Theoretical aspects and experimental results of STM studies in polar liquids

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Abstract. The physical nature of the aqueous tunnel barrier in a STM experiment is examined and the important role of spontaneous solvent dipole fluctuations, in providing microscopic trapping sites for electrons, is emphasized. Atomic resolution STM images of Au(111) surfaces in organic polar solvents are presented, which reveal detailed structural information on both the metallic substrate and the surface reconstruction.

1. Introduction

Electrochemical STM studies have as yet almost exclusively been performed in aqueous electrolyte solutions [1, 2]. Compared with the characterization of clean and adsorbate-covered metal surfaces *in vacuo* [3] the attainment of satisfactory lateral resolution in this environment has been much more difficult. To date we are aware of only two reports [4, 5] in which atomic details on a close-packed metal surface have been resolved. The origin of the difficulties encountered in aqueous STM applications has not been clearly identified yet. Most often it has been suggested that the interference of the faradaic current across the gap and chemical interactions of the tip or the sample with the liquid are the major sources of resolution degradation [1, 2].

There is, however, another puzzling observation in aqueous STM studies, which is related to the bulk of liquid water. Very low values (on average a few tenths of an eV) of the apparent tunnel barrier height φ_a [6], deduced from the variation of tunnel current with gap spacing, have consistently been reported [7–9] for aqueous environments. A general model to explain low values of φ_a has been proposed by Pethica and co-workers [10], in which the vertical scaling of the tip displacement is modified by tip–surface interaction forces. This effect is greatest at small tip–surface distances, typically less than 3 Å. Horn and Israelachivili [11] have shown that structural forces due to the molecular packing of liquids between surfaces in close proximity can also be observed. These forces may also modify the relationship between the tip–surface separation and the tip piezo-displacement. However, the data of Binggeli *et al* [7] for tunnelling in 0.5 M NaClO₄ were obtained at relatively large separations (>1 nm) for which the tip–surface interaction is expected to be much smaller and therefore expected not to influence the barrier-height measurement.
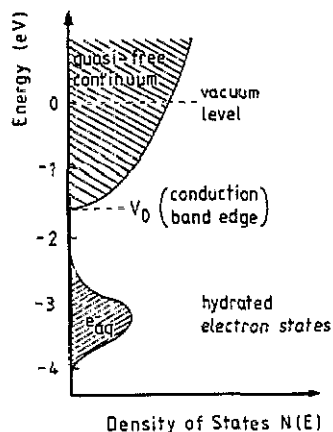
Figure 1. Schematic density-of-states diagram of electron energy levels in liquid water.
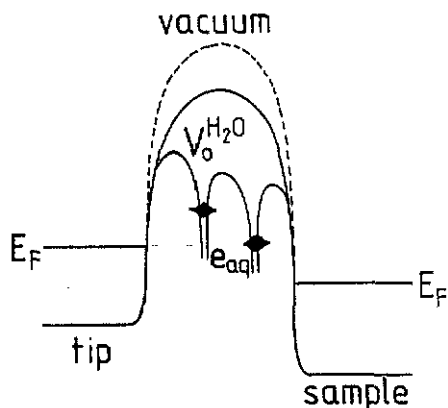

Figure 2. Compared with the situation in vacuum there are two contributions to the lowering of the tunnel barrier height in an STM with water (or another polar liquid) in the gap: $V_0^{H_2O}$ is the lowest non-bonding level (conduction-band edge), related to the fast electronic polarization of the liquid; e_{aq}^- levels are short-lived microscopic traps, resulting from either spontaneous or induced orientational polarizations.

In this paper we examine a different aspect, namely the physical nature of the aqueous tunnel barrier. We have made use of recent progress in the understanding of dynamical interactions between excess electronic charge and liquid water provided by molecular dynamics simulations [12–14] and ultra-fast spectroscopic experiments [15, 16]. It is proposed that polar solvents with a slower orientational response than water may provide favourable conditions for *in situ* STM imaging. Initial support for this claim seems to be provided by the greater ease with which the atomic resolution images, presented in the second part of this brief report, could be obtained in organic polar solvents as compared with water.

