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STM Visualization of C_{84} Fullerene on Gold

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Résumé. — La visualisation de molécules du fullérène C_{84} adsorbées sur une surface d'or est présentée. La préparation de l'échantillon par évaporation d'une solution et l'étude par STM ont été effectuées à l'air. Les vues montrent des détails intra moléculaires.

Abstract. — Visualization of C_{84} fullerene molecules adsorbed on gold is presented. Both, the coating of support and the STM study were done in air atmosphere. The images reveal intra-molecular details.

1. Introduction

Since 1990, fullerenes (mainly C_{60}/C_{70}) adsorbed on a variety of substrates have been extensively imaged using scanning tunneling microscopy (STM). Samples where frequently prepared ([1] and references therein) in vacuum by sublimation or epitaxy, sometimes coating of gold by evaporation of fullerene solution was used.

Recently, STM studies of C_{84} fullerene molecules were published [2, 3]. Both works were done in UHV conditions, using Si(100)2×1 [2] or cleaved GaAs(110) [3] as substrates. Samples were prepared in the high vacuum chamber by evaporation of fullerene, and generally an epitaxial growing of the molecular layer(s) occurred.

We want to present here our results of C_{84} fullerene purification and visualization in air on a Au(111) surface.

2. Experimental

C_{84} purification was performed by chromatography: 65 mg of a benzene extract (kindly provided by Krätschmer) of a crude soot was dissolved in 100 ml of toluene and then deposited on 20 g of

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neutral alumina (activity I). After removal of toluene, the obtained powder was placed on the top of a chromatography column (460 g of neutral alumina activity I). After elution of C_{60} (36 mg) and C_{70} (9 mg) with hexane / toluene (95/5) and (80/20) as eluent, elution with methylene chloride afforded a fraction (1 mg) containing mainly C_{84} (see mass spectrum Fig. 1).

