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NOTES

Preferential molecular ordering at the surface of a liquid perfluoropolyether revealed by x-ray photoelectron spectroscopy

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Many of the bulk properties of liquids are related to their microscopic surface structure. Why should a long chain alkane such as squalane (2,6,10,15,19,23-hexamethyltetracosane) exhibit a low surface tension (30 dyn/cm) than glycerol (63 dyn/cm) at room temperature is due to the difference in their surface chemical composition.[1] Glycerol exposes –OH groups of large surface free energy to the surface.[1] In contrast, the surface of the alkane is dominated by –CH$_2$ and –CH$_3$ groups which have low surface free energy.[1,2] Diverse properties of a liquid such as adhesion, lubrication, and wetting are similarly connected to its microscopic surface chemical structure. The dissolution of an incoming species in a liquid depends upon what it encounters up on its interaction with the liquid surface. Due to all these, the question of what constitutes a liquid surface has been of interest, especially because the bulk properties of liquids begin to appear approximately 4 Å beneath the liquid–vacuum interface.[2,3] A variety of tools has been used to answer this question. Most of the reports are on computer simulation;[2,4–11] molecular dynamics modeling of long chain alkanes[2] suggest that the liquid surface is mostly composed of the chain ends. Structural aspects of liquid surfaces have been inferred from rare gas scattering studies; investigations on a perfluoropolyether show that the incoming atoms get scattered from the protruding F atoms or –CF$_3$ groups in hard spherelike collisions.[12,13] In a recent study using low energy reactive ion beams, one of us has shown that the perfluoropolyether surface is primarily composed of fluorine atoms.[14] Reactive scattering, although surface sensitive, is not equally sensitive to all the different chemical species. There are a number of other methods potentially useful for the structural characterization of liquid surfaces. Light scattering is a powerful tool to study dynamic behavior of liquids,[15] but no molecular information can be derived. X-ray[16] and neutron[17] scattering have been used to study the properties of surfaces and interfaces involving liquids, but molecular information is yet to be derived from such studies. Nonlinear optical studies have been performed recently to understand the surface composition of liquid/vapor interfaces.[18] Liquids have been studied using electron spectroscopic techniques[19] as well as metastable atom scattering.[20] In the following, we present the results of a core level photoelectron spectroscopic investigation of the preferential molecular ordering at the liquid surface.

The techniques of electron spectroscopy, especially photoelectron spectroscopy, are extremely surface sensitive and the timescale of photoemission ($\sim 10^{-16}$ s) is much smaller than the time scale of molecular motion in a liquid. By vary-ing the electron takeoff angle, it is possible to make the technique either surface or bulk sensitive. The escape depth[21] of photoelectrons of ~ 1000 eV in an organic polymer is of the order of 15–30 Å, which is of the order of molecular dimensions of a liquid alkane. Keeping these in view, we performed an investigation of the molecular surface composition of a liquid using x-ray photoelectron spectroscopy (XPS). The measurements were carried out in a VG ESCALAB MKII spectrometer with Mg K_α radiation. Vacuum requirements of the spectrometer compelled us to use a low vapor pressure liquid, PFPE (Ref. 22) {perfluorinated polyether F[CF(CF$_3$)CF$_2$O]$_{27(\text{ave})}$CF$_2$CF$_3$, average molecular weight 4600, trade name Krytox 1625} having a vapor pressure of 3×10^{-10} Torr and a density of 1.87 g/cm^3 as our target surface. The surface was prepared by sheeting a 10 μm film of the liquid on a gold covered polished glass plate of 1 cm^2. The sample manufactured by DuPont was a gift from Professor R. G. Cooks. Base vacuum of the spectrometer was 8×10^{-10} Torr and it deteriorated to 2×10^{-9} Torr upon exposure to x-rays. To avoid possible surface changes that may result due to x-ray exposure, the flux was kept to a minimum of 15 W. The electron takeoff angle, defined as the angle between the photoelectron collection and the surface parallel was varied by rotating the sample. Takeoff angles in the range of 80°–40° were used. Both the x-ray and the photoelectron collection lens were held fixed. The XPS binding energies are referred to the Ag $3d_{5/2}$ peak of 368.2 eV. There was difference in the film thickness between measurements and consequently the extent of charging varied. The binding energies reported here are not precise due to this reason.

