PhysChemComm
Paper

# Distance tunnelling characteristics of solid/liquid interfaces: Au(111)/$Cu^{2+}$/$H_2SO_4$†

**Gabor Nagy, Dirk Mayer and Thomas Wandlowski**

*Research Center Jülich, Institute for Thin Films and Interfaces, ISG3, 52425 Jülich*

*Received 12th June 2002, Accepted 11th July 2002*

This study examined the liquid part of solid/liquid interfaces at the atomic level. By measuring distance tunnelling characteristics the height of the potential barrier between the tip and the sample, *i.e.*, the potential energy field the tunnelling electrons are exposed to, can be obtained, and this provides direct access to double layer properties. We found exponential IS-characteristics for the bare and the oxidised Au(111) surface, while non-exponential behaviour was obtained in the presence of ordered adlayers. The influence of the local environment just within the Helmholtz layer is strong enough to perturb the tunnelling process significantly. The electrolyte properties in the Gouy region do not change with electrode potential, the liquid in the tunnelling gap has only an average effect by lowering the barrier height.

This Poster Article is based on a poster presentation at Faraday Discussion 121. The original poster can be viewed here.

## Introduction

With the help of modern *in situ* techniques direct or indirect information can be obtained about the electronic states of adsorbed/deposited molecules. One of the most promising methods is scanning tunnelling microscopy (STM), which offers the possibility of detecting partial electron transfer processes. Recently, Tao *et al.*[2] gave an excellent review of the latest results on the field. A more elaborated way of obtaining electronic information is the use of modulation techniques of STM. With the so-called IV-spectroscopy (modulating the bias between the tip and the sample) the surface density of states can be measured as a function of the bias *i.e.* of the electron energy. Up to now, this method has not been used for functionalised, potential-controlled (*in situ*) electrochemical interfaces. Alternatively, the effective tunnelling barrier can be estimated directly with the so-called barrier height, or IS-characteristics measurements. In this way, the height of the potential barrier between the tip and the sample can be measured, coupled with the local work function of the sample. Several applications have been published about measurements in vacuum or in dry atmosphere. The first efforts of investigating solid|liquid interfaces by Siegenthaler *et al.*[3] showed tunnelling current ($i_T$) *vs.* distance curves with discontinuous jumps, measured for Pb UPD on Au(111) in perchlorate solution. The authors attributed these observations to reaching point contact. Lindsay *et al.*[4] suggested that local barrier height measurements are characteristic to the liquid phase of the interface. Halbritter and co-workers[5] found for Ag(111)|0.01 M $HClO_4$ that the IS-curves are exponential, but the potential barrier height depends on the electrode potential. Non-exponential tunnelling characteristics were found for HOPG|water and Pt(100)|water interfaces.[6,7] Similar results were obtained by Kang *et al.*[8,9] for HOPG and Au(111). Schultze *et al.*[10] pointed out the difficulties of these types of measurements on oxide-covered titanium. Kolb *et al.*[11] measured IS-characteristics on Cu-(1 × 1) UPD adlayer on Au(111) employing copper modified STM tip, and estimated an averge barrier height of 1.5 eV. Recently, Lee and co-workers[12] found exponential IS-characteristics for reconstructed Au(111) in humid air. Parallel to the first measurements, Schmickler[13] and Nitzan *et al.*[14] addressed the theoretical background successfully by using quantum chemical methods. On the basis of these examples we aimed to understand if it is possible to map the liquid part of the double layer perpendicular to the metal surface by measuring distance tunnelling characteristics.

## Experimental

The Au(111)|1 mM $Cu^{2+}$ + 50 mM $H_2SO_4$ system was investigated with a Molecular Imaging ECSTM under potential control. The IS-characteristics were measured as $i_T$ as a function of the relative tunnelling distance perpendicular to the surface ($\Delta s$). The results were considered acceptable only if atomic resolution of the surface was achieved. W and Pt-Ir tips were used giving identical results. The reprodicibility of measurements was found to be satisfactory.[1] All potentials are referred to the Cu/$Cu^{2+}$ couple (0.337 V *vs.* SHE).

