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Scanning tunneling spectroscopy of C_{60} adsorbed on Si(1 0 0)-(2 × 1)

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Abstract

A room-temperature scanning tunneling spectroscopy study has been conducted on single molecules and multilayers of C_{60} molecules adsorbed on the Si(1 0 0)-(2 × 1) surface without any post-annealing. For single isolated molecules, four peaks in the local density of states are observed that can be well attributed to molecular energy levels. Scanning tunneling microscope spectroscopy has also been carried out on molecules that are moved across the silicon surface. Spectroscopy on multilayers of C_{60} shows broad, smeared out features for the first monolayer, while the third layer results resemble those of single isolated molecules. We attribute the variations in electronic spectra to differing intermolecular interactions in the first and upper layers of C_{60}. © 2001 Published by Elsevier Science B.V.

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1. Introduction

Since its discovery [1] and subsequent production in significant quantities [2], the 'original' fullerene molecule, C_{60} has attracted significant attention from the surface science community. Through an understanding of molecule–substrate interactions, clues may be learned about the fundamental physical and chemical properties of these fullerenes. C_{60} adsorption on metal surfaces generally results in transfer of charge from the metal to the C_{60} molecules [3], and island formation due to the low surface electronic corrugation. For the case of semiconductor surfaces however, C_{60} molecules generally remain isolated, with a much lower degree of charge transfer. The two most widely studied semiconductor/C_{60} systems are Si(1 1 1)-(7 × 7)/C_{60} and Si(1 0 0)-(2 × 1)/C_{60}, due in part to the body of knowledge regarding the chemical and electronic nature of the pristine surfaces because of their technical importance. Despite a number of studies by scanning tunneling microscopy (STM) [4–8], scanning tunneling spectroscopy (STS) [9–11], and photoelectron spectroscopy [12–15] among other techniques, the interaction of C_{60} with these surfaces still remains contentious. Yao et al. [9] have recently investigated individual C_{60} molecules adsorbed on Si(1 0 0)-(2 × 1) by STS. However in their report it was noted that spectroscopy was not possible on molecules prior to annealing at $\sim$600 °C.

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This was due to the diffusion of molecules under the tip during STS measurements.

In this paper we present for the first time STS results on individual C_{60} molecules, as well as on multilayer coverages of C_{60} adsorbed on Si(1 0 0)-(2×1), with no post adsorption annealing. For our experiments we use p-type Si in contrast to Yao et al. [9] who used n-type. We speculate that this may cause a change in the alignment of surface states to molecular energy levels, thus changing the molecule/surface interaction strength. For individual isolated molecules we observe four peaks in the local density of states which strongly resemble the calculated HOMO − 1, HOMO, LUMO and LUMO + 1 levels for a free isolated molecule [10,16]. At 1 ML coverage of C_{60} the HOMO and LUMO related levels form broad shoulders which mask the outer lying energy levels. STS on third and upper layer islands of C_{60} again resembles the spectra found on isolated molecules on the Si(1 0 0)-(2×1) surface. We attribute these differences to variations in the nearest-neighbour separations and hence inter-molecular interactions between the first and third layers of C_{60}.

2. Experimental

All experiments were carried out using an STM [17] operating at room temperature in ultrahigh vacuum (base pressure 2.0×10^{-11} mbar). p-Type (0.1 Ω cm) Si(1 0 0) samples were prepared by degassing at 700 °C overnight, annealing to ∼1220 °C for several seconds, holding at 850 °C for 3 minutes and then cooling slowly (1 K/s) to room temperature. C_{60} (purity >99.9%) was sublimed from a Knudsen cell operating at 330 °C, onto room-temperature substrates at a rate corresponding to 1 ML in 30 min. During sample preparation and deposition of molecules the chamber pressure was kept below 2.0×10^{-9} mbar. All imaging and spectroscopy was performed using electrochemically etched tungsten tips which were cleaned in UHV by field emission. Topographic and spectroscopic data were recorded simultaneously in order to obtain unequivocal results and to overcome any effects of sample drift or tip changes during a measurement. In order to

