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Scanning tunneling microscopy and spectroscopy of C_{70} thin films

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Abstract. Scanning tunneling microscopy of C_{70} films deposited on HOPG and gold substrates has been carried out to investigate the 2D packing, defects and disorder. Besides providing direct evidence for orientational disorder, high resolution images showing the carbon skeleton as well as the molecular arrangement in a solid solution of C_{70} and C_{60} are presented. Tunneling conductance measurements indicate a small gap in the C_{70} film deposited on HOPG substrate.

Keywords. C_{70}; fullerenes; orientational disorder; scanning tunneling microscopy; tunneling spectroscopy.

1. Introduction

Scanning tunneling microscopy (STM) has emerged as a powerful technique to study solids and surfaces at atomic resolution. STM studies provide direct information on the morphology, local structure as well as the nature of defects in solids. The technique has been used recently for the study of fullerenes. Buckminsterfullerene, C_{60}, has been studied by STM in considerable detail (Narlikar *et al* 1992, 1994; Weaver 1992), high resolution images showing details of the carbon skeleton in the cage molecule. Orientational disorder in C_{60} also seems to be revealed by STM, although the spherical nature of the molecule makes it difficult to directly observe disorder from the images of the lattice. There have been few STM studies of C_{70} which show the occurrence of a hexagonal 2D lattice in films deposited on highly oriented pyrolytic graphite (HOPG) or gold (Liu and Kappes 1992; Zhang *et al* 1992). The presence of static orientational disorder has been observed in the STM images (Chen *et al* 1992), but not in sufficient detail. We have carried out a detailed investigation of C_{70} films deposited on solid substrates by STM, taking advantage of the ellipsoidal shape of the molecule (figure 1). The ellipsoidal shape, unlike the spherical shape of C_{60}, makes it easy to directly probe orientational disorder in solid C_{70}.

In this article, we describe the results of our study of C_{70} films deposited on HOPG and gold substrates, with respect to the packing of the molecules, orientational disorder, as well as the presence of defects. We have presented a high resolution image showing the partial structure of the carbon skeleton in the molecule, in addition to preliminary results on solid solutions of C_{60} and C_{70}. We also report tunneling conductance of C_{70} films deposited on HOPG.

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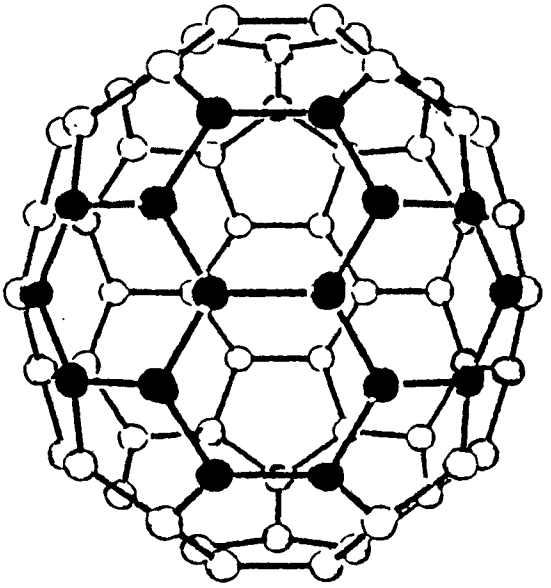


Figure 1. Structure of C_{70}.

