

Dynamics and spectroscopy of single C₆₀ molecules adsorbed on Au(1 1 1) at the liquid–solid interface

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Received 11 September 2002; accepted 7 October 2002

Abstract

The adsorption of C₆₀ molecules on Au(1 1 1) surfaces has been investigated by using scanning tunneling microscopy (STM) and spectroscopy (STS) at a liquid–solid interface and at room temperature (RT). At low coverage, C₆₀ decorates the step edges, forming two-dimensional islands on the terraces which indicate that the molecules have a high mobility even at RT. When the coverage is increased, the C₆₀ molecules form a close-packed $2\sqrt{3} \times 2\sqrt{3}R30^\circ$ structure on reconstructed Au(1 1 1) surface. It is demonstrated that STM in a liquid environment facilitates the performance of spectroscopy measurements and allows the manipulation of single molecules.

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Keywords: Self-assembly; Liquid–solid interface; Fullerenes; Organic–inorganic interface

1. Introduction

Fullerenes are often used as model adsorbates on various substrates [1–11]. Such studies are of interest not only from a fundamental point of view but also for technological applications of C₆₀. For these investigations the scanning tunneling microscopy (STM) has proven to be a very efficient tool because it provides information about structural and electronic properties on the nanoscale. In vacuum, detailed STM studies of C₆₀ overlayers have been performed on Au [1,4,6–8], Ag [1–4], Al [5], Cu [1,4,9], Ni [10], Pd [11]. STM has directly evidenced the close-packed hexagonal or quasi-hexagonal lattice of C₆₀ on threefold symmetry surfaces of noble metals. In spite of this large number of studies of vacuum-deposited C₆₀ films, there is surprisingly no investigations on fullerene adsorption at liquid–solid interfaces, which could promote technological applications. We report on an in situ STM investigation on the structure of C₆₀ overlayers formed at room temperature (RT) between a solution and Au(1 1 1) surfaces. We also demonstrate the possibility to manipulate single C₆₀ molecules and to carry

out spectroscopy measurements with an STM-tip in a liquid environment.

2. Experimental details

Gold substrates were prepared from gold films deposited in ultrahigh vacuum onto freshly cleaved mica heated at ~650 K. Before each measurement, the Au(1 1 1) substrate was annealed in a propane–air flame. Flamed samples revealed well known reconstruction lines [12] in air, but also in liquid *n*-tetradecane, C₁₄H₃₀ (99% purity, Aldrich). About 0.01 mg of C₆₀ were mixed with 1 ml of *n*-tetradecane, and after examination of bare gold by STM, a droplet of the solution was deposited on Au(1 1 1). In situ measurements were carried out by a molecular imaging STM, using a low current scanning head and a mechanically cut Pt–Ir (80:20) tip. Several STM images recorded in the constant current mode were obtained with different samples and different tips to check reproducibility and to confirm that results were free from artifacts. The recordings of local *I*(*V*) curves were performed in the limits of ±1.0 V by fixing the tip–substrate distance defined by imaging voltage and set tunneling current.

3. Results and discussion

Fig. 1(a) and (b) show two consecutive STM images of reconstructed gold covered by C₆₀. The molecules decorate

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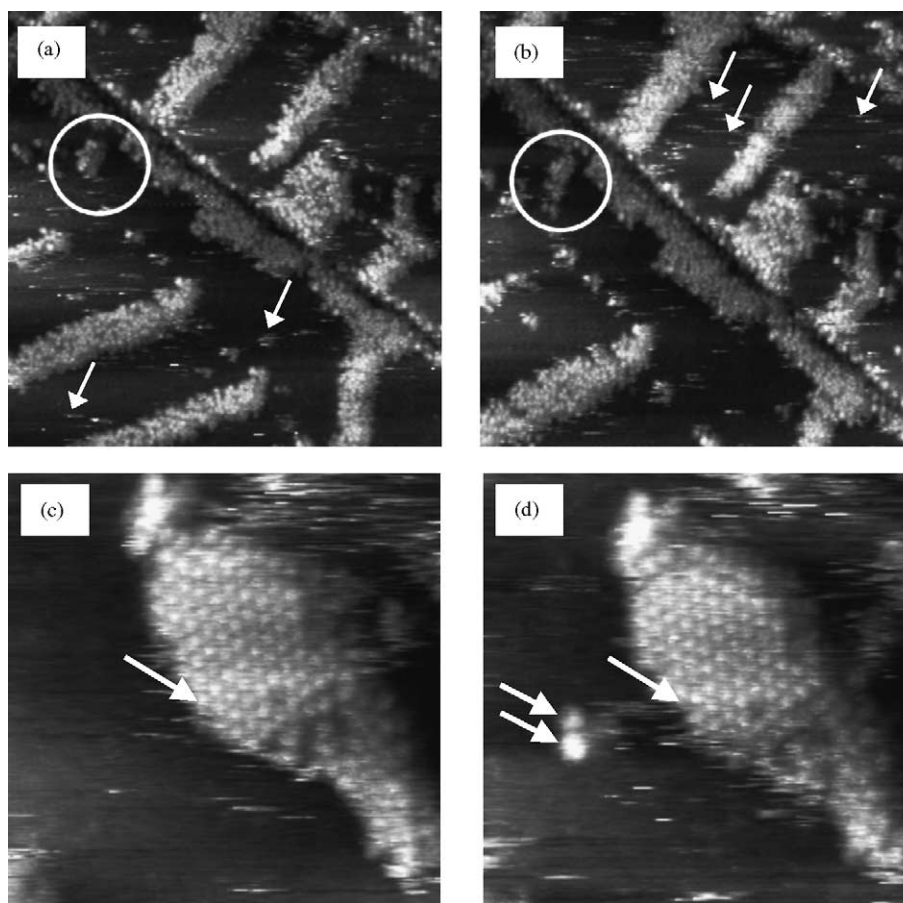


