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Angle resolved ion scattering spectroscopy at surfaces of pure liquids: topography and orientation of molecules†

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The topography of a liquid surface has not been the subject of experimental research because of a lack of experimental methods. The hereby outlined investigation shows how the topography of a liquid surface can be classified through the angular mode of neutral impact collision ion scattering spectroscopy. It further shows how concentration depth profiles with a high depth resolution are gained. These can be used as the basis to determine quantitatively the orientation of molecules. The substances investigated are the polar solvents formamide and benzyl alcohol.

Introduction

The investigation of the molecular structure of liquid surfaces is important for the understanding of their macroscopic properties like surface tension or surface potential. In the past decades methods have been developed to investigate the composition of the outermost layer, concentration depth profiles and orientation of molecules. Experimental methods used to determine concentration depth profiles are neutron reflectivity (NR)[1,2] and X-ray reflectivity,[3] angle resolved photoelectron spectroscopy (ARXPS)[4–6] and neutral impact collision ion scattering spectroscopy (NICISS).[7–9] The concentration depth profiles determined with these methods yield information about the orientation of the molecules. Another method used for this purpose is recoiling spectroscopy.[10] Metastable induced electron spectroscopy (MIES) is a perfect surface sensitive method that probes which orbital of a molecule is accessible for the metastable atom[11,12] and thus reveals also the composition of the outermost layer. Non linear optical methods like sum frequency generation are sensitive for interfaces and probe the interaction of differently polarized light with the molecules.[13–15] Both methods have been used to determine the orientation of molecules.

Another approach to the molecular structure of liquid surfaces are simulations, which form the basis for the investigation of a great variety of quantities like density profiles, diffusion constants, surface tension, orientation of molecules or concentration depth profiles.[16–20]

The topography of a liquid surface has not been the subject of experimental research because of a lack of experimental methods. The goal of this paper is to show how the homogeneity of the topography of liquid surfaces can be classified with the angular mode of NICISS (ARISS). Revealing the topography might be important for the interaction at the gas/liquid interface, especially for the uptake of gas molecules through the interface. NICISS has so far been used to determine concentration depth profiles at a single angle of incidence of the projectiles, the angle close to the surface normal.[8,9] Here we implicitly assumed that the influence of the topography on the concentration depth profiles may be neglected. This as-sumption is of course true *e.g.* for determining the surface excess from the depth profiles. Measurement of spectra at different polar angles reveals the topography around the atoms itself. The criterion for a homogeneous topography will be that the spectra of a liquid surface obtained at different polar angles can be fitted with a single depth profile. If this is the case, concentration depth profiles with a high depth resolution are also gained. These profiles can be used to determine quantitatively the orientation of molecules, which in itself is still a challenge, especially for small solvent molecules. Recently we have showed that in the case in which the topography is not homogeneous, the topography around an atom can be mapped out with the angular mode of NICISS (ARISS).[21]

The substances investigated are the polar solvents formamide and benzyl alcohol. The results will be compared with those obtained using MIES and computer simulations.

Experimental

In the context of the investigation of liquid surfaces NICISS has so far been used to determine elemental concentration depth profiles up to a depth of 300 Å with a depth resolution far below 10 Å.[7,8] The details are described elsewhere.[7] The target is bombarded with a pulsed beam of inert gas ions—mostly helium ions—with a kinetic energy of several keV. The energy of the projectiles back scattered from the atoms in the target is determined by their time of flight (TOF) from the target to the detector. The projectiles lose energy during the back scattering process. The extent of energy transfer depends on the mass of the target atom. Additionally the projectiles lose energy on their trajectory through the bulk due to low angle scattering and electronic excitations (stopping power), which is proportional to the depth of the target atom. The energy loss in the bulk is calibrated with self-assembled monolayers of alkanethiolates on gold and silver single crystals.[22] The depth that can be investigated with this method is limited by the broadening of the beam in the bulk due to low angle scattering. The maximum depth for investigation is about 300 Å at an energy of 5 keV. The dose of the He ions for this investigation was about 10^{10} ions cm^{-2}. This is very low compared to the typical number of atoms in a surface of about 10^{14} atoms cm^{-2}. Thus the damage of the surface and the influence of the impinging ions on the surface structure can be neglected.
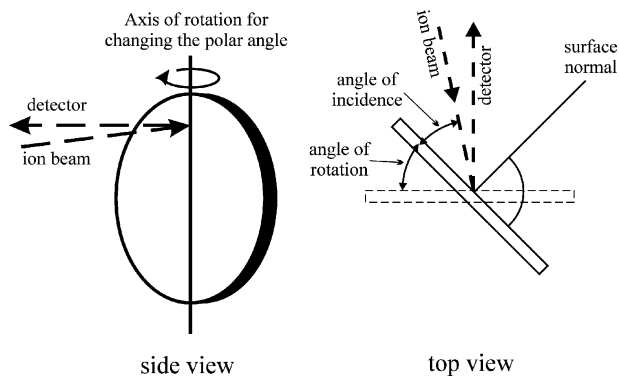
Fig. 1 Scheme of the target disk. The axis of rotation of the target has been placed on the surface of the rotating disk. The position on the disk used for the investigation has been on the axis of rotation.