## Results

### Au(111)-(1 × 1)

In this potential region the "bare" Au(111) surface can be imaged in the topographic STM mode. The IS-characteristics was found to be a simple exponential-type curve. The corresponding barrier height profile is almost a horizontal line fluctuating around the average barrier height of about 1 eV. This value is in accordance with literature data.[3–5] These results indicate that no strongly ordered adlayer exists in this potential region. Indeed, it is known from earlier works, that there is no long range order in the adlayer of sulphate ions co-adsorbed with water (hydronium ions) on the Au(111) surface under these conditions.[15,16]

---

†Presented at Faraday Discussion 121, The Dynamic Electrode Surface, Berlin, Germany, April 15-17, 2002.

DOI: 10.1039/b205720b

## Poster

### Introduction

The aim of this work is to characterise the liquid part of solid/liquid interfaces at the atomic level. By measuring the so-called potential barrier characteristics, or IS-characteristics, the height of the potential barrier between the tip and the sample, *i.e.* the potential energy field the tunnelling electrons are exposed to, can be obtained and this provides direct access to double layer properties.

### Experimental

The Au(111)|1 mM $Cu^{2+}$ + 50 mM $H_2SO_4$ system was investigated with a Molecular Imaging ECSTM under potential control. The IS-characteristics were measured as tunnelling current ($i_T$) as a function of the relative tunnelling distance perpendicular to the surface ($\Delta s$). The results were considered acceptable only if atomic resolution of the surface was achieved. W and Pt–Ir tips were used giving identical results. The reprodicibility of measurements was found to be satisfactory.[1] All potentials are referred to the Cu/$Cu^{2+}$ couple (0.337 V *vs.* SHE).

### Results

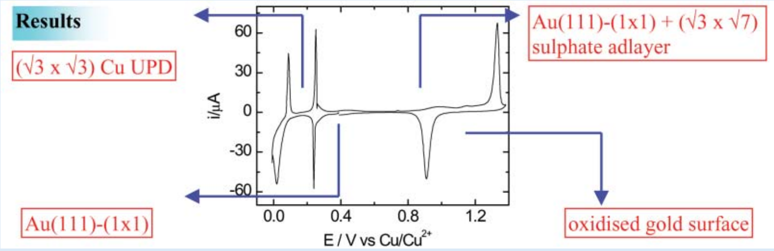

**Fig. 1** CV of Au(111)|1 mM $Cu^{2+}$ + 50 mM $H_2SO_4$ as measured *in situ* in the STM cell with 10 mV $s^{-1}$. For further results and discussion click to the corresponding subtitle.

### Discussion

At $i_T < 0.1$ nA, *i.e.* relatively far from the surface, all curves have simple exponential decay with an average barrier height of about 1 eV. For the bare or oxidised Au(111) surface, exponential $i_T$ *vs.* $\Delta s$ characteristics were obtained (Fig. 2 and 4). The calculated potential barrier profiles show no layering in the liquid phase. Non-exponential behaviour of $i_T$ *vs.* $\Delta s$ characteristics was obtained only in the presence of ordered adlayers (Fig. 3 and 5). The distance scale was calibrated by measuring topographic images as a function of setpoint current ($i_T$). We found for the Cu UPD adlayer that the image is strongly distorted if $i_T > 10$ nA implying that there is a strong interaction between tip and adsorbed layer. A similar effect was found for the ordered sulphate adlayer above 50 nA.