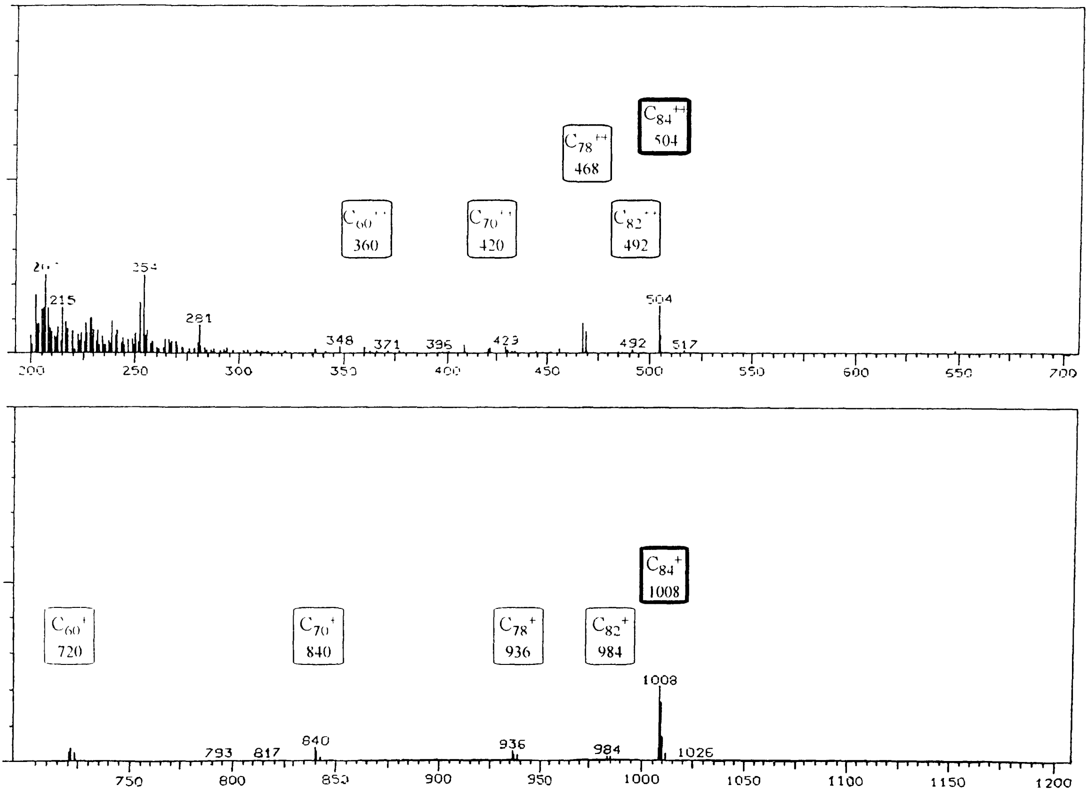


Fig. 1. — Mass spectrum of the C_{84} fraction (electro-impact ionization at 70 eV and thermal desorption on a Nermag R10 spectrometer).

Gold substrate was obtained by heating a small gold foil up to the melting point, with a H_2/O_2 torch. Samples were coated by spreading a few microliters of a C_{84} fullerene solution in toluene onto a freshly prepared gold support in air atmosphere. After evaporation of the solvent in air, the sample was ready for STM examination.

STM observations were done on a Nanoscope II apparatus, equipped with mechanically formed commercial Pt/Ir nanotips. For best high resolution images, operating conditions being tunnel current in the range 150 to 200 pA and voltage bias between 15 mV and 200 mV in the constant current mode, in air atmosphere and room temperature. The scanning speed was in the extent of 30 to 90 nm/s. Recorded images were 200 × 200 pixels sized, and are slightly low pass filtered for noise attenuation.

3. Results and Discussion

High resolution visualization is easily obtained, displaying motionless molecules in an unorganized coverage of the field. The contrast of images is not clearly depending on the tunneling conditions, for values in the range indicated in the experimental part (*vide supra*). On 15 × 15 nm^2 areas (Fig. 2), numerous fullerene molecules are seen in an amorphous coverage of the gold substrate. As the thickness of the adsorbate is not controlled in the easy procedure for sample preparation, the deposited layer is multinanometers thick. Such a layer appears to have a sufficient electric conductivity to perform stable STM analysis, as observed in studies of well- ordered two dimensional arrays [2, 3].

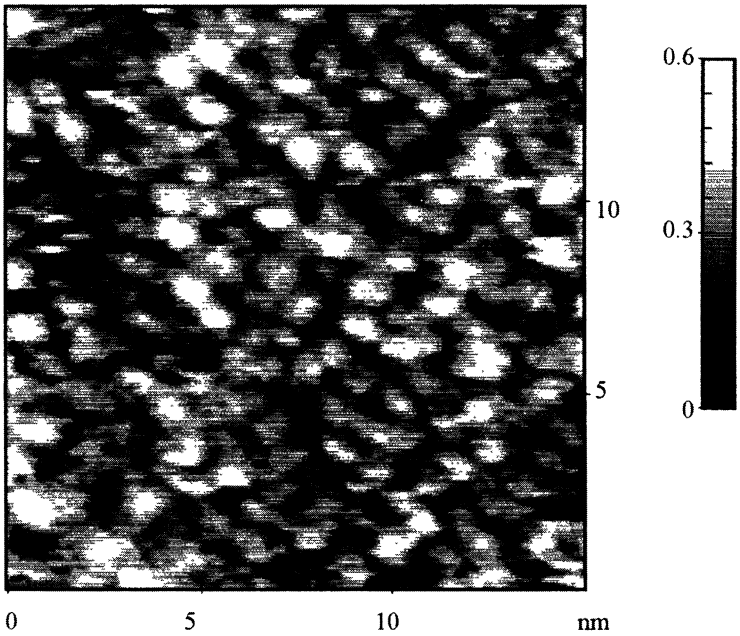


Fig. 2. — STM of fullerene (mostly C_{84}) molecules on Au(111); field of 15 × 15 nm^2 (0.15 nA and 15 mV).