The liquids investigated are the polar solvents formamide and benzyl alcohol. At the temperature chosen for the measurements (6 °C) formamide has a vapour pressure of 6×10^{-3} mbar and benzyl alcohol 1.3×10^{-3} mbar (-10 °C).

The liquid surface is generated as a liquid film with a thickness of several tenths of a millimeter on a rotating disk, which is partially immersed into a reservoir filled with the investigated liquid. After emerging from the reservoir the disk passes by a skimmer. At this position a fresh surface is created.

For the ARISS measurements the target has to be aligned in such a way that the distance for the TOF measurements is constant at all angles used for the measurements. Thus the axis of rotation of the target has to be placed on the surface of the rotating disk as sketched in Fig. 1 and also the position at which the liquid surface is investigated. The accuracy of the alignment is crucial for the data evaluation. The spatial full width half maximum (FWHM) of the ion beam was kept below 0.7 mm and did not influence the spectra.

Results

The spectra of the different elements are derived from the NICIS spectra as described in detail in ref. 7. Fig. 2a shows the TOF spectra of oxygen of formamide at the angles of incidence of 78° *i.e.* close to the surface normal, as well as at 13° *i.e.* at grazing incidence. Both spectra are almost the same. Since the correlation between the TOF scale and the depth scale is different for all angles of incidence, the only concentration depth profile of oxygen, which fits to these spectra, is a step profile with the onset at the surface. The calculation of the ratio between the energy loss and the depth is given in the ESI.† The finding is that the slope of the onset of the oxygen step is finite, although the concentration depth profile is a step function. The reason for this finding is discussed below.

The spectra are converted to the energy scale according to ref. 8 and plotted over the energy loss scale in Fig. 2b. The energy loss is the energy of the back scattered projectiles minus the energy of a projectile being back scattered from the outermost layer, thus a projectile which did not suffer an energy loss in the bulk. The conclusion that the depth profile of oxygen is a step with the onset at the outermost layer leads to the further conclusion that it is possible to determine the energy of those projectiles that are back scattered from oxygen from the outermost layer. Thus the zero mark of both the energy loss scale and the depth scale can be determined and the gauging can be used also for all oxygen spectra irrespective of the substance investigated.

