

# Chemical constitution of a perfluoropolyether liquid surface. A photoelectron spectroscopic study

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## Abstract

Angle resolved X-ray photoelectron spectroscopy from a liquid perfluoropolyether shows that its surface is primarily composed of chain ends oriented nearly perpendicular to the surface. Indirect evidence suggests that the ether oxygens may not be available for any of the surface processes. The results are in agreement with recent atomic beam scattering experiments and molecular dynamics simulations.

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## 1. Introduction

The surface chemical structure of liquids is of great interest to scientists of diverse disciplines. Most of the available information is derived from computer simulations [1–9]. Molecular dynamics studies of long chain alkanes [1] suggest that the liquid surface is mostly composed of chain ends. Various experimental approaches have also been used to understand the liquid surface structure. Rare-gas atomic beam scattering from a perfluoropolyether shows that incoming atoms undergo direct scattering from the protruding F atoms or CF<sub>3</sub> groups in hard sphere like collisions [10,11]. A recent study of the liquid surface using reactive ion beams showed that a perfluoropolyether surface is primarily composed of fluorine atoms [12]. An important disadvantage of reactive ion beam scattering is that the probe beam although sensitive to surface functional groups, is not equally sensitive to all the surface species. Light scattering is a powerful tool to understand the dy-

amic behaviour of liquids [13], but it is hard to derive molecular information. X-ray total reflection [14] has been employed to study liquid–vapor interface, but little is known on the molecular orientation at the liquid surface. Neutron scattering [15] has also been applied to study liquids and the information available is similar to that of X-rays. Nonlinear optical spectroscopic investigations have been used to probe liquid surfaces and such studies have revealed a good deal of structural information [16]. Electronic structures of liquids have been studied by electron spectroscopic techniques [17] and metastable atom scattering [18].

In this Letter, we present an angle-resolved photoelectron spectroscopic investigation of a perfluoropolyether liquid surface and conclusively show that its surface is composed of molecular chain ends. The study is an extension of that reported earlier with better quality data on a different, but chemically similar liquid [19]. As is well-known, photoelectron spectroscopy (PES) is highly surface sensitive and

the time scale of photoemission ( $\approx 10^{-16}$  s) is orders of magnitude lower than the time scale of molecular motion in a liquid. The electron take-off angle, defined as the angle between the electron acceptance lens and the surface plane, controls the depth to which the technique is sensitive. By varying this parameter, the technique can be made either surface or bulk sensitive. The escape depth of photoelectrons of  $\approx 1000$  eV in organic polymeric films [20] is of the order of 15–30 Å. Thus at extremely low electron take-off angles such as  $30^\circ$ , the depth to which the photoelectrons are sensitive to is only about 8 Å. Since the liquid surface essentially means a distance of about 5 Å beneath the top layer, below which the bulk properties commence [21,22], X-ray photoelectron spectroscopy can be effectively used to study it. X-ray PES requires ultra high vacuum as a prerequisite and only liquids compatible with UHV can be used in these experiments.

## 2. Experiment

Measurements were performed with a VG ESCALAB MKII spectrometer at a base pressure of  $8 \times 10^{-10}$  Torr. A 0.2 mm film of the liquid was sheeted on a gold coated glass substrate. The liquid used was a perfluoropolyether [23], trade name krytox 16256, with an average molecular weight of 11000 and an approximate molecular formula of  $F[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_{65(\text{ave})}\text{CF}_2\text{CF}_3$ . The liquid has a vapour pressure of  $10^{-14}$  Torr, a density of 1.92 gm/cm<sup>3</sup> and a viscosity of 2717 centistokes (all at 20°C). The liquid was a gift from Professor R.G. Cooks of the Purdue University. No change in the spectrometer vacuum was observed during X-ray exposure. The photoelectron spectra were measured with Mg K $\alpha$  radiation at an X-ray flux of 80 W. All the spectra are averages of 10 scans of 60 s duration. Photoelectron spectra at take-off angles of  $90^\circ$ – $30^\circ$  were measured. The positions of X-ray gun and the electron acceptance lens were fixed and the take-off angle was varied by rotating the sample. The binding energies are referred to the Ag 3d<sub>5/2</sub> peak at 368.2 eV. There was small change in the film thickness between measurements and the extent of charging varied. Therefore, the binding energies reported are not exact.