### Conclusions

(1) For the bare and the oxidised Au(111) surface, exponential IS-characteristics were obtained with an effective barrier height of approximately 1 eV.
(2) Non-exponential behaviour of the IS-characteristics was obtained only in the presence of ordered adlayers: the ($\sqrt{3} \times \sqrt{3}$) Cu UPD and the ($\sqrt{3} \times \sqrt{7}$) sulphate phases.
(3) The distance scale was calibrated by measuring topographic images as a function of the $i_T$.
(4) Although the structure of ordered adlayers is known there is no simple correlation between the barrier height profiles and the molecular/atomistic models. Moreover, the role of co-adsorbed water has to be clarified.
(5) The above findings suggest that the influence of the local environment just within the Helmholtz-layer is strong enough to perturb the tunnelling process significantly. The electrolyte properties in the tail of the Gouy-region do not change with electrode potential, the liquid in the tunnelling gap has only an average effect by lowering the barrier height.

### Au(111)-(1 × 1) + ($\sqrt{3} \times \sqrt{7}$) sulphate adlayer

In this potential region the ($\sqrt{3} \times \sqrt{7}$) sulphate adlayer with co-adsorbed water (hydronium ions) can be imaged in the topographic STM mode.[15,18,19] The IS-curve was found to be non-exponential at larger tunnelling currents. The corresponding potential barrier profile, like in the case of Cu UPD, contains characteristic peaks clearly showing the layering within the double layer. By measuring topographic images in the function of setpoint current we "calibrated" our distance scale and found that we probed the structure of adsorbed layer, therefore the peaks in the potential barrier profile can be related to the ordered structure of sulphate and water species. Further away from the surface ($\Delta s > 0.4$ nm) the IS-characteristics becomes exponential and the corresponding barrier height is about 1 eV [*cf.* disordered sulphate on Au(111)-(1 × 1)]. Although the structure of the ordered adlayer is known it is not easy to relate it to the peaks in the barrier height profiles without assuming not only molecular but atomic contributions from sulphate ions and water to the potential barrier. From the peak positions one may deduce the position of electron rich species and the charge distribution may be estimated.[1]

### Oxidised Au(111) surface

By oxidising the Au(111) surface small $AuO_x$ clusters form with an average size of 1–3 nm. Similarly to the case of the disordered sulphate adlayer on Au(111), the IS-curve was

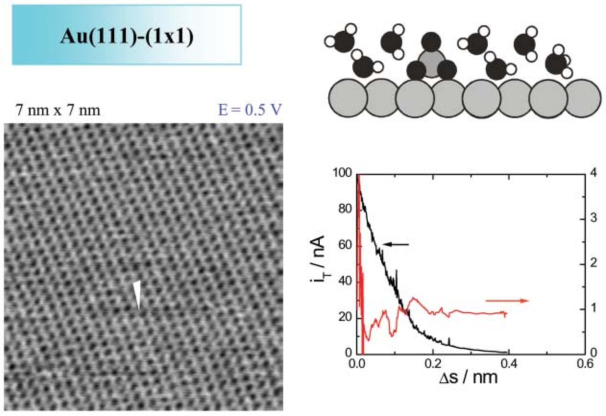

**Fig. 2** IS-characteristics ($i_T$–$\Delta s$ - black line) and the calculated[7] one-dimensional potential barrier height ($\phi$ - red line) profile at $E = 0.5$ V *vs.* Cu/Cu$^{2+}$. The zero of the distance scale is arbitrary. The IS-characteristics were measured simultaneously with the corresponding topographic image ($i_T = 1$ nA). The actual adlayer structure[15,16] is depicted as a side view.

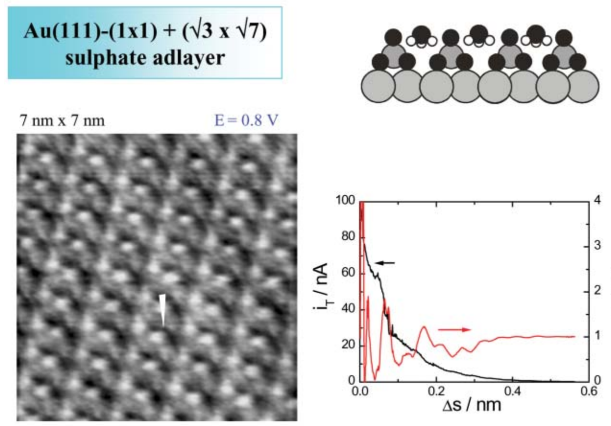

**Fig. 3** IS-characteristics ($i_T$–$\Delta s$ - black line) and the calculated[7] one-dimensional potential barrier height ($\phi$ - red line) profile at $E = 0.8$ V *vs.* Cu/Cu$^{2+}$. The zero of the distance scale is arbitrary. The IS-characteristics were measured simultaneously with the corresponding topographic image ($i_T = 1$ nA). The actual adlayer structure[17] is depicted as a side view.