The oxygen spectrum at 78° converted to the depth scale is shown in Fig. 2c. Additionally the deconvoluted concentration depth profile is shown. The deconvolution of the spectra at all angles was carried out with the genetic algorithm as described
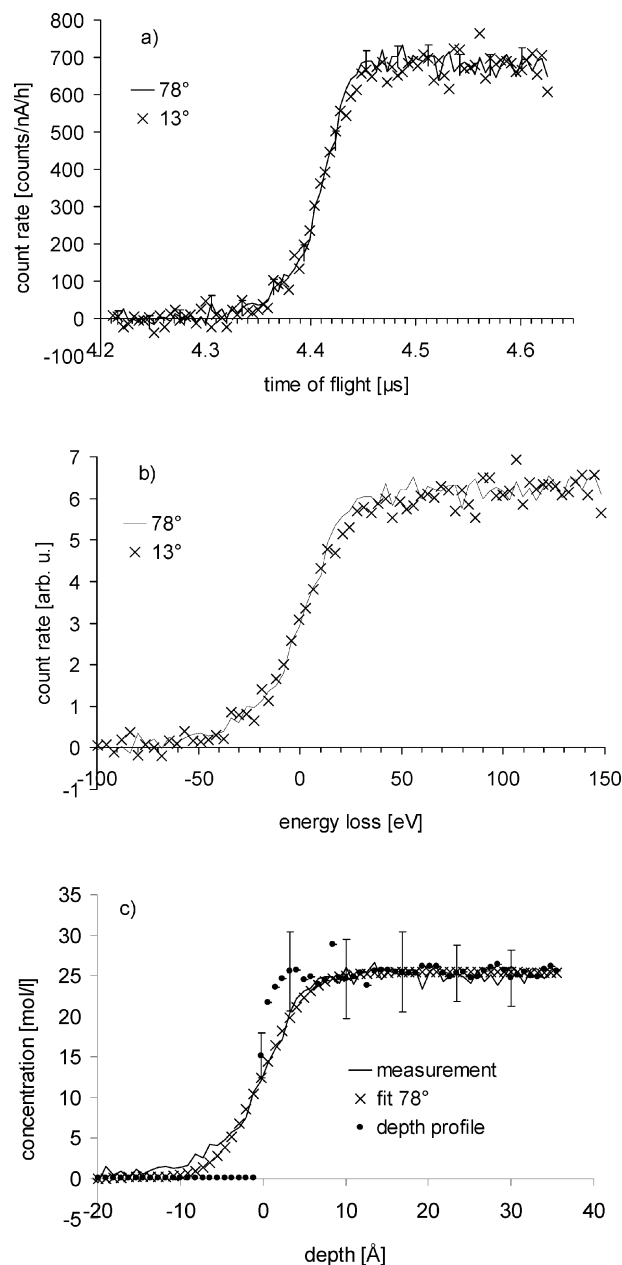

Fig. 2 (a) Time of flight spectrum (TOF) of oxygen of formamide at an angle of incidence close to the surface normal (78°) and at grazing incidence (13°). (b) The same spectra as that in (a) but as energy loss spectra. Since the spectra are the same at both angles they can be used to gauge the zero mark of the energy loss scale. (c) Spectrum of oxygen converted to the depth scale with the fitted depth profile appearing as a step function. The error bars are determined from the statistics of the fit procedure.

in ref. 8 with the concentrations as the fit parameters. The FWHM of the Gaussian curve used for the deconvolution was varied. The spectra at all angles could be fitted best with a step function and a FWHM of the Gaussian curve of 45 eV. The onset of the oxygen spectrum has a finite slope, although the concentration depth profile are found to be a step function. The reason for the finite slope is the energy resolution of the method, which is given mainly by the distribution of inelastic processes during the back scattering process. The FWHM of the Gaussian curve used for the deconvolution shows the distribution of inelastic processes during back scattering. It must be emphasized here that the shape of the onset of the measured oxygen spectrum is not due to the density profile at the formamide surface but only due to the reason mentioned above.
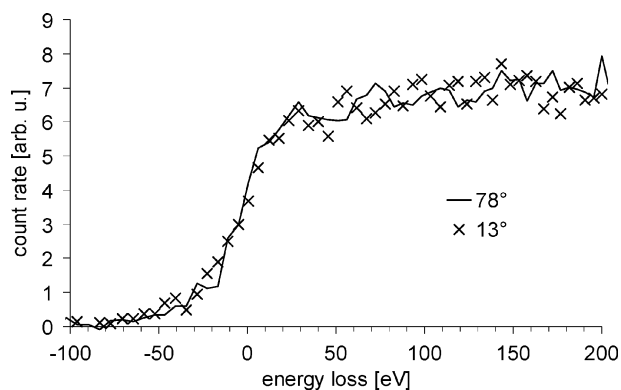
Fig. 3 Energy loss spectra of nitrogen of formamide. Since the spectra are the same at both angles they can be used to gauge the zero mark of the energy loss scale.

Fig. 3 shows the energy loss spectra of nitrogen of formamide at the angles of incidence of 78° and 13°. The spectra are the same. Thus it can be concluded for nitrogen the same as for oxygen as regards the depth profile, the zero mark of the energy loss scale and the depth scale.

The spectra of carbon were not evaluated as the recoil hydrogen background has an inflection point close to the onset of the carbon step. Thus the precision in determining the carbon spectra would be worse than that of oxygen and nitrogen.

