

TOWARDS HIGH RESOLUTION NEAR-FIELD MEASUREMENT OF THE LIQUID-LIQUID INTERFACE

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Keywords: *near-field optics, liquid-liquid interface, Raman scattering*

Abstract: This contribution reports on the investigation of the water/carbon tetrachloride interface by a high resolution method combining Raman spectroscopy and near-field microscopy. Trans phase boundary Raman profiles were measured with a spatial resolution of 200 nm. The observed blue shift of the OH water band indicates a weakening of the hydrogen bond while approaching the interface.

Liquid-liquid interfaces are relevant to many biological processes. For example, the hydrocarbon-water interface is a simple model of a biological membrane [1]; oil-water interfaces can be used to analyse drug delivery processes [2-3]. Although important information can be gained from the characterisation of the liquid-liquid interface with optical methods, absorption by the liquids and scattering by the glass surface of the cuvette have always put a limitation in the techniques employed for the study of the interface at molecular level.

In this work, the investigation of the interface has been performed using a near-field tip as illumination source. The Raman light scattered by the liquids has been detected using an objective tilted at 45° with respect to the interface in order to reduce the change of the optical path caused by the meniscus forming at the sides of the cuvette [4]. Theoretical calculations have shown that given an aperture size of 150 nm, the decay length of the evanescent field is only 20 nm [5]. Therefore, the small decay length of the evanescent field outside a near-field probe combined with vibrational spectroscopy allows to study structural changes at variable distances from the interface with high resolution. The positioning of the tip at the beginning of the experiment is of fundamental importance for the performance of the measurement; a step-by-step procedure has been identified and will be described in details.

The system investigated is the water/carbon tetrachloride interface. The choice of these liquids comes mainly from the properties of this interface. Interesting biological aspects can be indeed investigated through this interface since water with its hydrogen bonding is important in a wide range of biological processes like protein folding and membrane formation.

The water/carbon tetrachloride interface was approached in steps of 200 nm. After each movement, a Raman spectrum was recorded. The Raman band of the water was fitted with a Gaussian curve. The intensity and the central peak position of the fitted curves are plotted in Fig. 1 as a function of the distance covered by the cuvette. These parameters were calculated with a confidence interval of 95% and the resulting error is plotted in the graphs as well. On the x-axis, the tick mark '0' simply represents the starting point of the experiment.

Fig. 1a shows a plateau with a constant value of the water band intensity followed by a step-like decrease of the signal (highlighted in grey shade in the graph). This is the behaviour expected in the region of the interface when the near-field tip passes from the upper to the lower phase. Correlated to the intensity decrease is a shift of the water band peak in the interface region (Fig. 1b). In the upper phase, the peak position is, apart from fluctuations, constant. Then a sudden increase is

noticed. The interaction of water with large non-polar surfaces has always been explained on the basis of hydrophobic hydration derived from the investigation of the interaction of water with small non-polar solutes [6-7]. As result of these studies the water molecules, when approaching the interface, are expected to undergo a structural rearrangement corresponding to a strengthening of the hydrogen bond among neighbouring water molecules. In contrast, one of the first experimental data, obtained through non linear vibrational spectroscopy [8] on the water/carbon tetrachloride interface, showed a different picture: a weakening of the hydrogen bond among neighbouring interfacial water molecules was detected. The shift of the water peak observed in our experiment supports these results since a weaker intermolecular interaction among the water molecules corresponds to a blue shift of the Raman peak.

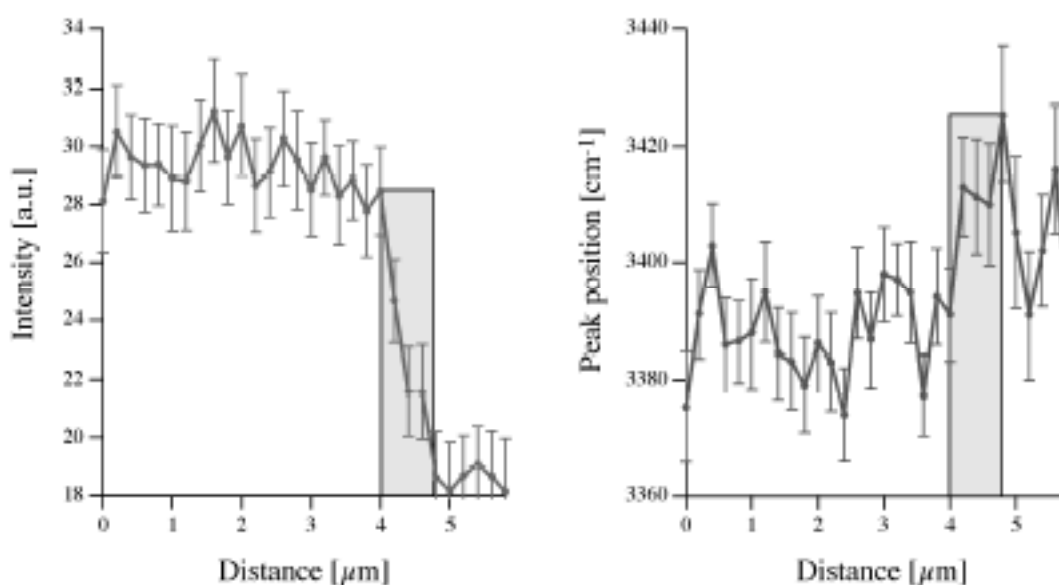


Fig. 1. a: Plot of the Raman band intensity of water vs. the distance covered by the cuvette.
b: Plot of the Raman band central peak position of water vs. the distance covered by the cuvette.

Acknowledgements:

Financial support from the Alexander von Humboldt Stiftung, the ZIP program of the German federal Government and Forschungskommission of ETH Zürich (grant no.TH-0-20680-99) is highly acknowledged.

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