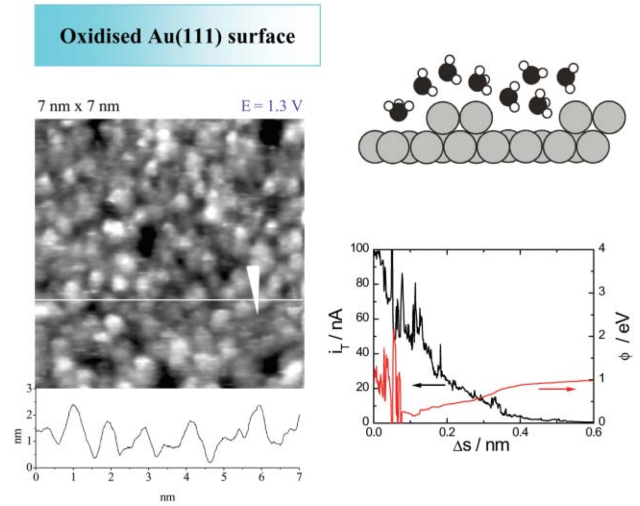

**Fig. 4** IS-characteristics ($i_T$–$\Delta s$ - black line) and the calculated[7] one-dimensional potential barrier height ($\phi$ - red line) profile at $E = 1.3$ V *vs.* Cu/Cu$^{2+}$. The zero of the distance scale is arbitrary. The IS-characteristics were measured simultaneously with the corresponding topographic image ($i_T = 1$ nA). The white line in the topographic image indicates the position of the separately plotted cross-section. The actual adlayer structure is depicted as a side view.

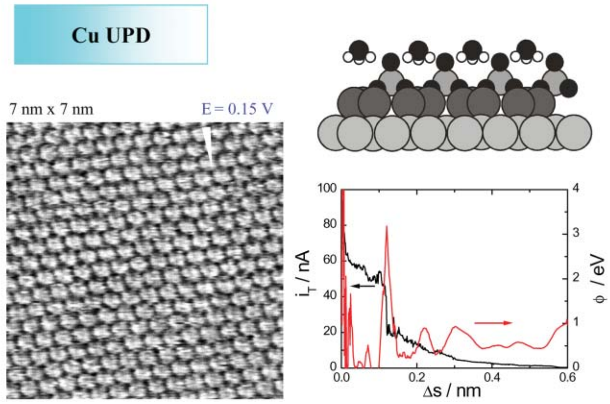

**Fig. 5** IS-characteristics ($i_T$–$\Delta s$ - black line) and the calculated[7] one-dimensional potential barrier height ($\phi$ - red line) profile at $E = 0.15$ V *vs.* Cu/Cu$^{2+}$. The zero of the distance scale is arbitrary. The IS-characteristics were measured simultaneously with the corresponding topographic image ($i_T = 1$ nA). The actual adlayer structure[21,22] is depicted as a side view.

found to be exponential-type. The corresponding potential barrier profile is approaching the average barrier height of 1 eV. The same qualitative picture was found for the disordered sulphate on Au(111)-(1 × 1). These results indicate that no strongly ordered adlayer exists in this potential region. The fact, that the calculated barrier height values are very similar for the bare Au(111) surface and for the oxidised Au(111) surface, may indicate no big, discontinuous changes in the