Looking at neighbour molecules of the same apparent level, the shortest distance between centers of two molecules is about 1.0 nm. This value is close to the one measured for an array of C_{84} onto GaAs(110) [3]. On a Si(100)2×1 surface, the nearest-neighbour distance is described to be 1.21 nm for multiple layers coverage [2].

By a high resolution observation of small areas (Figs. 3a-b: 7.5 × 7.5 and 6 × 6 nm^2), submolecular data are revealed, as recently seen in UHV environment and interpreted in [2b] and [3] as internal structure of the fullerenes molecules. Such an observation indicates no (or negligible) molecular rotation.

Molecules are generally seen as oval shaped (labelled A on views Fig. 3), a few being circular (labelled B on views Fig. 3). This fact may be interpreted by a random orientation of identical molecules (*vide infra*), or as an indication of the presence of isomers, or of another fullerene as an impurity.

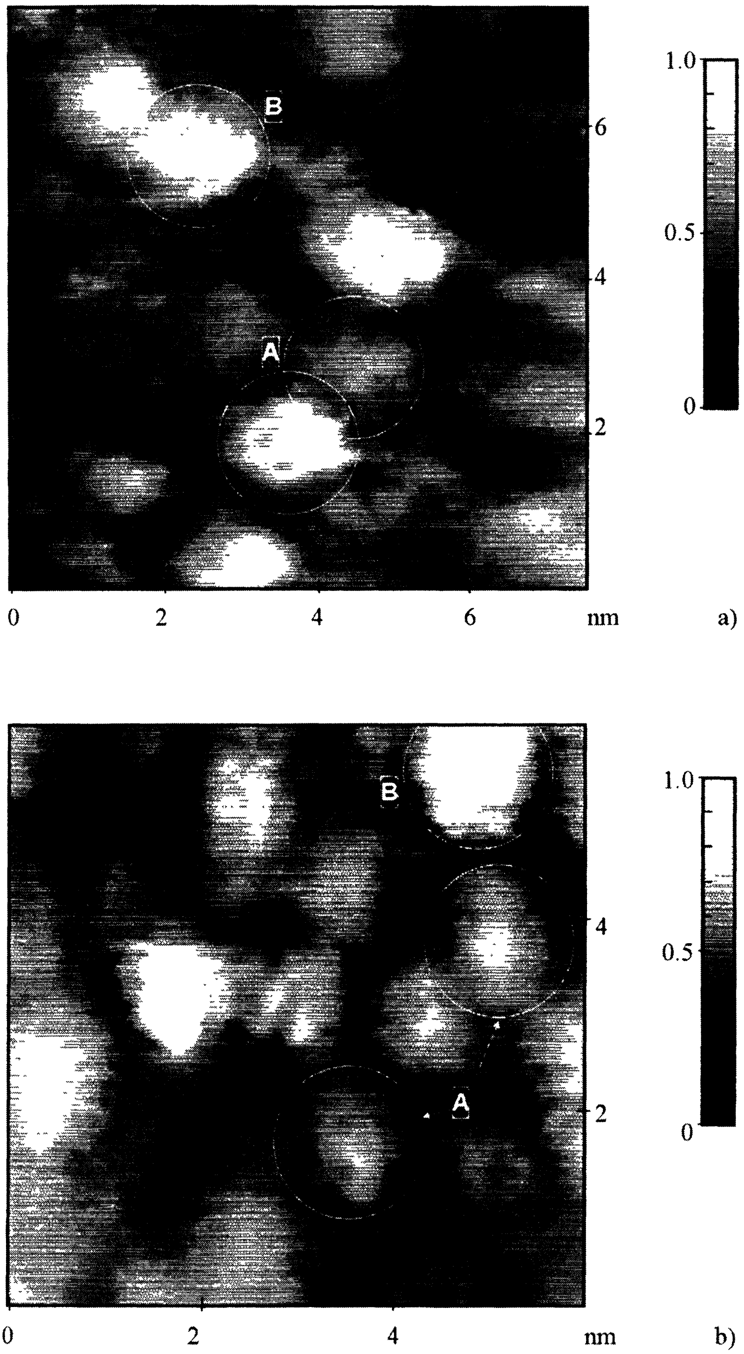
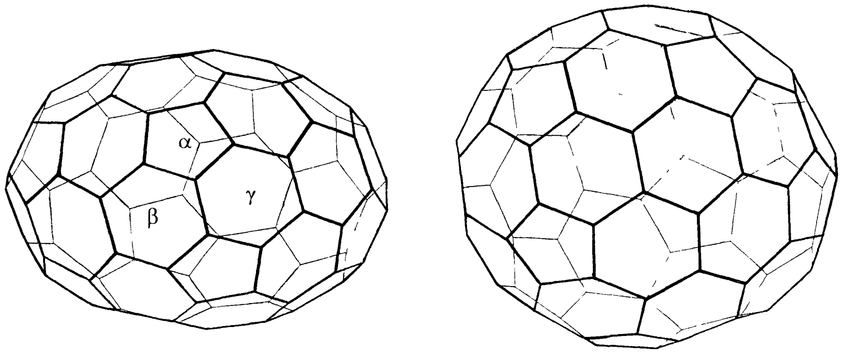