2. Experimental

C_{70} was prepared by the contact arc evaporation of graphite under He pressure of 1 atm. This evaporation technique first yields a mixture of fullerenes. After soxhlet extraction with CS_2, C_{70} was separated from the mixture by flash column chromatography (Govindaraj and Rao 1993). C_{70} thus obtained is generally 95% pure. Further purification was carried out by column chromatography on neutral alumina with 5% toluene in petroleum ether solvent. The purity of C_{70} obtained this way was above 99% which was confirmed by UV-visible spectroscopy. The C_{70} sample so obtained was dried at 473 K under vacuum (10^{-6} torr) for 12 h and then cooled. The dried sample was taken in a pyrex glass tube which was sealed at one end with its other end fused to a ground joint. This tube was vertically connected through the ground joint arrangement to a high vacuum system. The clean solid substrate on which the film was to be deposited was placed vertically inside a small furnace which was maintained at a temperature of 673 ± 10 K under dynamic vacuum of 10^{-6} torr. C_{70} sublimes around 648 K on the substrate forming a polycrystalline film. Solid solutions of C_{60} and C_{70} were also sublimed similarly. The solid substrates used were HOPG (gift from Dr A W Moore, Union Carbide) or gold/glass.

STM studies of the C_{70} films were carried out in a Nanoscope-II scanning tunneling microscope operating in air at room temperature. The images were obtained with fine Pt-Ir tips using the Nanoscope in constant current mode with typical current of 0·2–1·5 nA and bias voltages of 20–2000 mV. Images obtained were quite stable and reproducible with different tips. C_{70} with its HOMO-LUMO gap (band gap) of 1·6 eV would be quasi-insulating making it unsuitable for STM studies. However, it has been possible to image the films deposited on HOPG as

well as gold substrate possibly as a result of charge transfer from the substrate to the film which renders it sufficiently conducting for STM purposes.

We show a typical low magnification STM image of C_{70} film deposited on HOPG in figure 2a. The image shows uniform C_{70} coverage containing ellipsoidal microcrystallites typically of 10–15 nm. Each such microcrystallite appears to contain 10–12 molecules with the spacing between individual molecule around 1·04 nm which agrees well with the hexagonal packing arrangement. The surface roughness of the film varies between 2–4 nm. In figure 2b, we show a C_{70} island formed at the surface step with a step height of 0·8 nm which acts as a nucleation site. We see some brighter spots in such islands which are at 1 nm height indicating the growth of a second layer before the completion of the first layer. Such a variation in the heights of features within an island reveals a small variation in the thickness of the film.

We show a lattice-resolved STM image of a C_{70} film deposited on gold/glass in figure 3. The image clearly shows the ellipsoidal nature of the molecule. The line profiles taken across the minor and major axes shown in figure 3 give the size of a typical molecule to be 1·07 nm × 1·17 nm with an aspect ratio of more than 1 as expected. We will be discussing the lattice structure as well as high-resolution STM images of these films later in the discussion.