In Fig. 4a the energy loss spectra of the oxygen of benzyl alcohol are shown for the polar angles 78° and 13°. The spectra are different and the spectrum at 13° shows a maximum at an energy loss of about 90 eV. The spectra at all polar angles can be fitted in the same way as that of formamide with a single depth profile, but with a non-constant depth profile. The measured spectra converted to the depth scale, the fitted spectra and the depth profile are shown in Figs. 4b and c. There is a depletion of the oxygen at the surface and an enrichment at a depth of about 4 to 5 Å. The determination of the carbon spectra of benzyl alcohol is subject to the same problem as that of formamide. Nevertheless if one is to assume that the sum of the oxygen and the carbon depth profiles is constant then the depth profile of oxygen determines the carbon depth profile as carbon is the only other element in the molecule apart of hydrogen. In order to prove whether the carbon depth profile determined in this way is in agreement with the spectra the so found carbon spectra are subtracted from the NICIS spectra. The criterion for the validity of the carbon depth profile is whether the remaining recoil hydrogen background is smooth. This is the case within the statistics of the spectra as can be seen in Fig. 5a. In Fig. 5b the carbon spectrum at 13° is shown together with the depth profile and the fit of the spectrum. The spectrum was obtained by subtracting a smooth curve fitted to the recoil hydrogen background after subtracting the carbon depth profile calculated from that of oxygen.

Discussion

It was found that the ARIS spectra of both formamide and benzyl alcohol can be fitted with a single depth profile for all angles of incidence. The depth profiles for oxygen and nitrogen of formamide are constant whereas that of oxygen of benzyl alcohol shows a depletion at the surface and a maximum below the surface at about 4 to 5 Å. The finding in the case of the solutions of the surfactants tetrabutylammonium iodide (Bu_4NI), tetrabutylphosphonium bromide (Bu_4PBr) and the inorganic salt potassium iodide (KI) was different. The ARIS spectra of iodide, bromide and phosphorous could by no means be fitted with a single depth profile for all angles of incidence.[21] The spectra could be fitted only by assuming that
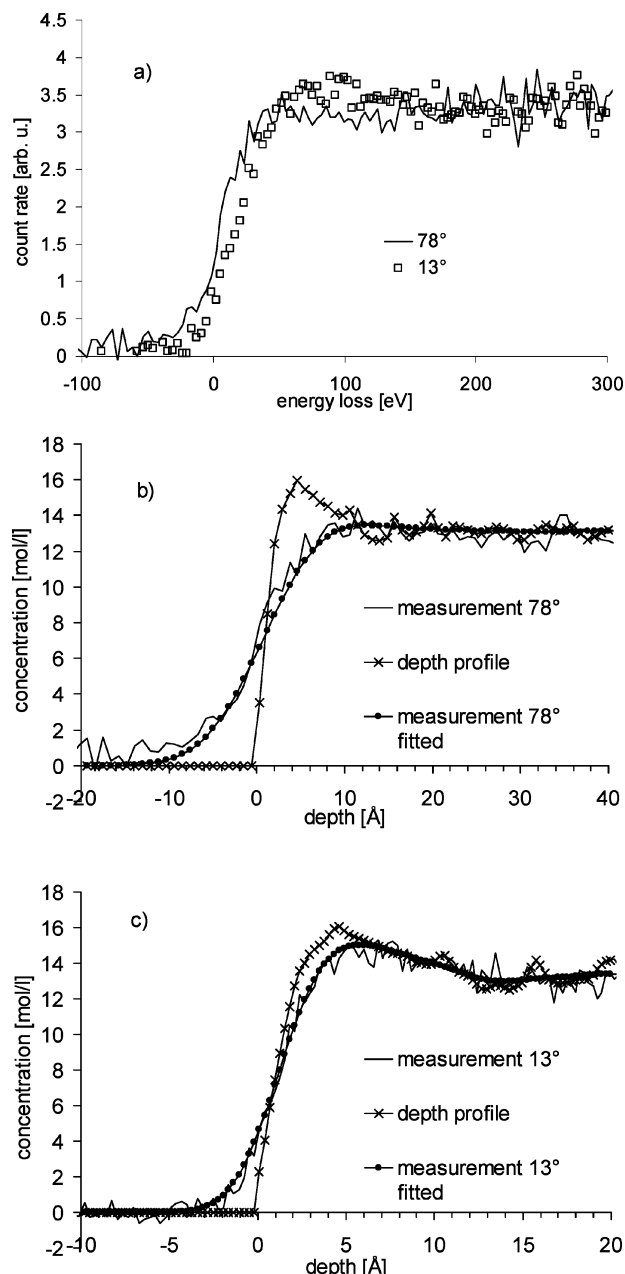