optimize the signal to noise ratio in our spectroscopy measurements, we used relatively high tunnel current set points (∼0.5–1.0 nA). The starting bias voltage used for spectroscopy was the same as that used for the tunnel-current feedback loop during scanning. This was typically ±3 V, with the voltage sweep for STS extending over a range of 6 V. Note that in order to eliminate singularities arising around zero bias, we have applied a gentle numerical smoothening to the local density of states (LDOS) plots. This removes these noise-related zero bias features but does not shift or adjust the remaining peaks in the spectra. Apparent features arising between ±0.3 V should be regarded as noise.

3. Results and discussion

A topographic STM image showing isolated C_{60} molecules on the Si(1 0 0)-(2×1) surface is shown in Fig. 1(a). The C_{60} molecules appear as white spheres and the (2×1) reconstructed dimer rows run diagonally across the image. A Si terrace step runs across the centre of the scan where the dimer rows change phase by 90°. In agreement with previous studies [18,19] we find that molecules are located in the troughs between dimer rows above the four dimer site (see Fig. 1(b)). All the spectroscopy for isolated molecules presented in this paper was performed away from step edges and defects. To ensure reliable spectroscopy, I–V curves were additionally recorded on locations on the bare Si surface beside molecules. Here we observe the typical π and π^* bands also reported in the literature [20]. The spectroscopy curves presented in this paper are plotted as $(V/I)(dI/dV)$ vs V, as this is the best approach to indicate the peak positions in the LDOS [21].

Typical spectra, representative of many hundreds of I–V curves for isolated C_{60} molecules and the bare Si surface are plotted in Fig. 2. Spectra for molecules reveal four peaks in the local density of states at −1.8, −0.6, +1.1 and +2.24 eV. The relative intensity of these peaks is generally consistent between measurements, with the peak at −0.6 eV always the smallest, +2.24 eV always the largest, and the remaining two peaks at intermediate heights. The calculated energy levels for a free

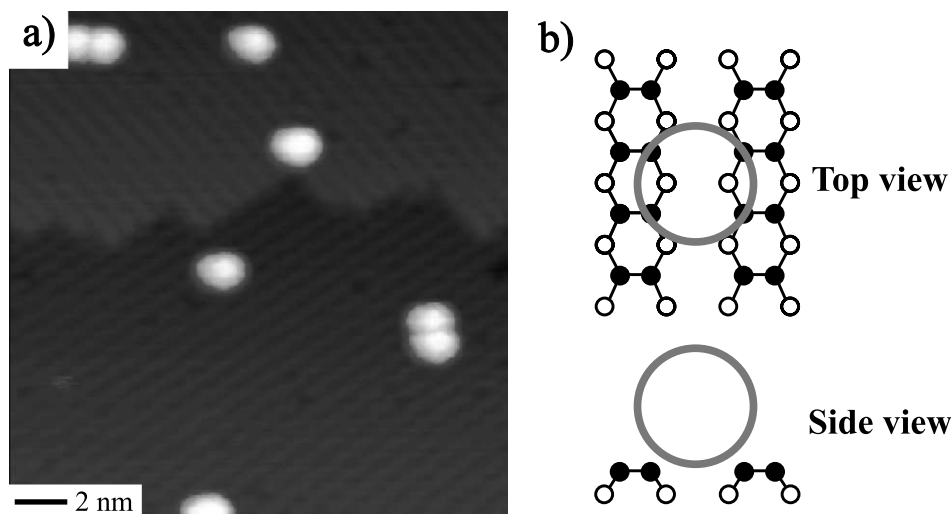Fig. 1. (a) 20 nm × 20 nm STM image showing isolated C_{60} molecules on the Si(1 0 0)-(2 × 1) surface. A Si terrace step runs horizontally across the centre of the image. Scan parameters: −2.0 V, 0.1 nA, (b) schematic diagram of a C_{60} molecule above a four dimer site in the trough between Si dimer rows.
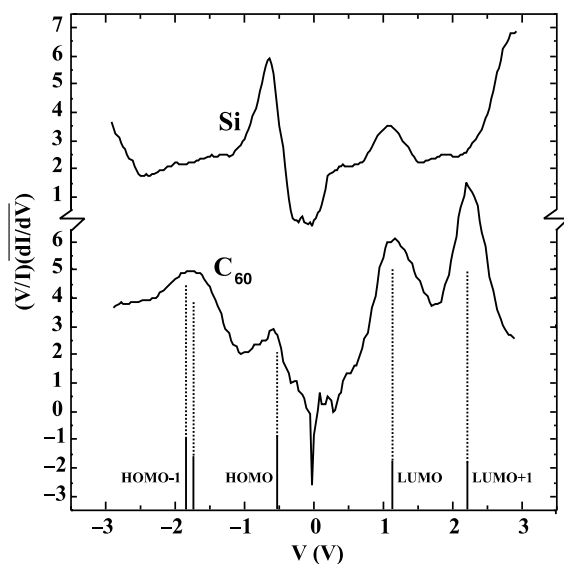