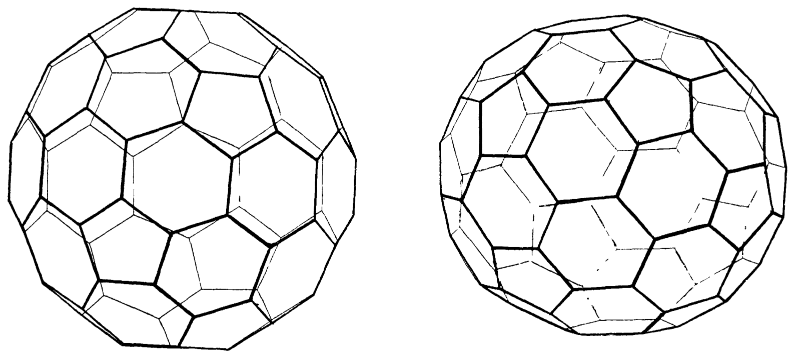
Fig. 3. — High resolution STM views of C_{84} on Au(111), displaying intramolecular details: a) field of 7.5 × 7.5 nm^2 (0.16 nA and 20 mV); b) field of 6 × 6 nm^2 (0.15 nA and 30 mV).

According to NMR studies [4], among the 24 isolated-pentagon C_{84} fullerenes [5], only two D_2 symmetry [D_2 (22) and D_2 (5)] and one D_{2d} (23) have to be considered (Fig. 4), with a D_2 to D_{2d} ratio of 2:1 [4]. The case is not simple for the D_2 isomers of C_{84} fullerene. Considering energy calculations, the D_2 (22) is the most favoured isomer [6, 7]. In a STM study, an ordered layer of C_{84} on Si(100)2×1 was described as fitting the D_2 (22) isomer geometry [2b]. Nevertheless of energy considerations, a mechanism for the formation of higher fullerenes predicts a ratio of D_2 (5) and D_{2d} (23) of 2:1 respectively [8], the same ratio as determined by NMR study [4]. However, it seems possible that a selective step in the process can influence the isomeric composition. In fact, an X-ray diffraction study of the iridium complex, $(\eta^2 - C_{84})Ir(CO)Cl(PPh_3)_2,4C_6H_6$, shown that the D_{2d} (23) isomer can be selectively obtained [9]. The growth of a regular array of C_{84} onto GaAs(110) was found to fit, this time, the D_2 (5) geometry [3]. These experiments have a selective step such as the chemical reactivity and the crystallization in the formation of the iridium complex or formation of a 2D crystal array fitting the substrate structure in epitaxially grown layers.



a) b)

$D_2(5)$



a) b)

$D_2(22)$

Fig. 4. — Drawings of two C_{84} D_2 isomers, obtained by molecular modeling. The D_2 (5) isomer is shown oval shaped a) and as a large circle b); whereas D_2 (22) isomer is nearly spherical, a) and b).