2. The nature of the aqueous tunnel barrier

The traditional phenomenological picture [17] of excess electron states in water, as well as in other liquids, distinguishes between quasi-free, delocalized levels (not unlike a *conduction band*) and localized, solvated configurations e_{aq}^-, which are equilibrated with the solvent dipole orientations. This is schematically illustrated in figure 1 in terms of a density-of-states representation. The conduction-band edge of V_0 level is located approximately 1.5 eV below the vacuum level [18] and the centre of the hydrated electron levels another 1.0–1.5 eV lower in energy [19]. Both of these effects would produce a lower φ_a than produced in the operation in UHV.

Recent molecular dynamics simulations [12–14] and ultra-fast spectroscopic experiments [15, 16] have, however, added some refinements to the nature and energetic distribution of the excess electron states. First, it has been found [15, 16] that electrons created in the conduction band are initially confined to prehydrated, 'wet' states between

the V_0 and the e_{aq}^- levels before they are fully hydrated. Second, there is evidence that the thermal fluctuations of water molecules in the hydrogen-bonded network produce dipole configurations with a very attractive electrostatic potential, which in rare but significant cases may be as low in energy as the fully hydrated state [12].

The importance of solvent dipole fluctuations, producing particularly favourable configurations with low probability [20], has been emphasized in conjunction with a recent molecular dynamics simulation of the Fe^{2+}/Fe^{3+} homogeneous charge-transfer reaction [14]. The physical difference in the case of tunnelling across an aqueous STM gap is the thermodynamic determination of the energy levels in the charge-donating tip relative to the charge-accepting levels in the sample, which is enforced by the external bias voltage. Whereas in redox reactions the energy levels of the donor and the acceptor can fluctuate individually up and down to produce the resonant transition state [20], only the height and shape of the barrier between the tip and the sample are affected by solvent fluctuations in the gap.

We propose, therefore, that in addition to the barrier lowering caused by the V_0 level (c.f. figure 1), which has recently been considered [21], there is a further substantial reduction due to the dynamical occurrence of microscopic trapping sites [12]. These short-lived sites in the gap can be exploited by electrons in the tip, due to the much larger frequency of the tunnelling attempts compared with the rate of successful charge-transfer events [3, 20, 21]. In figure 2 this distinction between tunnelling through a vacuum barrier and an aqueous barrier is schematically illustrated, with the understanding that there are picosecond fluctuations of the locations and energies of the e_{aq}^- sites. Due to the complicated three-dimensional topography of the fluctuating potential energy surfaces in the gap [22] it is, of course, not possible to quantify the effects of these traps on the apparent barrier-height measurements, but an explanation for the experimental observations of very low φ_a values can definitely be based on these considerations.

In addition to the spontaneous occurrence of microscopic sites with a favourable electrostatic potential, it may be worth considering another possibility for the formation of attractive electron sites. The orientational dielectric response of liquid water appears to be ultra-fast, with librational rearrangements occurring in $\sim 10^{-14}$ s [12, 13]. Such times are short enough to be related to recent estimates [23] of the transmission time of electrons through barriers with parameters appropriate to our considerations. It is therefore conceivable that in the course of the electron tunnelling through the STM gap the water molecules have time to respond to the excess electronic charge and to reorientate rapidly, such that the barrier is lowered again in a similar way to that discussed above for the spontaneous fluctuations. In fact, these two mechanisms may occur co-operatively, with a spontaneous trapping site providing the initiation of the electron transmission and the subsequent induced polarization stabilizing the lower energy site [24].

Recently Berthe and Halbritter [25] have proposed that localized electron states of adsorbates on the tip, such as W–OH–HOH result in resonant tunnelling and that a Coulomb barrier occurs in this channel. Consequently, in comparison with direct tunnelling where $j_S \propto e^{-2kd}$ one expects that $j_{RT} \propto e^{-kd}$ when resonant tunnelling dominates. This has an important effect in determining the value of φ_a. For instance, the values of $\varphi_a \sim 0.2$–0.3 eV based on normal tunnelling [7] would be $\varphi_a \sim 0.8$–1.2 eV using $j_{RT} \propto e^{-kd}$. These values are quite close to those estimated from the expected lowering due to the V_0 level and hydrated electron levels. This interpretation of the barrier is quite appealing, although a microscopic description of the associated charging blockade is not yet available. Given the experimental difficulties associated with performing tunnelling spectroscopy in liquids we have adopted a different approach to the

investigation of the role of liquids in the tunnel gap. We propose that an investigation of tunnelling in a wide range of polar and non-polar liquids with different electronic structure may reveal systematic trends in the values of φ_a.