Fig. 4 (a) Energy loss spectra of oxygen of benzyl alcohol at an angle of incidence close to the surface normal (78°) and at grazing incidence (13°). (b) Spectrum of oxygen at 78° converted to the depth scale with the fitted depth profile. (c) Spectrum of oxygen at 13° converted to the depth scale with the fitted concentration depth profile.

iodide, bromide and phosphorous are located in the outermost layer in a valley-like structure. Thus, the evaluation of ARISS data allows to test whether the assumption of lateral homogeneity of the topography is justified, irrespective of whether the corresponding depth profile is constant or not. The concept "lateral homogeneous topography" means that there is no correlation between the position of an element or a subunit of a molecule or a molecule and the topography in its local environment. Thus the surface is flat in this case. A surface with a lateral homogeneous topography is sketched on the left side of Fig. 6. There is no correlation between the topography of the surface and the indicated atom. On the right side of the figure the indicated atom is positioned in a valley-like structure and there is a correlation between the position of the atom and the topography. Thus the topography on the right side has to be classified as inhomogeneous.

If the topography of a surface can be classified as homogeneous, we will be able to use the concentration depth profiles
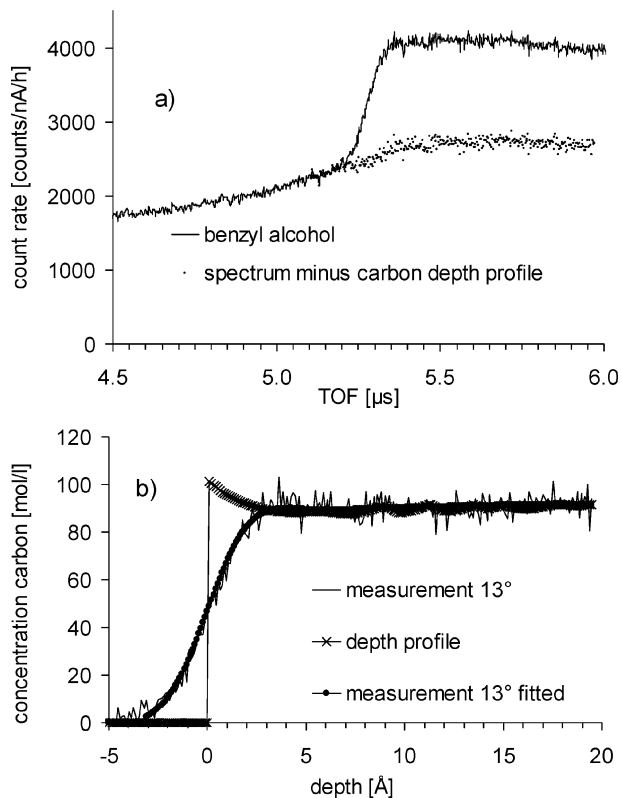
Fig. 5 (a) TOF spectrum of benzyl alcohol and the remaining recoil hydrogen background after subtracting the carbon step. (b) The spectrum of carbon at 13° converted to the depth scale with the concentration depth profile calculated from the fitted oxygen concentration depth profile.

for determining the orientation of the molecules at the surface. It must be emphasized here that the depth resolution with ARISS is much better than in the case that only a single spectrum is measured at an angle of incidence close to the surface normal.

The constant depth profile of oxygen and nitrogen of formamide could be due to either a random orientation or a preferred orientation of the molecules parallel to the surface. The conclusion which follows is that the latter is the case since this orientation was found by means of MIE spectra by Keller
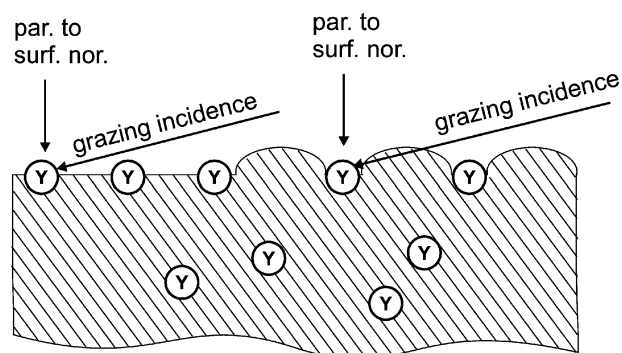