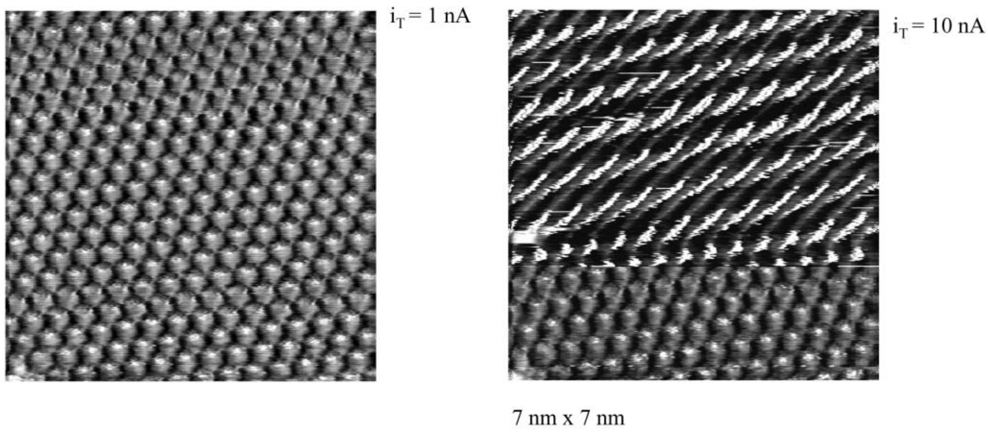

**Fig. 6** Setpoint dependence of the topographic images for the ($\sqrt{3} \times \sqrt{3}$) Cu UPD on Au(111) at 0.15 V *vs.* Cu/Cu$^{2+}$.

work function due to the surface oxide formation. This is in accordance with the work function measurements for polycrystalline gold by Kolb *et al.*[20]

### Cu UPD

In this potential region an ordered Cu sub-monolayer (2/3) with an ordered sulphate adlayer (1/3) and co-adsorbed water adsorbed on-top can be imaged in the topographic STM mode.[21–23] The IS-curve was found to be non-exponential at larger tunnelling currents. The corresponding potential barrier profile, like in the case of the ordered sulphate adlayer, contains characteristic peaks clearly showing the layering within the double layer. We "calibrated" our distance scale by measuring topographic images in the function of the setpoint current ($i_T$) and found that we indeed probed the structure of the adsorbed layer. Therefore, the peaks in the potential barrier profile can be related to the Cu UPD structure. Further away from the surface ($\Delta s > 0.4$ nm) the IS-characteristics becomes more or less exponential and the corresponding barrier height is about 0.8 eV which is lower than the value for the disordered sulphate on Au(111)-(1 × 1). Despite the complexity of the Cu UPD there appears to be a clear correlation between the shape of the calculated barrier height profile and the structure of the adlayer. The two steps in the IS-characteristics, and the corresponding two large peaks in the barrier profile may be related to the copper adlayer and the adsorbed sulphate layer. In order to prove these types of correlations, a systematic study of related, but distinctly different systems is necessary. Moreover, the role of co-adsorbed water should also be clarified.