In the PFPE sample, there are four distinctly different carbon atoms. Per molecule, there are 28 –CF$_3$, 29 –CF$_2$, and 27 –CF groups. There are two kinds of –CF$_2$ groups, one in the repeating unit attached to oxygen and other in the chain ends. There are only two latter types of –CF$_2$ groups per molecule and we will not be able to differentiate this minority contribution from the other 27 –CF$_2$ groups. It is expected that the core level C 1s binding energies of –CF$_2$O and –CF$_3$ groups will not be significantly different and with the unmonochromatized source, we will not be able to differentiate the two. The –CF carbon will have a lower binding energy.[23] Thus the C 1s region of PFPE will exhibit two peaks corresponding to –CF and –CF$_2$/–CF$_3$. Assuming similar cross sections for the various carbon atoms, the peaks will be roughly in 1:2 intensity ratio for the free molecule. When the x-ray probes the liquid surface, the intensities of these peaks will vary with the electron takeoff angle if there
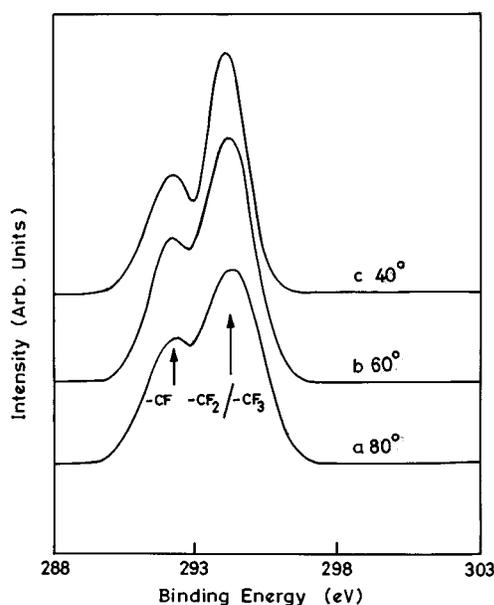
FIG. 1. The x-ray photoelectron spectrum of the C 1s region of Krytox 1625 at various electron takeoff angles; (a) 80°, (b) 60°, and (c) 40°. Note the decrease in relative intensity of the –CF peak as the electron takeoff angle decreases. There were small differences in the C 1s binding energies between a set of measurements since the extent of charging varied with the sample thickness which could not be held constant.

is preferential orientation. If all the molecules lie horizontal to the surface, it is expected that the C 1s spectrum would be the same with two components of roughly 1:2 intensity ratio, at all angles regardless of whether it is bulk or surface sensitive. If the molecules lie nearly normal to the surface, as the electron takeoff angle decreases, there will be an increase in intensity of photoelectrons from the terminal –CF$_3$ and –CF$_2$ groups than from the –CF groups assuming similar angular dependence for all the carbons. Thus the intensity of the low binding energy peak (due to –CF) with respect to the –CF$_2$/–CF$_3$ peak will decrease as the takeoff angle decreases.

The photoelectron spectra shown in Fig. 1 can be rationalized on the basis of the above reasoning. At nearly normal takeoff angle [Fig. 1(a)], the spectrum shows two bands at nearly 1:7 intensity ratio at 292.3 and 294.3 eV; the first one is due to –CF and the other is due to –CF$_2$ and –CF$_3$. The larger intensity of the –CF feature can be understood on the basis of the helical structure[24] of the molecule which exposes more –CF groups than the –CF$_3$ groups (present in the monomer units). As the electron takeoff angle decreases, relative intensity of the –CF peak decreases (see Fig. 1). This observation cannot be explained if the surface of the liquid is in random order. However, if one considers that the surface of the liquid is primarily composed of molecule ends, it is understandable. On such a surface, as the technique becomes more surface sensitive, there are more –CF$_2$ and CF$_3$ groups than –CFs contributing to the C 1s intensity. As the contribution to the photoelectron intensity changes from 10 to 5 to 3 [CF(CF$_3$)CF$_2$O] monomer units, the CF to CF$_2$/CF$_3$ peak intensity would decrease from 9/21 to 4/11 to 2/7. Although the actual intensities would be affected by other fac-

tors, the general trend would follow the above pattern as reflected in Figs. 1(a)–1(c). In conclusion, the results show that the terminal –CF$_3$ groups primarily constitute the surface.

The F 1s and O 1s regions were also studied as a function of electron takeoff angle. The F 1s appears as a single peak at 688.6 eV as expected and there was no change in the peak shape with takeoff angle. The O 1s appears at 536.8 eV and no change in the peak shape was observed with angle, although intensity decreased significantly at lower takeoff angles. The surface of the liquid was remarkably clean from any contaminants. Up on deliberate exposure of the surface to molecules such as water, no adsorption was observed suggesting that the ether oxygens are beneath the surface.

It is interesting that a more direct technique such as photoelectron spectroscopy can be used in understanding the chemical nature of a liquid surface. The present study agrees with the previous ion/surface reactive scattering and rare gas atom scattering measurements. Experiments are currently underway to understand the surface chemical structure of other low vapor pressure liquids by photoelectron spectroscopy. We are exploring the changes in the surface chemical constitution of the liquid as it solidifies. We are also investigating the possibility of changing the surface composition of the liquid by providing some highly reactive species at the surface.

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