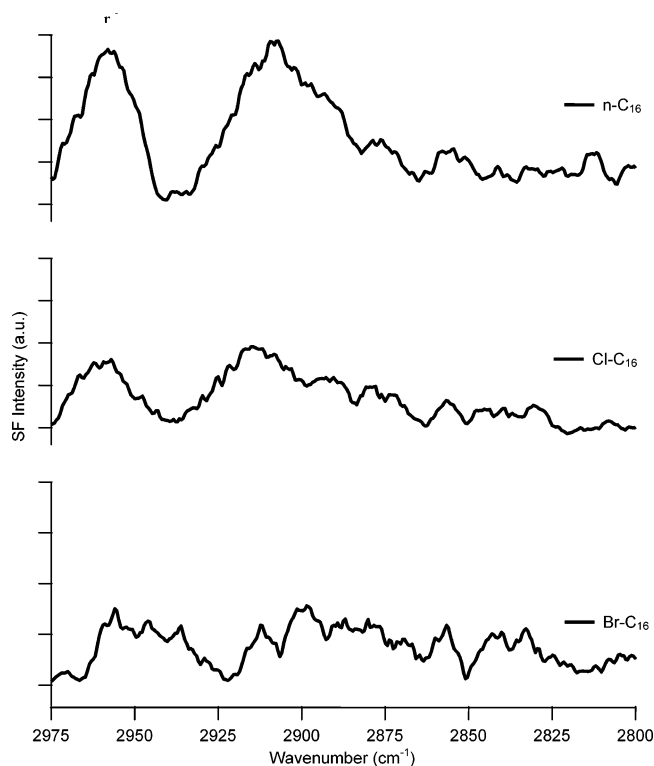


**Figure 2.** Sum-frequency spectra of *n*-hexadecane (*n*-C<sub>16</sub>, top), 1-chlorohexadecane (Cl-C<sub>16</sub>, middle), and 1-bromohexadecane (Br-C<sub>16</sub>, bottom) under  $S_{st}P_{vis}P_{ir}$  polarization condition, observing only the vibrational transition moments that have out-of-plane components. Black lines are background-corrected data, gray lines show the multi-peak fit spectra, and dashed lines show the individual features for the CH<sub>2</sub> and CH<sub>3</sub> symmetric stretches.

us to continuously vary the bandwidth of the visible light and, thus, control the resolution of the SF spectra. Autocorrelation of the manipulated visible beam showed that the beam could be stretched from 200 fs ( $\sim 67$  cm<sup>-1</sup> fwhm) to 3 ps (5 cm<sup>-1</sup> fwhm). Typical experimental conditions used 2-ps visible pulses with a bandwidth of  $\sim 7.5$  cm<sup>-1</sup> fwhm. The SF spectra were collected by overlapping the IR and visible beams at the liquid/vapor interface at incidence angles of 36° and 68°, respectively, with respect to the surface normal. The approximate diameters of IR and visible beams were 250  $\mu$ m and 1 mm, respectively, with energies of  $\sim 4$   $\mu$ J for each. The generated SF signal is dispersed onto a thermoelectrically cooled CCD (Spec-10:100, Roper Science) with a 100  $\times$  1340 pixel array via a monochromator (Acton SP300i). Background corrections were applied to all collected spectra. Composite spectra presented in this work reflect the sum of seven or more individual spectra taken with different IR-centered wavelengths. The choice of these wavelengths ensures constant infrared power across the entire spectral region of interest. More details will be forthcoming in a separate study.