3. STM images of Au(111) surfaces in organic polar solvents

We shall now direct our attention to our recent STM investigations in organic electrochemical fluids. The ability to select the molecular architecture and electronic structure of a polar solvent is particularly appealing for testing theoretical concepts and experimenting with the STM in the spirit of the previous discussion. We started by investigating two fundamental classes of solvents; protic and aprotic (either hydrogen-bonded or not), of which glycerol (protic), ethylene glycol (protic) and propylene carbonate (aprotic) were chosen because of their low vapour pressures.

Despite apparently successful reports of imaging graphite in a variety of organic oils and other liquids, including water, where the characteristic hexagonal atomic structure of C(0001) was resolved [26] we decided against this substrate for several reasons. It has been recognized for some time that the tip–surface force can mediate the observed corrugation amplitude [10, 27] and even in UHV it has been reported that this effect is dependent on the contamination levels at the surface [28]. Hence it is quite possible that liquid molecules are effectively squeezed out of the gap region during tunnelling. Our choice of substrate stems from surface physics experiments on Au(111) reconstructed surfaces [29] where both the gold atoms and the reconstruction have been resolved by STM. Preparation of Au films deposited on Pyrex and then flame annealed and quenched in methanol have been shown to produce excellent reconstructed (111) facets that can be imaged with atomic resolution in air [22, 30].

Figure 3(a) shows an overview STM image of a 2200 × 2200 Å^2 area of a Au(111) film imaged in propylene carbonate. In this area, large flat terraces are observed, separated by atomic steps with a height of ~2.4 Å. The straight step edges are orientated along the principle [110] directions of the close-packed lattice, resulting in triangular terraces due to the threefold symmetry of the (111) surface.

Figure 3(b) shows a higher resolution image of a (111) terrace (1340 × 1340 Å^2) obtained in ethylene glycol. In this picture, pairs of lines are clearly visible running from the top to the bottom of the image. These lines are due to the ($\sqrt{3}$ × 23) surface reconstruction of Au(111). The rearrangement in the topmost layer is due to a compression of ~4.3% in the ⟨110⟩ direction which reduces the stress in the first layer [29]. The distance between twinned lines is approximately 25 Å, the unit-cell dimension is 63 Å and the corrugation amplitude normal to the surface is on the order of 0.15–0.20 Å. This particular image shows a degree of disorder in the step edge region where the reconstruction lines do not traverse the step from one terrace to another (c.f. top left hand corner). The explanation for this may be the irregular shape of the step edge. In other images the reconstruction continues across the step edges when the corrugation lines are perpendicular to the steps. In cases where this is not true some distortion or termination of the reconstruction lines occurs as seen in this image.