## 3. Results and discussion

In a single molecule of PFPE, there are 64 CF, 66 CF<sub>2</sub> and 66 CF<sub>3</sub> groups. The CF<sub>2</sub> groups are of two kinds, 64 in the repeating monomer and two in the chain ends. It is hard to differentiate the contribution from the terminal two CF<sub>2</sub> groups from the remaining CF<sub>2</sub>s. The CF<sub>2</sub> groups in the repeating units are attached to oxygen atoms and therefore, the C<sub>1s</sub> binding energies of the CF<sub>2</sub> and CF<sub>3</sub> groups will be close to each other and will be hard to separate the two with non-monochromatic X-ray source. The CF carbon, however, will have a substantially lower binding energy. The above reasoning suggests that the C<sub>1s</sub> region of the photoelectron spectrum of PFPE will have two peaks corresponding to CF and CF<sub>2</sub>/CF<sub>3</sub> ionizations with the latter group having higher binding energy. As regards intensities, assuming cross sections of various carbons to be the same, the intensities of the CF and CF<sub>2</sub>/CF<sub>3</sub> peaks would be in the ratio 1 : 2.

The actual intensities depend upon additional factors: firstly, the electron take-off angle and secondly the molecular ordering in the liquid. If no order exists, the spectrum will not show any change with angle regardless of whether surface or bulk is examined. If the molecules lie horizontal to the surface, then again no variation in spectral features is expected. If the molecules are ordered laterally with the molecular axis lying perpendicular to the surface, a variation in electron take-off angle can have a significant effect on the various C<sub>1s</sub> intensities. Here it is assumed that the angular dependence of photoelectron intensity is similar for all the different forms of carbons; which is a reasonable assumption. As the electron take-off angle decreases, the contribution from the terminal CF<sub>3</sub> and CF<sub>2</sub> groups will increase with respect to the CF groups.

Let us look at the intensities in more detail. Assuming a linear structure for the molecules with a photoelectron mean free path of 20 Å, there are about five CF<sub>3</sub>, six CF<sub>2</sub> and four CF groups per molecule contributing to the C<sub>1s</sub> XPS intensity for a perpendicularly ordered structure. However, the structure of a perfluoroether is helical in nature, with CF<sub>3</sub> groups inhibiting the close packing and ether oxygens enhancing the flexibility of the carbon skeleton [24]. Thus, due to helicity, the CF<sub>2</sub>/CF<sub>3</sub> : CF

intensity at 90° angle will be lower than the expected 11:4. As the technique becomes more surface sensitive, fewer and fewer monomer units contribute to the intensity. This will make the intensity ratio increase from 9:3 to 7:2 to 5:1, as observation angle decreases. Although the exact values depend on the extent of helicity, the general trend is quite obvious.

The marked change in the intensity ratio is reflected in the photoelectron spectra. In Figs. 1a–d, we show the  $C_{1s}$  PE spectra at electron take-off angles of 90°, 70°, 50° and 30°, respectively. The two peaks are labelled as CF and  $CF_2/CF_3$ . The 90°

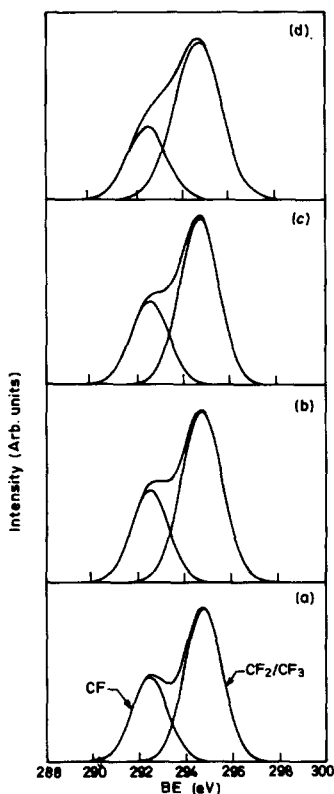


Fig. 1. The X-ray photoelectron spectrum of the  $C_{1s}$  region of krytox 16256 at various photoelectron take-off angles. (a) 90°; (b) 70°; (c) 50° and (d) 30°. The peaks are labelled. The observed spectrum has been fitted with two symmetric Gaussians. Note the decrease in the CF peak intensity with decrease in the electron take-off angle. There was significant extent of charging which varied slightly with the angle due to differences in the liquid film thickness. The binding energies were calibrated with respect to Ag  $3d_{5/2}$  peak at 368.2 eV.