Fig. 6 On the left side a lateral homogeneous topography is sketched. There is no correlation between the position of the indicated atom and the topography and the surface is flat. On the right side there is a correlation between the position of the indicated atom and the topography and the topography is classified as inhomogeneous. The spectra of a surface on the left side can be fitted with a single depth profile for all angles of incidence. On the right side the situation is different. Projectiles impinging on the surface close to the surface normal see an uncovered atom while projectiles impinging at grazing incidence have to pass matter—the adjacent hills—before hitting the atom in the outermost layer.
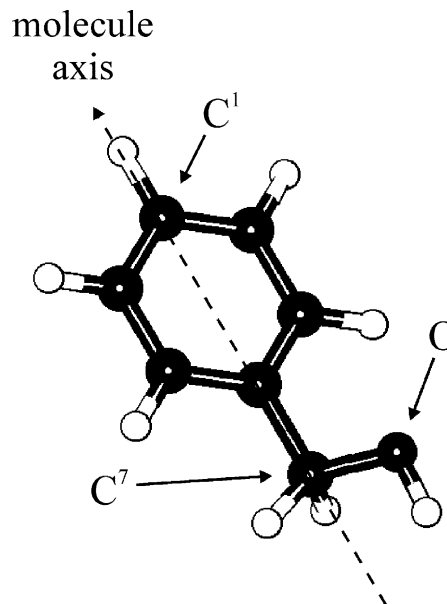

Fig. 7 Scheme of the benzyl alcohol molecule with the molecule axis.

et al.[11] and by means of computer simulations by Oberbrodhage.[20]

It is obvious that the depletion of oxygen at and the enrichment below the surface is due to the orientation of the benzyl alcohol. But it has to be clarified first, which possible configurations the molecules can have. The only possibility to achieve different configurations is by turning the C–O bond around the molecule axis. The molecule axis is given by the direction between the carbon atom close to the alcohol group (C^7) and the carbon atom of the benzene ring opposite to it (C^1) (see Fig. 7). The measured quantity is the depth profile. Configuration and orientation cannot be determined independently from one another. Thus in order to determine the orientation of the molecule axis we must average over the different possible configurations whilst neglecting possible correlations between the orientation of the O–C^7 axis and the molecule axis. The result of the average is the projection of the oxygen atom position on the molecule axis. The average distance between the oxygen atom and the carbon atom of the benzene ring opposite to the oxygen (C^1) is in this case 4.6 Å. The orientation of the benzyl alcohol is determined by using the concentration depth profile of the oxygen as starting point and fitting the carbon concentration depth profile with the orientation as fit parameters. As a result we find that the benzyl alcohol is tilted from the surface normal about $(68 \pm 8)°$ on average.

The preferred orientation of benzyl alcohol was already found qualitatively by Ballard et al.[23] with ultraviolet photoelectron spectroscopy (UPS) and Stietz[12] with MIES. It was concluded from the findings that in the UP spectra the relative intensity of the lone pair orbital of oxygen was smaller compared to that in the gas phase spectra and missing in the MIE spectra. Dietter and Morgner[16] determined from computer simulations quantitatively the distribution of the orientations of the benzene ring but also that of the bond between oxygen and its next neighbor carbon atom. They found that the benzyl alcohol is tilted on average about 42° from the surface normal. The depth profile of oxygen of Dietter and Morgner[16] are shown additionally in Fig. 8. The depth scale of the computer simulation was converted to that of the ion scattering scale by

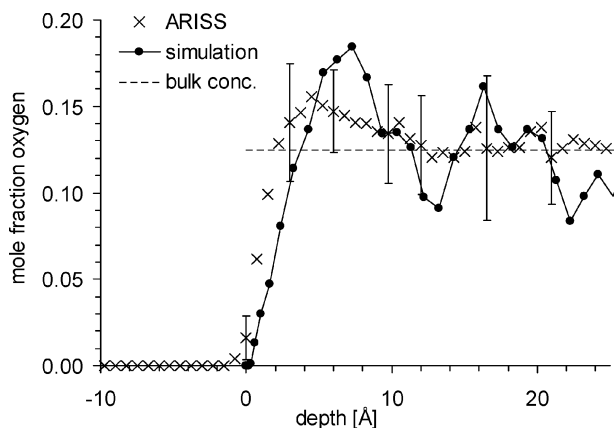$$z(z') = \int_{-\infty}^{z'} z'' \cdot \frac{\rho(z'')}{\rho_{bulk}} dz'' \qquad (1)$$