Fig. 2. STS data for the bare Si(1 0 0)-(2 × 1) surface (upper line) and for isolated C_{60} molecules (lower line). V = −3.0 V, 1.0 nA. Vertical bars along the x-axis represent the calculated energy levels for a free C_{60} molecule (from Ref. [10]).

isolated C_{60} molecule [10] are indicated as well. We have applied a rigid shift to the calculated energy levels so that the LUMO aligns with the first observed peak in the density of states on the positive bias side.

It is striking that a corresponding peak can be observed in the experimental data for every calculated energy level. A rather high degree of broadening is evident in our experimental molecular spectra which may be expected when one considers the fact that molecules reside not in free space but are adsorbed on a surface. (It is interesting to note that the broadest experimental peak measured is the one at −1.8 eV. This should be compared to the calculated energy levels which reveal a doublet at this energy.) In this respect, our results resemble those reported by Wang et al. [10] in a similar STS study of isolated C_{60} molecules adsorbed on the Si(1 1 1)-(7 × 7) surface. Our results on the Si(1 0 0)-(2 × 1) surface differ however, in that we do not observe additional peaks beside those calculated for a free isolated C_{60} molecule. Differences in surface states between the Si(1 1 1)-(7 × 7) [22] and Si(1 0 0)-(2 × 1) [21] surfaces may account for this, because variations in the electronic spectra of these surfaces may subtly alter the molecular orbital/Si dangling bond orbital mixing, and hence the molecular energy spectrum.

Photoelectron spectroscopy conducted on the C_{60}/Si(1 0 0)-(2 × 1)–H system [15] following

annealing, strongly suggested the formation of covalent bonds between the C_{60} molecules and the Si surface. This was evident through the appearance of a peak in the valence band spectra located between HOMO and HOMO − 1 levels, spaced 0.8 eV from the HOMO − 1. Upon identifying the lowest lying peak in our STS results near −1.8 V as the HOMO − 1 level, we would expect to see this feature near −1.0 V. A peak is not observed here however. It is worth of noting that De Seta et al. [15] observed an increase in the number of Si/C_{60} bonds following annealing. For our experiment, we deposit molecules onto room-temperature Si substrates. The fact that we do not observe this peak may simply point to a reduced number of Si–C_{60} bonds, as our experiments do not involve an annealing step. Another point worth noting is that for our experiments, we are able to locally probe the electronic structure of single molecules adsorbed only at the four dimer sites, whereas photoemission studies will also average the electronic information for molecules adsorbed at step edges and defects, where the Si–C_{60} interaction is stronger.