## Results and Discussion

In this study, we have investigated the surface structure of neat, 1-chloro-, and 1-bromo-hexadecane, using  $S_{st}P_{vis}P_{ir}$  and  $S_{st}P_{vis}S_{ir}$  polarization combinations to understand how molecular structure affects the surface structure. Figure 2 shows the SF spectra of *n*-C<sub>16</sub>, Cl-C<sub>16</sub>, and Br-C<sub>16</sub>, acquired under SSP polarization conditions. Black lines are the background corrected data, gray lines show the multi-peak fit spectra, and dashed gray lines show the vibrational bands of individual features. The *n*-C<sub>16</sub> spectrum is quantitatively consistent with that reported by Shen



**Figure 3.** Sum-frequency spectra of *n*-hexadecane (*n*-C<sub>16</sub>, top), 1-chlorohexadecane (Cl-C<sub>16</sub>, middle), and 1-bromohexadecane (Br-C<sub>16</sub>, bottom) under  $S_{st}P_{vis}S_{ir}$  polarization condition observing only the vibrational transition moments that have in-plane components. Data are background-corrected.

and co-workers.<sup>9</sup> The two low-energy features in the spectrum at 2850 and 2872 cm<sup>-1</sup> are assigned to the methylene symmetric stretch (CH<sub>2</sub>-SS, d<sup>+</sup>) and the methyl symmetric stretch (CH<sub>3</sub>-SS, r<sup>+</sup>), respectively. As is common in alkyl vibrational spectra, the higher-energy features are not well-resolved. This band has been fit with three contributions, corresponding to a methylene Fermi resonance (CH<sub>2</sub>-FR, d<sub>FR</sub><sup>+</sup>) at 2907 cm<sup>-1</sup>, the methylene asymmetric stretch (CH<sub>2</sub>-AS, d<sup>-</sup>) at 2922 cm<sup>-1</sup>, and the methyl Fermi resonance (CH<sub>3</sub>-FR, r<sub>FR</sub><sup>+</sup>) at 2934 cm<sup>-1</sup>. All of these assignments are based on previous bulk and surface studies of the alkyl vibrational structure.<sup>1,7-9,17</sup> The haloalkane spectra are qualitatively similar to those of *n*-C<sub>16</sub>, except for the significantly diminished relative intensity of the r<sup>+</sup> band. In addition, bands corresponding to the d<sup>+</sup>/d<sup>-</sup>/r<sub>FR</sub><sup>+</sup> features are markedly sharper. The r<sup>+</sup>/d<sup>+</sup> ratio of intensities is used frequently as a measure of conformational order at surfaces containing alkyl chains. For example, *n*-hexadecane in its *all-trans* conformation possesses inversion symmetry along the carbon chain meaning that the r<sup>+</sup> and d<sup>+</sup> modes are SF inactive. In principle, the r<sup>+</sup> and d<sup>+</sup> modes can contribute to a SF spectrum only when this inversion symmetry is broken by gauche defects along the chain or when the two ends of the molecule are subjected to different forces. For the spectra in Figure 2, the r<sup>+</sup>/d<sup>+</sup> ratios are 0.3 for *n*-C<sub>16</sub> and  $\leq 0.1$  for Cl-C<sub>16</sub> and Br-C<sub>16</sub>. Several factors could account for this decrease and will be discussed below.

As mentioned previously, different polarization combinations can provide information about the orientation of vibrational transition moments by comparing relative band intensities in spectra acquired under SSP and SPS polarization conditions (see Figures 2 and 3, respectively). For *n*-hexadecane, the absence of the CH<sub>3</sub>-AS (r<sup>-</sup>) feature in the SSP spectrum (top, Figure 2), coupled with a clear r<sup>+</sup> band, implies a net CH<sub>3</sub> orientation