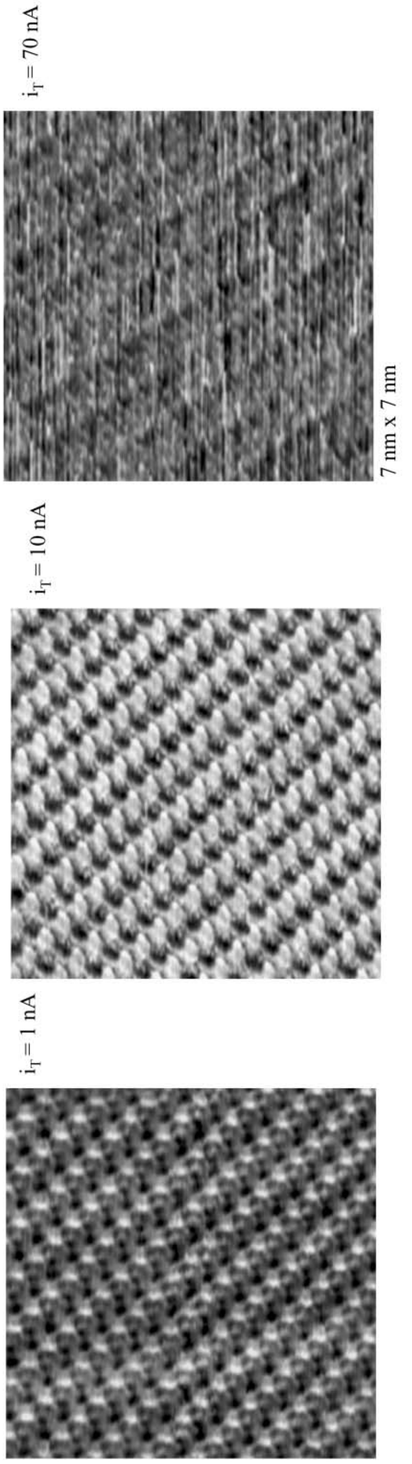

**Fig. 7** Setpoint dependence of the topographic images at for the ($\sqrt{3} \times \sqrt{7}$) ordered sulphate adlayer on Au(111) at 0.8 V *vs.* Cu/Cu$^{2+}$.

### Cu UPD: setpoint dependence

To determine an approximate absolute tip-surface distance we measured topographic images in the function of $i_T$. In this way we "calibrated" our distance scale. For the Cu UPD adlayer we found that the image is distorted if $i_T > 10$ nA implying that the tip is so close to the surface that there is a strong interaction between tip and the adsorbed layer. From the shape of the distortion we may conclude that an attractive interaction between tip and adlayer becomes important in this case. If we use higher setpoint currents the tip probably gets in contact with the copper layer. Thus, we may conclude that during the IS-characteristics measurements the tip probes the interfacial region in the immediate vicinity of the Cu UPD adlayer.

### Au(111)-(1 × 1) + ($\sqrt{3} \times \sqrt{7}$) sulphate adlayer: setpoint dependence

To determine an approximate absolute tip-surface distance we measured topographic images in the function of $i_T$. In this way we "calibrated" our distance scale. We found that the image is distorted if $i_T > 70$ nA implying that the tip is so close to the surface that there is a strong interaction between tip and adsorbed sulphate layer. From the shape of the distortion we may conclude that the short range, repulsive interaction between tip and adlayer becomes important in this case. It is probable, that at very "high" tunnelling currents (100 nA) the tip is already within the adsorbed layer. This allows us to conclude that during the IS-characteristics measurements the tip probes the interfacial region in the immediate vicinity of the ordered sulphate adlayer.

## Discussion and conclusions

At $i_T < 0.1$ nA, *i.e.* relatively far from the surface, all curves have simple exponential decay with an average barrier height of about 1 eV. For the bare or oxidised Au(111) surface exponential $i_T$ *vs.* $\Delta s$ characteristics were obtained (Fig. 2 and 4). The calculated potential barrier profiles show no layering in the liquid phase. Non-exponential behaviour of $i_T$ *vs.* $\Delta s$

characteristics was obtained only in the presence of ordered adlayers (Fig. 3 and 5). The distance scale was calibrated by measuring topographic images as a function of setpoint current. We found for the Cu UPD adlayer that the image is strongly distorted if $i_T > 10$ nA implying that there is a strong interaction between tip and adsorbed layer. A similar effect was found for the ordered sulphate adlayer above 50 nA. We conclude that:

(1) For the bare and the oxidised Au(111) surface exponential IS-characteristics were obtained with an effective barrier height of approximately 1 eV.

(2) Non-exponential behaviour of the IS-characteristics was obtained only in the presence of ordered adlayers: the $(\sqrt{3} \times \sqrt{3})$ Cu UPD and the $(\sqrt{3} \times \sqrt{7})$ sulphate phases.

(3) The distance scale was calibrated by measuring topographic images as a function of $i_T$.