Fig. 1. (a) and (b), consecutive STM images with a low coverage of C_{60} , registered within the interval of about 2 min. The molecules decorate the step edges. White circles mark the growth of an island. White arrows design smeared spots accounting for tip-induced mobility along scanning direction. Visible shift of image (b) compared to image (a) corresponds to thermal drift ($U_t = 110$ mV, $I_t = 0.1$ nA, 100 nm \times 100 nm). (c) and (d): consecutive images demonstrating possibility of nanomanipulation. Two molecules were grasped from the edge of the island (marked by the white arrows) and stabilized on the terrace (30 nm \times 30 nm, $I_t = 0.140$ nA, $U_t = 0.270$ V).

the step edges of Au(1 1 1), forming two-dimensional islands on the terraces which indicate that the molecules have a high mobility even at RT. The fact that nucleation appears near step edges is not surprising because it is known that Au(1 1 1) presents a high local density of states at the step edge, due to the formation of a standing wave of surface state electrons [13]. In contrast with the results obtained for adsorption of long-chain molecules at the *n*-tetradecane/Au(1 1 1) interface [12], some C_{60} islands decorate gold steps or form alignments along some particular directions of the substrate. Such adsorption behavior is also observed in UHV [7]. In between islands, STM images present no signal from the gold surface (neither the reconstruction stripes nor the atomic resolution are observed) or from any self-organized monolayer of *n*-tetradecane molecules [12]. Most of the islands exhibit boundaries parallel to a preferential direction, which is related to a particular orientation on the Au(1 1 1) substrate. This direction, perpendicular to the edges of triangular terraces, is then parallel to $\langle 1\ 1\ 2 \rangle$. The measured height of C_{60} islands is equal to 0.4 nm, which is smaller than the C_{60} di-

ameter (1 nm). Such an apparent reduced height, previously reported for a C_{60} monolayer on Au(1 1 1) in UHV, is related to the electronic structure of adsorbed C_{60} molecules [7,8]. Fig. 1(c) and (d) bring additional evidence for the mobility of C_{60} molecules at the liquid/Au(1 1 1) interface. The shape of the island boundary is being changed and some parts of islands disappear or grow (see white circles). This high mobility of C_{60} in liquid contrasts with results obtained in UHV and could be related to an energy transfer from the solvent. Numerous smeared spots in between islands (see white arrows) evidence a tip-induced mobility along the scanning direction. As it will be shown below, this effect can be used for manipulations of single molecules.

Fig. 1(c) and (d) show an hexagonal closed-packed island, very stable and with molecular resolution. In the limits of this uniform domain the lateral separation between the centers of the molecules is equal to 1 ± 0.05 nm and close to $2\sqrt{3}a \approx 0.998$ nm, where a is the gold lattice constant ($a \approx 0.288$ nm). This structure is assigned as $2\sqrt{3} \times 2\sqrt{3}R30^\circ$ and schematically shown in Fig. 2. Fig. 1(c) and (d) give

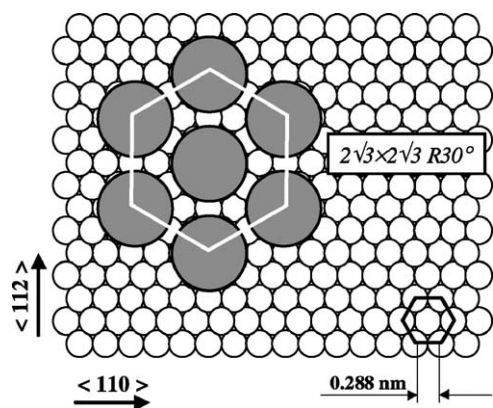


Fig. 2. Structural model for C_{60} packing at the n -tetradecane/Au(111) interface.

also evidence of a possible nanomanipulation of single molecules at a liquid–solid interface. It has been shown that on several substrates, surface atoms or adsorbed molecules can be picked up and displaced with a tip by adapting the tip–sample separation [14]. As distance between tip and substrate is defined by tunneling current and applied voltage, these parameters are commonly used to reduce the tunneling gap. But the same effect can be obtained by taking advantage of a non-ideal feedback loop. It is, for example, possible to decrease shortly the parameters controlling integral gain, or to increase scan speed. The tip can then strike against impediments, in particular against single molecules on flat surfaces. We succeeded in grasping two molecules by a decrease of integral gain. The tip removed these molecules from the edge of the island designed by the arrow in Fig. 1(c), after what they were stabilized on the flat terrace, possibly thanks to a local defect, as shown in Fig. 1(d).