While the interaction of C_{60} with the Si(1 0 0)-(2 × 1) surface is relatively strong [13,15], it is still possible to translate molecules across the surface [7] by using the STM tip to overcome the diffusion barrier. This is achieved by moving the tip closer to the surface by increasing the tunnel-current set point and decreasing the bias voltage, and then sweeping it over the position of a molecule. As noted above, we use relatively high tunnel current values (∼0.5–1.0 nA) to ensure stable spectroscopy results. This did, on rare occasions, result in the translation of a molecule during a spectroscopy measurement. While this effect is generally undesirable, and in fact prevented previous studies on n-type Si [9,11], we have found that reliable spectroscopy is still possible on *moving* molecules. This allows an investigation of the dependence of the STS spectra on the molecular bonding site and C_{60} orientation (see Fig. 3).

Fig. 3(a) shows a STM topograph of two isolated C_{60} molecules. The fast scan direction is from left to right, perpendicular to the dimer row direction, and the slow scan direction is from bottom to top. Note the translation of the upper right
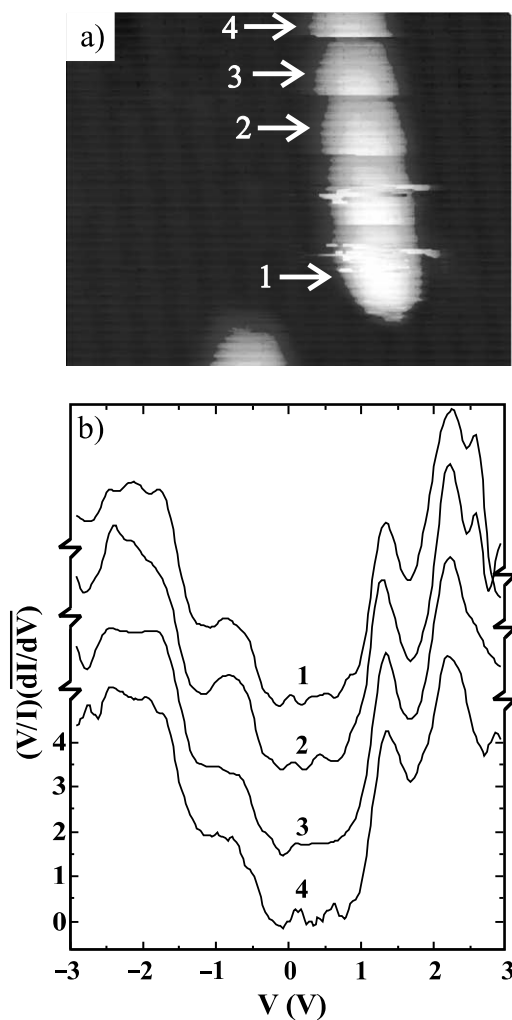

Fig. 3. (a) STM topographic image during which STS was recorded at every third data point. Dimer rows run vertically up the image. Note the tip assisted diffusion of the right hand molecule up a single dimer row. (b) STS data recorded in (a) at positions 1–4. V = −3.0 V, 1 nA.

molecule along a dimer row in a number of discrete steps from bottom to top. It is interesting to note that it is the top of the molecule that is imaged each time before it is moved upwards by the tip. This is clear evidence that the tip has exerted an attractive force to the molecule, thereby 'pulling' it up a dimer row. This result is in contradiction to previous proposals on the tip-induced manipulation of C_{60} molecules on the Si(1 0 0)-(2 × 1)

[7] and Si(1 1 1)-(7 × 7) [8,23] surfaces, which sug-
gested a repulsive tip–molecule interaction. We
have performed molecular manipulation experi-
ments [24] and have also observed a repulsive in-
teraction when moving C_{60} molecules along dimer
rows. In the above case however, the tip scan di-
rection is perpendicular to the dimer row direction
and hence to the direction of molecular motion. A
satisfactory explanation for this new effect is
lacking.