Figure 3(c) shows an atomic resolution image of the Au(111) reconstruction in glycerine (70 × 70 Å^2). The hexagonal structure corresponds to the arrangement of the Au atoms in the (111) lattice. Superimposed upon the atomic structure are the bright reconstruction lines, which reflect the periodic transition from FCC to HCP stacking [31]. The lines run parallel to the [211] direction, giving rise to three possible domains rotated
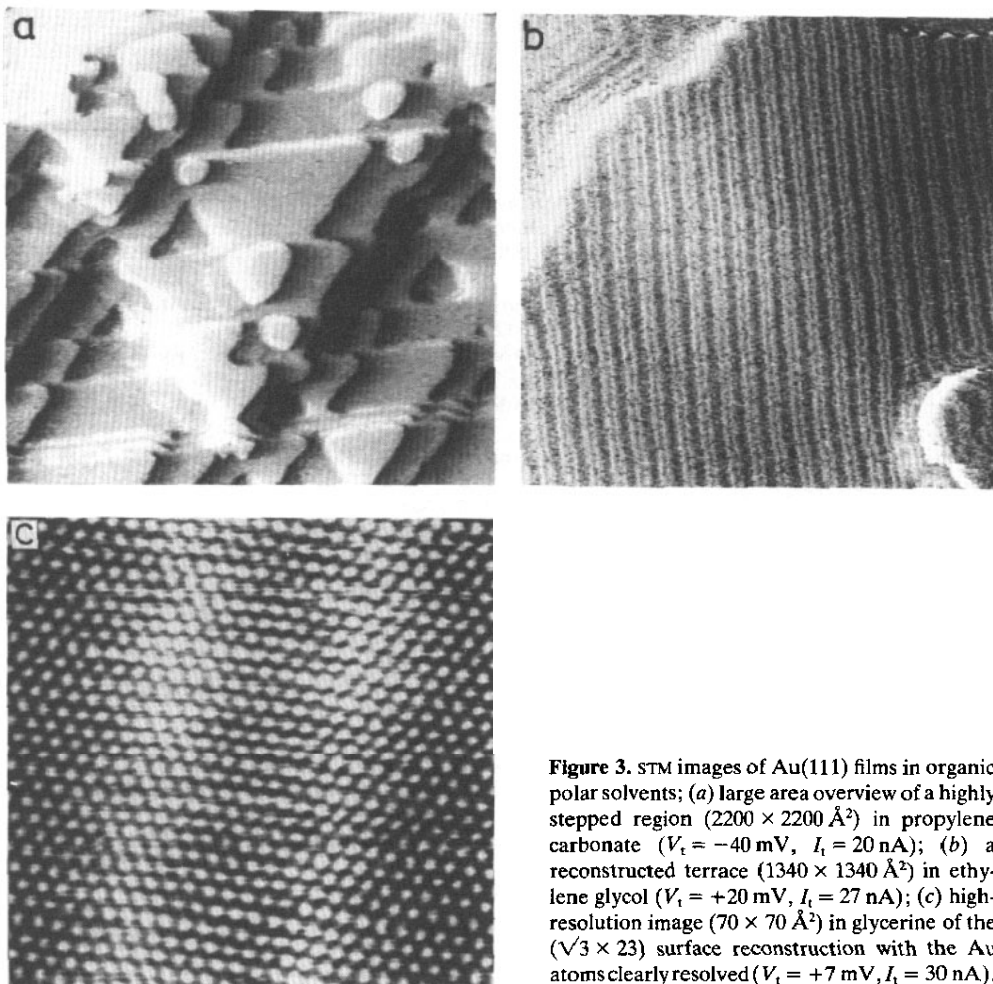
Figure 3. STM images of Au(111) films in organic polar solvents; (*a*) large area overview of a highly stepped region (2200 × 2200 Å^2) in propylene carbonate ($V_t = -40$ mV, $I_t = 20$ nA); (*b*) a reconstructed terrace (1340 × 1340 Å^2) in ethylene glycol ($V_t = +20$ mV, $I_t = 27$ nA); (*c*) high-resolution image (70 × 70 Å^2) in glycerine of the ($\sqrt{3} \times 23$) surface reconstruction with the Au atoms clearly resolved ($V_t = +7$ mV, $I_t = 30$ nA).

by 120° with respect to each other. In this image only a single domains is visible. Domain sizes ranging from a hundred ångstroms up to a thousand ångstroms have been observed.

We wish to note here, specifically, that the surface reconstruction persists and can be imaged in the presence of a variety of solvents, which themselves appear transparent to the tunnelling process. In our initial work, tunnelling through water, we find that it is also possible to produce images with atomic resolution, albeit with greater difficulty than in the organic solvents. These preliminary observations are encouraging and we plan to study a wider range of protic and aprotic liquids, with the aim of learning more about the fundamental mechanisms of tunnelling in polar liquids and the dependence of the apparent barrier height [6] on the specific properties of different solvents.

Acknowledgments

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