Fig. 8 Comparison of the oxygen depth profile derived from ARISS and from the computer simulation of Dietter and Morgner[16] as shown in ref. 27.

where z is the depth scale of the ion scattering spectroscopy, z' the depth scale of the simulation, $\rho(z'')$ the density of the simulation and ρ_{bulk} the bulk density. This conversion is necessary for the comparison, since determining the depth scale in the ion scattering spectra makes use of the stopping which is proportional to the density. Thus the depth scale of the computer simulation shrinks in an ion scattering experiment in the region where the density rises from that of the gas phase to that of the bulk. In Fig. 8 it can be seen, that the depletion zone of oxygen at the surface is thicker in the simulation than that determined with ARISS, that the maximum of the oxygen concentration is located somewhat deeper (6 to 8 Å) and that the maximum is greater.

To compare the results of the computer simulation and ARISS the influence of the differences in the methods has to be discussed. First there is the difference in the depth scale. Ion scattering spectroscopy treats the depth as the product of distance and density thus as amount of matter per unit area. This was already taken into account comparing the depth profiles determined with ARISS and computer simulations. The uncertainty of the depth scale in the absolute numbers in the experiment is proportional to the uncertainty of the experimentally determined stopping power,[22] which is about 15%. The other possibility to determine the stopping power is Bragg's rule[24] and using the extrapolation of the stopping power of the pure elements measured at higher kinetic energies.[25] The stopping power in the latter case is about 10% greater than the experimentally found values. Using the stopping power derived from Bragg's rule would even cause a shrinking of the depth scale of the experiment. Thus the deviation between experiment and simulation would become greater. Second, when the orientation was determined with ARISS it was not taken into account, that there could be a correlation between the orientation of the molecule axis and the C–O axis. The simulation of Dietter and Morgner[16] show also for the C–O axis a preferred orientation but the correlation between both angles mentioned was not evaluated. If there was a correlation between the distribution of both axes, our assumption over the distance between the oxygen atom and the carbon atom of the benzene ring opposite to the oxygen would be erroneous. We assume that the possible error due to this assumption is small as the difference in the concentration depth profiles of the oxygen point in the same direction. A shift of the maximum to a greater depth and an increase in the thickness of the depletion zone correlates with smaller angles between surface normal and the molecule axis. Reasons within the computer simulation for the discrepancy could be either that no polarization terms were taken into account or that the oxygen–hydrogen interaction, causing the formation of the

hydrogen bonds in the molecule chains, is too strong, thus that the charges on the atoms have been too great.

Conclusion

The topography of liquid surfaces can be classified by the application of ARISS. A surface can be classified as having a lateral homogeneous topography whenever it is possible to fit the spectra at different polar angles with a single depth profile. The surfaces of formamide and benzyl alcohol were found to have a lateral homogeneous topography.

We expect that revealing the topography of a liquid surface will have impact on the understanding of reactions at the gas/liquid interface. The interaction of a gas molecule impinging on the surface will not only be determined by whether or not a molecule is part of the outermost layer but also by whether or not the interaction with a specific atom or group of a molecule of the liquid surface is sterically hindered. The interaction of metastable helium atoms with the liquid surfaces is used for spectroscopic purpose but is also an example of the interaction between gas molecules and the liquid surface. MIE spectra show a difference in the reaction rate about a factor of 9 between the anions iodide and bromide of the surfactants Bu_4NI and Bu_4PBr,[26] while the surface excess differs only by a factor of 2.[8] The reason is most likely the difference in the local topography around both ions caused by the difference in the strength of the interaction with their next neighbours.

From the depth profiles and with the help of MIES it could be determined that formamide molecules are lying flat on the surface. In the case of benzyl alcohol the molecules are tilted from the surface normal about $(68 \pm 8)°$ on average. The orientations of the molecules could be determined quantitatively and are similar to that found in the computer simulations by Dietter and Morgner.[16] It may be worth investigating whether incorporating polarization terms or changing the charges on the benzyl alcohol molecule in the simulation would lead to an orientation which comes closer to that found in the experiment.

Acknowledgements

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