(4) Although the structure of ordered adlayers is known there is no simple correlation between the barrier height profiles and the molecular/atomistic models. Moreover, the role of co-adsorbed water has to be clarified.

(5) The above findings suggest that the influence of the local environment just within the Helmholtz-layer is strong enough to perturb the tunnelling process significantly. The electrolyte properties in the tail of the Gouy-region do not change with electrode potential, the liquid in the tunnelling gap has only an average effect by lowering the barrier height.

## Acknowledgements

G. N. is indebted to the Alexander von Humboldt Stiftung for a research fellowship. This work was also partially supported by the Volkswagen Stiftung under grant no. I75-262 and the Research Center, Jülich.

## References

1 G. Nagy and T. Wandlowski, *Z. Phys. Chem., special issue for the 60th birthday of Professor D. M. Kolb*, submitted, 2002.
2 N. J. Tao, C. Z. Li and H. X. He, *J. Electroanal. Chem*, 2000, **492**, 81.
3 M. Bingelli, D. Carnal, R. Nyffenegger and H. Siegenthaler, *J. Vac. Sci. Technol. B*, 1991, **9**, 1985.
4 S. M. Lindsay, T. W. Jing, J. Pan, D. Lampner, A. Vaught, J. P. Lewis and O. F. Sankey, in *Nanoscale Probes of the Solid/Liquid Interface*, ed. A. A. Gewirth and H. Siegenthaler, NATO ASI Series, vol. 288, Kluwer Academic Publishers, The Netherlands, 1995, p. 25.
5 J. Halbritter, G. Repphun, S. Vinzelberg, G. Staikov and W. J. Lorenz, *Electrochimica Acta*, 1995, **40**, 1385.
6 G. Nagy, *Electrochimica Acta*, 1995, **40**, 1417.
7 G. Nagy, *J. Electroanal. Chem.*, 1996, **409**, 19.
8 J. R. Hahn, Y. A. Hong and H. Kang, *Appl. Phys. A*, 1998, **66**, S467.
9 Y. A. Hong, J. R. Hahn and H. Kang, *J. Chem. Phys*, 1998, **108**, 4367.
10 C. Kobusch and J. W. Schultze, *Electrochim. Acta*, 1995, **40**, 1395.
11 G. E. Engelmann, J. C. Ziegler and D. M. Kolb, *Suf. Sci*, 1998, **401**, L420.
12 M.-B. Song, J.-M. Jang, S.-E. Bae and C.-W. Lee, *Langmuir*, 2002, **18**, 2780.
13 W. Schmickler, *Surf. Sci.*, 1995, **335**, 416.
14 U. Peskin, A. Edlund, I. Bar-On, M. Galperin and A. Nitzan, *J. Chem. Phys.*, 1999, **111**, 7558 and references therein.
15 O. M. Magnussen, J. Hagenböck, J. Hotlos and R. Behm, *Faraday Discuss.*, 1992, **94**, 329.
16 K. Ataka and M. Osawa, *Langmuir*, 1998, **14**, 951.
17 Th. Wandlowski, K. Ataka, S. Pronkin and D. Diesing, *PhysChem. ChemPhys.*, submitted, 2002.
18 G. J. Edens, X. Gao and M. Weaver, *J. Electroanal. Chem.*, 1994, **375**, 357.
19 L. J. Wan, S. L. Yau and K. Itaya, *J. Phys. Chem.*, 1999, **99**, 9507.
20 D. L. Rath and D. M. Kolb, *Surf. Sci.*, 1981, **109**, 641.
21 O. M. Magnussen, J. Hotlos, R. Nichols, D. M. Kolb and R. J. Behm, *Phys. Rev. Lett.*, 1990, **64**, 2929.
22 M. F. Toney, J. N. Howard, J. Richer, G. L. Boges, J. G. Gordon and O. R. Melroy, *Phys. Rev. Lett.*, 1995, **75**, 4472.
23 E. Herrero, L. J. Buller and H. Abruna, *Chem. Rev.*, 2001, **101**, 1897.