that is, on average, perpendicular to the surface. Supporting this picture is the strong  $r^-$  band in the SPS spectrum (top, Figure 3) with no detectable signal in the  $r^+$  region. Because of the difficulty of assigning the  $d^-$  feature unambiguously, we cannot determine a net molecular orientation. However, the perpendicular orientation of  $\text{CH}_3$  groups will constrain the orientation of the first methylene group and create a weak  $d^+$  feature in the SSP spectrum. The fact that the  $d^+$  band is much stronger than the  $r^+$  band implies considerable conformational disorder that is likely to randomize the orientation of the second methyl group. Consequently, we expect little contribution from the second methyl group to the SF spectrum. Despite the small  $r^+/d^+$  intensity ratio observed at the  $n\text{-C}_{16}$  surface, the presence of any intensity in the  $r^+$  band requires that a disproportionate number of methyl groups adopt an orientation with their symmetry axes parallel to the surface normal. This picture of a semi-ordered surface structure contrasts with the description presented from X-ray surface scattering studies of  $n\text{-C}_{16}$ , where no long-range order was reported and a highly disordered surface structure was implied.<sup>10</sup> As mentioned in the Introduction, differences between X-ray and vibrational studies may be due to the experimental limitations constraining each technique. X-ray experiments are sensitive to static, long-range order and require a regular array of molecules to produce well-defined scattering patterns. The SFG technique, on the other hand, requires only that functional group (i.e.  $-\text{CH}_3$ ) transition dipoles adopt a net, anisotropic polar ordering. In other words, SFG is more sensitive to small, less-ordered details of the surface structure than X-ray scattering measurements.

Spectra from the haloalkane/vapor interfaces support this model of an interface that has considerable surface structure. The narrower line widths of the  $d^+$  and  $d_{\text{FR}}^+$  bands suggest a more homogeneous environment for those  $\text{CH}_2$  groups that contribute to the SF spectra. The dramatic decrease in the  $r^+$  band intensity (and the  $r^+/d^+$  intensity ratio) in the  $\text{Cl-C}_{16}$  SSP spectrum (middle, Figure 2) indicates that either fewer methyl groups exist at the surface, compared to  $n\text{-C}_{16}$ , or that the methyl groups at the surface do not have their transition dipole oriented along the surface normal. An in-plane methyl orientation is not supported by the SPS spectrum (middle Figure 3) that shows a noisy but significant  $r^-$  band for  $\text{Cl-C}_{16}$ . The SPS spectrum of  $\text{Br-C}_{16}$  (bottom, Figure 3) does not contain any discernible features, implying that the surface is completely isotropic within the interfacial plane. Correlated with the decrease in the  $r^+$  band intensity in the haloalkane spectra is a significant narrowing of the multicomponent feature centered near  $2925\text{ cm}^{-1}$ , where narrowing can be attributed to a loss of intensity in the  $r_{\text{FR}}^+$  band.

Typically, evaluation of the surface structure of different alkyl systems involves comparing the  $r^+/d^+$  intensity ratios from different spectra and interpreting differences in terms of the relative degree of conformational order at each interface. Several difficulties preclude such a direct comparison between the SFG spectra of the  $n\text{-C}_{16}$  and  $\text{Cl-C}_{16}$  (or  $\text{Br-C}_{16}$ ) systems. First, the  $\text{Cl-C}_{16}$  molecule has one less methyl group than  $n\text{-C}_{16}$ ; therefore, even a simple, statistical consideration would reduce the surface methyl groups at the  $\text{Cl-C}_{16}$  surface and diminish the intensity of the  $r^+$  band. In addition, the surface number density of the  $\text{Cl-C}_{16}$  system would be less than that of  $n\text{-C}_{16}$  because of the larger cross-sectional area of the terminal chloromethyl ( $-\text{CH}_2\text{-Cl}$ ) group compared to that of the terminal methyl group. Finally, every interfacial methyl ( $-\text{CH}_3$ ) group that is replaced by a chloromethyl group ( $-\text{CH}_2\text{Cl}$ ) leads to an enhancement in the  $d^+$  band because of the  $\text{CH}_2$  unit that is part of the terminal

chloromethyl group. Nevertheless, based on the relative intensities of the  $r^+$  features in the  $\text{C}_{16}$  and  $\text{Cl-C}_{16}$  spectra, one can conclude that the terminal chloromethyl groups *do not* preferentially sequester themselves in bulk solution, leaving a methyl-terminated surface exposed to the vapor.