If the observation of a few molecules is considered to be representative of the sample composition, and neglecting the interference due to impurities, the presence of D_2 (5) isomer is found to be more in agreement with the STM observations (Fig. 3) than the D_2 (22). The D_2 (5) structure (Fig. 4) has a more elongated (a) or a large circular shape (b), depending on the projection axis, while the D_2 (22) is nearly spherical (Fig. 4). The difference between maximum and minimum diameters is almost 0.3 nm for D_2 (5) structure, while the difference is only 0.07 nm for the D_2 (22) isomer [2, 3]. On one of the oval shaped molecules of Figure 5, probably due to helping contrast, we can distinguish two C_6 rings (β, γ) and one C_5 ring (α). If this is not an artifact, such a case is easy to found in the D_2 (5) isomer of C_{84}, as labelled α, β and γ in Figure 4 D_2 (5) a).

In our observations, selectivity should not be excluded. The adsorption of C_{84} molecules on Au(111) yields a random coverage of the surface in which the D_2 (5) isomer is preferentially seen.

Medium sized fullerenes, mostly C_{84}, will be soon obtained in larger amount by optimization of a thermal treatment of extracted soot residues [9]. Such a larger avaibility opens the,way for C_{84} chemistry leading to a better knowledge of its isomers [10].

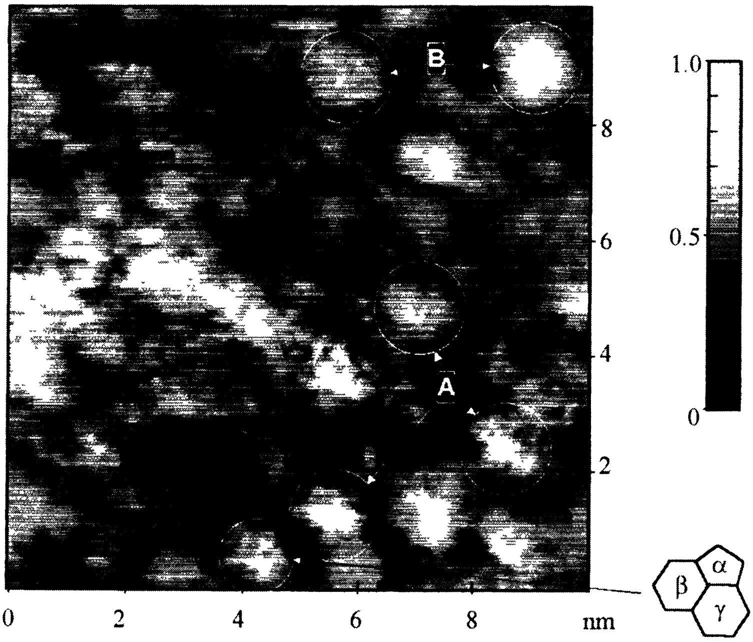


Fig. 5. — View of a 10 × 10 nm^2 field of C_{84} on Au(111), showing interesting molecular details (0.15 nA and 15 mV).

4. Conclusions

The STM results presented here were obtained in an air atmosphere on a gold surface. Observed samples were prepared by the coating of Au(111) substrate with a toluene solution of C_{84}, followed by air evaporation of the solvent. In the environment of an organic chemistry laboratory, we have been able, by this simple procedure, to visualize fullerene molecules adsorbed on gold.

A random coverage of the substrate is more difficult to elucidate than a regular array. Well organized array of unspherical molecules in a 2D crystal always show the same part of molecules, whereas in an unorganized layer the molecules display various orientations.

In such a case of an air stable adsorbate-substrate combination, a STM equipment working in the air yields results complementary to these obtained with more sophisticated apparatus.

Acknowledgements

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