Despite the large number of STM studies of C_{60} overlayers, only a few involve STS. We use it in order to screen the effects of packing and adsorption on charge transfer through C_{60} in solution on Au(111).

We first registered IV curves on bare gold (dark regions in Fig. 1(c) and (d)). The typical behavior we observed is given by the dashed curve in Fig. 3(a). This symmetric curve presents a linear part between -0.4 and $+0.4$ V. On top of single C_{60} molecules, we registered very reproducible IV curves for more than 20 images. An average value of 10 of these curves is given by the solid graph in Fig. 3(a). As compared to gold, C_{60} single molecules present a rectifying behavior. A comparison with UHV data enlightens two major similarities with STS in liquid–solid interface. First, IV curves taken on top of adsorbed C_{60} have a quasi-linear behavior between -0.2 and $+0.2$ V, as reported by Joachim and Gimzewski [15]. The second similarity concerns the position of the LUMO level of adsorbed C_{60} . The normalized differential conductance curve given in Fig. 3(b) reveals two peaks at approximately -0.9 and 0.8 V in the considered range of energies. The sharpness of the peak at 0.8 V accounts for a weak perturbation of the molecular orbitals

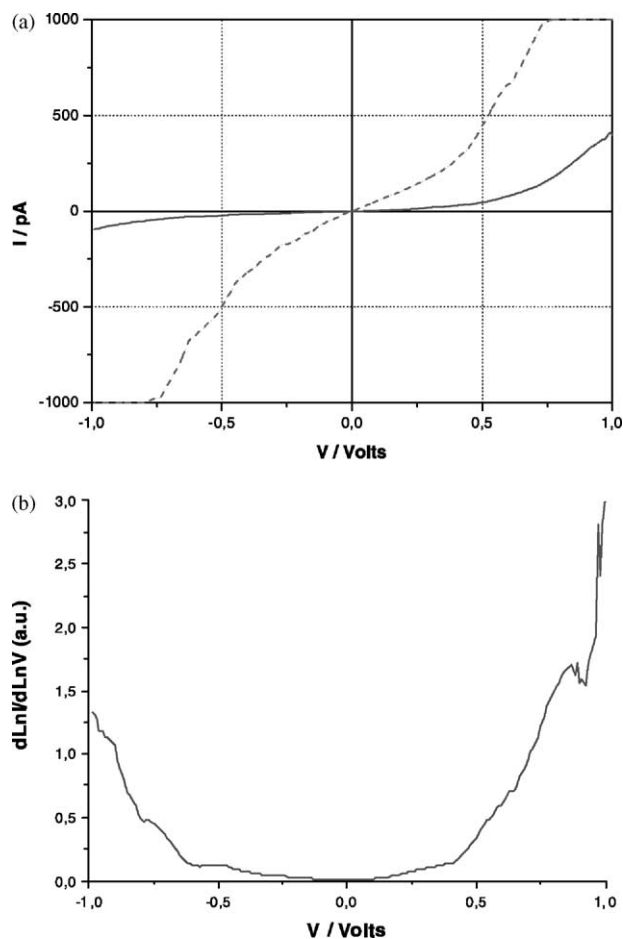


Fig. 3. (a) The solid line represents current versus bias (I - V) spectra acquired on top of single molecules. The dashed line corresponds to the Au(111) I - V curve in tetradecane. (b) Normalized differential conductance ($d \ln I / d \ln V$) of single C_{60} molecules versus bias plot.

by interaction with the substrate. It can consequently be attributed to the LUMO level peak, also observed by Rogero et al. [16] in vacuum. The other variations of this curve probably correspond to the tunneling levels of electrons, generated by the mixing of gold and C_{60} orbitals.

4. Conclusion

The adsorption of C_{60} molecules on Au(111) surfaces has been investigated at RT by using STM and spectroscopy at a liquid–solid interface. At low coverage, C_{60} decorates the step edges, forming two-dimensional islands on the terraces which indicate that the molecules have a high mobility even at RT. At higher coverage, the C_{60} molecules form close-packed $2\sqrt{3} \times 2\sqrt{3}R30^\circ$ structures. We also demonstrated for the first time that STM in a liquid environment allows the performance of spectroscopy measurements and the manipulation of single molecules. These results can be used for the development of nanotechnologies in liquid environments [17].

Acknowledgements

A. Marchenko would like to thank DRECAM/CEA and Departement des Sciences Chimiques du CNRS for financial support.

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