The spectroscopy results for the moving mole-
cule, presented in Fig. 3(b), show the same features
as the spectroscopy data for static molecules (Fig.
1). (The small features between 0 and 0.6 V are
near the noise limit and can be disregarded.) As
shown by Moriarty et al. [7] the molecule is likely
to rotate as it is moved along the dimer row. Our

STS results therefore show that the precise orien-
tation and location of C_{60} molecules on the
Si(1 0 0)-(2 × 1) surface has no effect upon their
electronic structure.

We now present results on multilayer coverages
of C_{60}. After depositing C_{60} for 80 min onto room-
temperature substrates, we observe second and
third layer islands coexisting with regions of
monolayer C_{60}. We find that the first layer of C_{60}
is rather disordered but it has a tendency to
form two partially ordered domains (see Fig. 4a).
The c(4 × 4) domain has a molecular nearest-
neighbour separation of 10.9 Å while the c(4 × 3)
domain has a lower nearest-neighbour separa-
tion of 9.6 Å [5] as illustrated in Fig. 4(c) and (d).
In contrast, the molecules of the upper layers
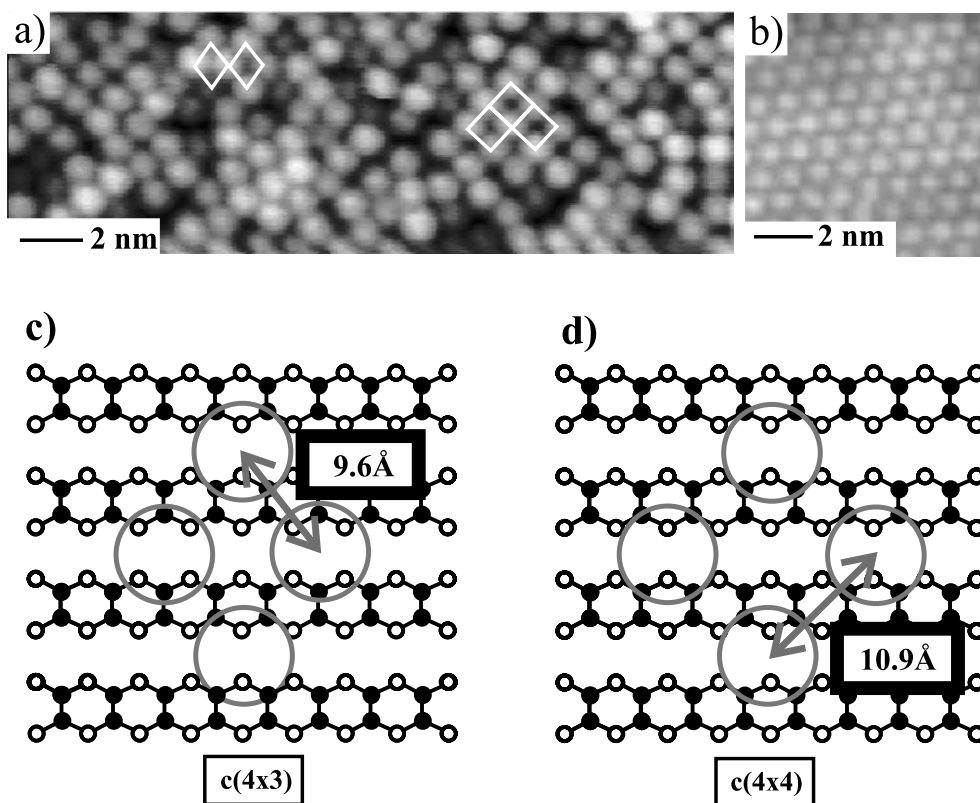exhibit a clear hexagonal ordering with a nearest

