Comment on "Identifying Molecular Orientation of Individual C_{60} on a Si(111)-(7×7) Surface"

In a recent work Hou *et al.* [1] report scanning tunneling microscopy (STM) images of C_{60} molecules adsorbed on Si(111)-(7 × 7), which reveal clear intramolecular features. Their comparison with electronic structure calculations [2] allows them to clearly identify the adsorption sites and the molecule orientation. An important issue in their work is the dependence of the images with the applied bias voltage: They claim that images of the molecular cage are obtained only at positive bias voltages.

We have also performed STM experiments on C_{60} molecules adsorbed on Si(111)-(7 × 7). Our results coincide in many respects, but certain important differences are critical to the conclusions. In particular, we do not observe any bias voltage dependence in the STM images, which have been reproduced with many different tips. Figures 1(a)–1(d) show four representative STM images with a well-defined and clear intramolecular structure related to the molecule orientation. They are zooms of larger images showing excellent molecule and substrate resolution, and a large variety of similar molecules. The applied voltages were +2, −1.5, +2, and −2 V, respectively. Figures 1(e)–1(h) show images generated from standard density functional calculations of the isolated C_{60} molecule. To simulate the symmetry-breaking effect of the substrate, a small uniaxial compression was applied in the vertical direction, except in Fig. 1h, where the strain direction was inclined 30°. The effect of the strain is to split the fivefold degenerated highest occupied molecular orbital (HOMO), and the figures show the highest-energy orbitals after this splitting. This procedure is completely heuristic, and we can justify it only by the excellent agreement between the theoretical and experimental images. In principle, the HOMO should be probed only at negative sample bias, but we observe it at both polarities, in strong contradiction with [1]. Moreover, we found that any MOs other than the HOMO, or energy integrations including more MOs than the HOMO, gave a substantially poorer comparison. Also, the agreement with experiment was not improved by calculations of the molecule adsorbed on the silicon surface.

We agree with Hou *et al.* on the critical role played by the tip in high resolution STM images. Thus, understanding the imaging mechanism at different bias voltages in this relatively complex system is not as straightforward as in noble metal surfaces. A full explanation of both experiments may require calculations beyond the Tersoff-Hamann theory used in [1], including the whole substrate-molecule-tip system.

J. I. Pascual,[1] J. Gómez-Herrero,[2] A. M. Baró,[2]
Daniel Sánchez-Portal,[3] Emilio Artacho,[2]
Pablo Ordejón,[4] and José M. Soler[2,5]
[1]Fritz-Haber-Institut
Faradayweg 4-6
D-14195 Berlin, Germany
[2]Departamento de Física de la Materia Condensada, C-III, and Instituto Nicolás Cabrera
Universidad Autónoma de Madrid
28049 Madrid, Spain
[3]Department of Physics and Materials Research Laboratory
University of Illinois
Urbana, Illinois 61801
[4]Instituto de Ciencia de Materiales de Barcelona
08193 Bellaterra, Spain
[5]Lyman Laboratory, Department of Physics
Harvard University
Cambridge, Massachusetts 02138

Received 4 November 1999
PACS numbers: 82.65.My, 61.16.Ch, 61.48.+c, 71.15.Mb

[1] J. G. Hou, Y. Jinlong, W. Haiqian, L. Qunxiang, Z. Changgan, L. Hai, B. Wang, D. M. Chen, and Z. Qingshi, Phys. Rev. Lett. **83**, 3001 (1999).
[2] J. Tersoff and D. R. Hamann, Phys. Rev. B **31**, 805 (1985).

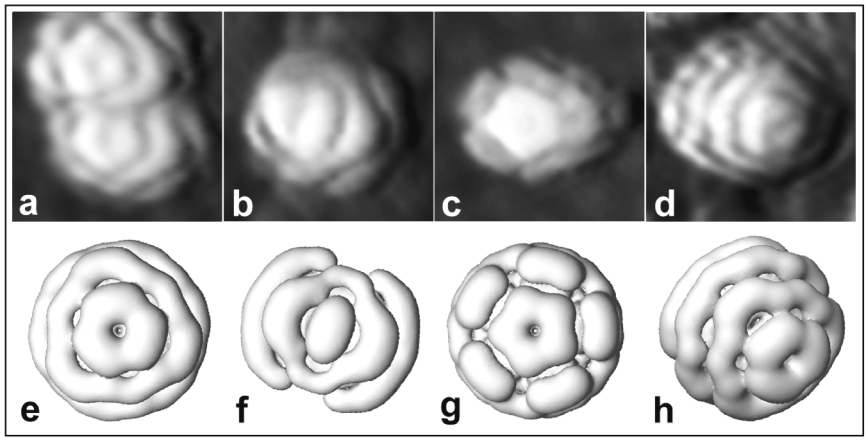

FIG. 1. Comparison of experimental STM images of individual molecules (a)–(d) with calculated shapes of C_{60} HOMO's (e)–(h). The applied voltages and tunnel currents are 2 V, 0.2 nA (a); −1.5 V, 0.2 nA (b); 2 V, 1 nA (c); and −2 V, 1 nA (d). The theoretical images correspond to isosurfaces of constant HOMO density. Reprinted from J. I. Pascual *et al.,* Chem. Phys. Lett. **321**, 78 (2000) with permission.