Energetic concerns also prevent a direct comparison between  $n\text{-C}_{16}$  and  $\text{Cl-C}_{16}$  surfaces. The  $\text{C-Cl}$  bond is sufficiently polar ( $\mu \approx 2.0\text{ D}$ ), so that dipole-dipole interactions can lead to enhanced surface structure and surface activity of the halogenated ends. Molecular dynamics simulations of  $\text{Cl}$ -terminated self-assembled monolayers by Benjamin and co-workers have suggested that dipolar interactions could lead to an enhanced surface structure.<sup>18,19</sup> However, there exist enough differences between the SAMS simulations and the liquid/vapor systems studied here that any direct comparison should be considered tenuous at best. At a surface, the end group dipoles of  $\text{Cl-C}_{16}$  can organize without the steric hindrance that would inhibit dipole-dipole interactions in bulk solution. A higher dipole density at the surface will also lead to a higher surface free energy that is reflected in the  $\text{Cl-C}_{16}$  surface tension of  $30\text{ mN/m}$ , relative to  $26\text{ mN/m}$  for  $n\text{-C}_{16}$ . Additional  $\text{CH}_2\text{Cl}$  end groups at the surface would increase the  $d^+$  band intensity considerably, because of the surface-induced polar ordering, and intermolecular interactions between the adjacent end-groups will lead to a more homogeneous distribution of terminal methylene groups. In fact, the  $d^+$  band in the  $\text{Cl-C}_{16}$  spectrum is 40% narrower than that in the  $n\text{-C}_{16}$  spectrum. If the halogenated end group did not alter the overall conformational order within the chain significantly, the contribution to the  $d^+$  band intensity from the rest of the chain would be comparable to contributions from the  $n\text{-C}_{16}$  molecules, meaning that the  $d^+$  band would remain quite broad (as it is in the  $n\text{-C}_{16}$ ). We note that the methylene group adjacent to the terminal  $\text{Cl}$ -methyl group can, in principle, also contribute to the SF spectrum (due to the inherent asymmetry in the molecule).

Observed features of the  $\text{Br-C}_{16}$  surface spectra match closely the data acquired from the  $\text{Cl-C}_{16}$  surface. In the SSP spectrum (bottom, Figure 2), an increase in the relative intensity and bandwidth of the  $r^+$  feature is observed compared to  $\text{Cl-C}_{16}$ . No features were observed in the SPS spectrum (bottom, Figure 3). The observed differences can be correlated with the size difference of the halogenated end groups. The bigger the halogen, the fewer the number of  $\text{CH}_2\text{X}$  end groups at the surface. This will cause a net reduction in the contribution to the  $d^+$  band. Moreover, there will be more free volume for the  $\text{CH}_3$  end groups at the liquid/vapor surface, causing an increase in the  $r^+$  band intensity and bandwidth.

In conclusion, we have studied the structural effect on the surface organization of very similar molecules in their bulk properties. We have observed that there is a preferential orientation only at the surface side of the alkanes and the remainder of the molecule is highly disordered. The thickness of the ordered region is likely too small to be observed via X-ray diffraction studies, explaining why the surface induced polar-ordering has largely escaped notice until now. For haloalkanes, we also suggest a mixed surface composition with mainly  $\text{CH}_2\text{X}$  (where  $\text{X} = \text{Cl}$  or  $\text{Br}$ ) and  $\text{CH}_3$  end groups oriented toward the vapor phase. These results demonstrate that small changes in molecular structure can have a profound impact on the surface structure at a liquid/vapor interface.

**Supporting Information Available:** We thank J. Stephenson and K. A. Briggman for helpful discussions and instrumental assistance. This work was supported by NSF-CRIF (under No.



CHE-9982190) and CAREER (under No. CHE-0094246) awards. R.A.W. thanks the Alfred P. Sloan Foundation for additional support of this research.

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