Fig. 4. STM image of the first monolayer (a) and a third layer island (b) on the Si(1 0 0)-(2 × 1) surface. c(4 × 3) and c(4 × 4) domains
are indicated in the left and right of (a) respectively. Dimer rows run horizontal in these images. Scan parameters: −3.0 V, 0.1 nA. (c)
and (d) schematic diagrams of the c(4 × 3) (c), and c(4 × 4) (d) domains of C_{60} in the first monolayer on Si(1 0 0)-(2 × 1) (from Ref. [5]).
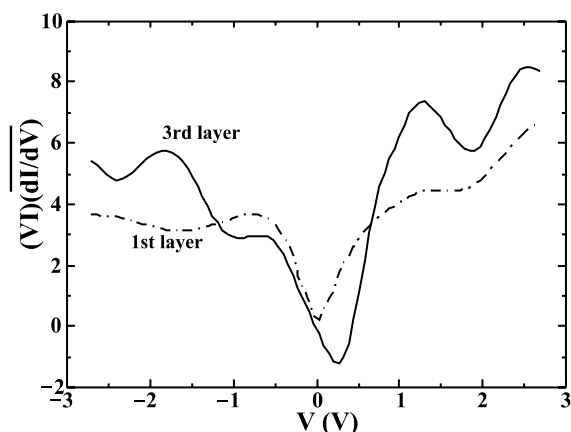Note the nearest-neighbour distance of 9.6 Å for the c(4 × 3) domain.

Fig. 5. STS of the first (lower line) and third layers (upper line) of C_{60} on Si(1 0 0)-(2 × 1). STS parameters: −3.0 V, 1.0 nA.

neighbour separation of about 10 Å (see Fig. 4b).

In Fig. 5 we present a summary of STS data recorded on regions of first and third layer C_{60}. Inconclusive results were obtained on second layer islands. The lower line shows the LDOS for the monolayer, averaged over many tens of molecules. The onset of the HOMO and LUMO levels are apparent, albeit significantly broadened, while the outer lying levels are smeared out altogether. In contrast to the results of Wang et al. [5] we do not observe a feature at the Fermi energy. In this respect our data is in agreement with recent photoemission studies [12,15]. Our results for the third layer islands of C_{60} are markedly different from those for the first monolayer. Here we observe four distinct peaks in the density of states. Comparison with spectra for isolated C_{60} molecules on the bare Si surface (Fig. 2) reveals a striking similarity both in peak positions and relative heights. As this spectrum is somewhat more noisy due to the lower signal-to-noise ratio (because of the lower tunnel current), the data perhaps give the appearance of some density of states within the band gap, but it would be incorrect to conclude the absence of a band gap in the third layer from that.

We attribute the differences in the electronic spectra of the first and third layers of C_{60} to the variations in the intermolecular spacings of these layers. The value of 9.6 Å for the first monolayer is important as it is below the van der Waals separation of 10.05 Å. Thus it is reasonable to assume that some of the molecules in the first monolayer will have overlapping molecular orbitals, and hence a modified electronic structure compared to upper layers of C_{60}. Both our STS on isolated molecules, and photoemission experiments [12,15] show that at room temperature, the Si–C_{60} interaction does not significantly affect the electronic spectra of C_{60}. Hence we propose that the spectral broadening observed for the first monolayer is due to electronic interactions between adjacent molecules, which as mediated by the interaction with the substrate, have a minimum intermolecular separation of 9.6 Å. Molecules in third layer islands, due to their larger bulk-like separation of above 10 Å, exhibit a spectra similar to individual C_{60} molecules.

4. Conclusion

We have investigated the electronic structure of C_{60} molecules on the Si(1 0 0)-(2 × 1) surface at sub-monolayer and multilayer coverages by STS. For single isolated molecules, we observe four peaks in the density of states which bear a strong resemblance to the calculated energy levels of a free isolated molecule [10]. STS on multilayer coverages of C_{60} reveals broad smeared-out features for the first monolayer, in contrast to the third layer which resembles that of single molecules on Si. We propose that the differences in electronic spectra between the first and upper layers is due to the fact that for a lower nearest neighbour distance, the C_{60} molecular orbitals overlap between nearest neighbours that are at a variety of distances, down to distances as small as 9.6 Å in the first monolayer.

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