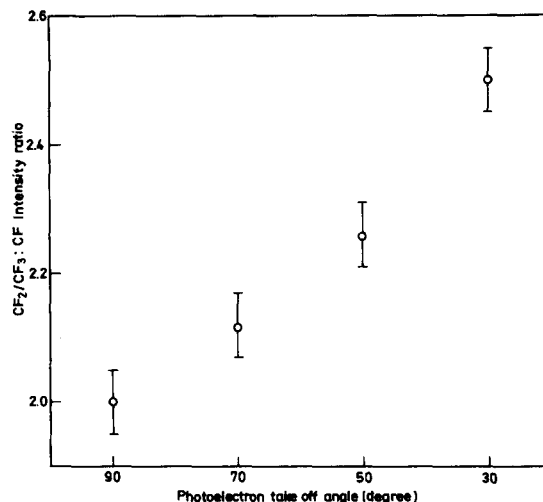


Fig. 2. A plot of the variation of the  $CF_2/CF_3 : CF$  intensity ratio with the photoelectron take-off angle.

spectrum (Fig. 1a) gives an intensity ratio of 2.00 for  $CF_2/CF_3 : CF$ . As the electron take-off angle decreases, the  $CF_2/CF_3 : CF$  intensity ratio increases. The actual values are 2.00 at 90°, 2.12 at 70°, 2.25 at 50° and 2.50 at 30°. The spectrum does not show the emergence of any new peaks, only a variation in intensity is observed. This change can well be accounted for on the basis of the reasoning given above. The results suggest that the molecular chain ends of the ether protrude towards the liquid surface. It should be mentioned that the increase in  $CF_2/CF_3$  peak intensity can only be due to the terminal groups; a variation in the intensity of  $CF_3$  or  $CF_2$  group in the chain body should proportionately enhance the CF group intensity. In Fig. 2 we summarise the variation of the  $CF_2/CF_3 : CF$  intensity ratio with the photoelectron take-off angle. Significant increase in the intensity ratio is seen with a decrease in the take-off angle.

The  $F_{1s}$  and  $O_{1s}$  regions of the PFPE were also studied as a function of electron take-off angle. The  $F_{1s}$  region shows only one peak at 688.6 eV. The peak shape does not show any change with the electron take-off angle as expected. A similar behavior was observed with  $O_{1s}$  which gave a single peak at 536.8 eV. The  $O_{1s}$  intensity, however, showed a decrease at lower take-off angles.

An experiment was performed in which the sur-

face was exposed to a few adsorbants. Even after prolonged exposure to air,  $\text{PCl}_3$  and methanol, neither of the species was detected in the XPS spectra. The exposure was performed in the analysis chamber and the measurements were performed soon after. The surface was remarkably clean after the exposure, no change in the peak positions of  $\text{C}_{1s}$ ,  $\text{F}_{1s}$  and  $\text{O}_{1s}$  was observed. In PFPE, oxygens are the only absorbing sites, although they are expected to be weak bases due to the lone pair stabilization by the electron withdrawing fluorine atoms [25]. Our study shows that these oxygens may not be available on the surface to become involved in adsorption.

Investigation of the surface of a chemically related perfluoropolyether by XPS has shown that its surface is primarily composed of chain ends [19]. The present study together with the ion/surface and molecular beam scattering experiments suggest that there is a high degree of order on these liquid surfaces. It may be noted that such a surface structure does not imply ordering in the bulk. Taken together with molecular dynamic simulations, it may be generalised that long chain molecular liquids surfaces are composed of chain ends. Some of the properties of these liquids such as lubrication, surface tension, wettability and chemical inertness can be correlated with this surface order. Experiments are currently in progress to understand the changes in the surface ordering with temperature. Although the requirement of ultra high vacuum imposes restrictions on the type of liquids that could be studied, we are looking into the possibilities of applying the method to different chemical systems.

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