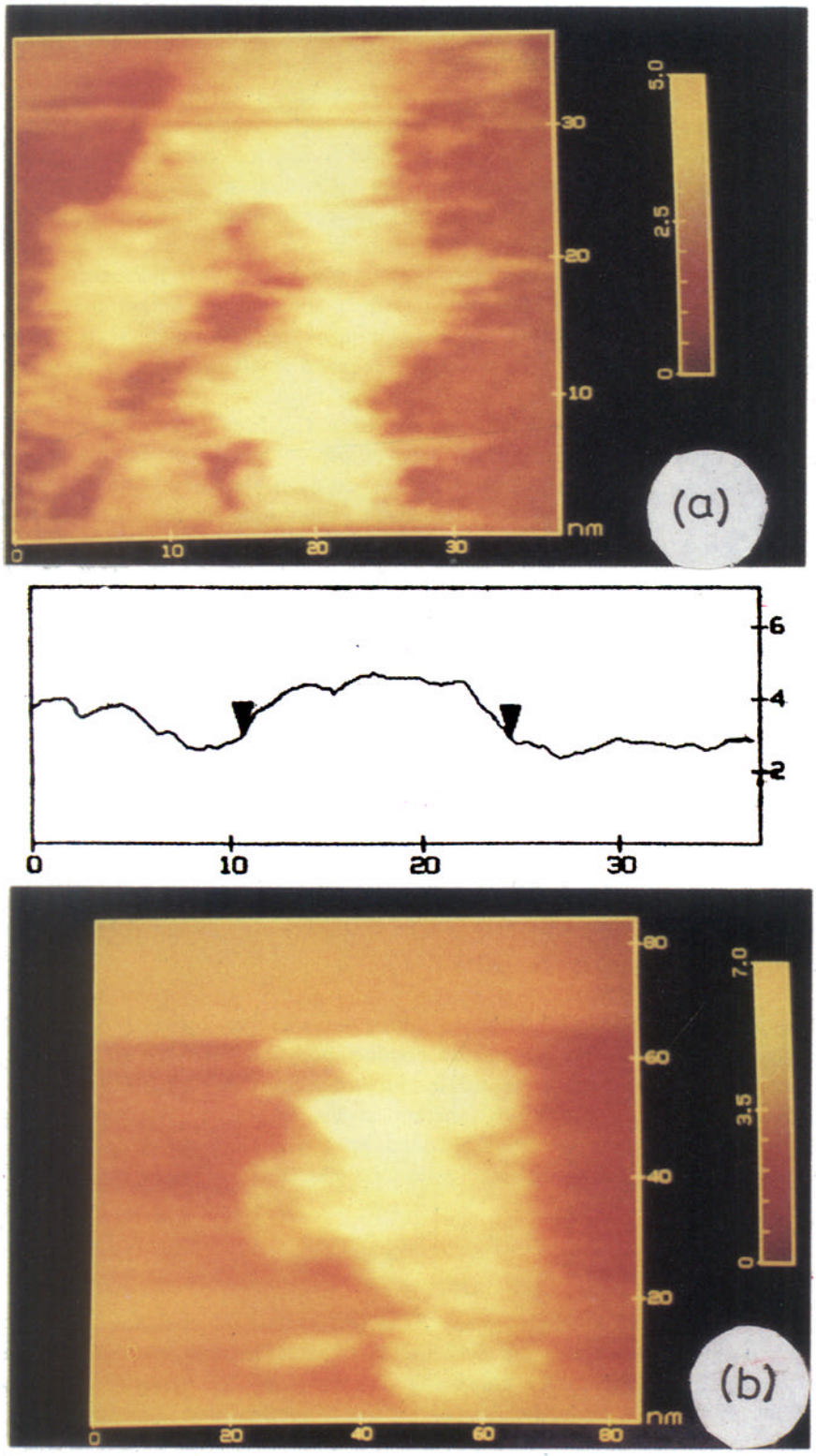
Scanning tunneling spectroscopic (STS) measurements were performed at different points on the C_{70} film deposited on HOPG by opening the feedback loop and monitoring the current [and normalized conductance $(\mathrm{d}\ln I/\mathrm{d}\ln V)$] while sweeping the bias voltage over a range. With the active feedback, as the bias voltage is ramped over a range, at fixed tunneling current, the tip-sample distance constantly adjusts itself. With the increase in voltage, the lateral resolution degrades whereas with the decreasing voltage the conductance $(\mathrm{d}I/\mathrm{d}V)$ diverges to infinity in the zero bias region. This problem was overcome by opening the feedback loop and measuring the I–V curves at a constant tip-sample distance. Adverse effects of the tip-sample transmission factor (which distort the features in the spectra) were eliminated by plotting the normalized conductance,

$$(\mathrm{d}\ln I/\mathrm{d}\ln V) = [(\mathrm{d}I/\mathrm{d}V)/(I/V)],$$

against the bias voltage, V. This was done through the software options which allow one to compute the normalized conductance $(\mathrm{d}\ln I/\mathrm{d}\ln V)$ as a function of the bias voltage. However, there are certain instabilities due to the tip encountered in STS measurements which are inherent to the technique. We report a typical normalized conductance spectrum obtained on a C_{70} film, the features in which were quite reproducible at different points on the film.

3. Results and discussion

Figure 4 shows a real-time grey scale STM image in 3-dimensional perspective at 60° pitch over a scan area of 8·47 nm × 8·47 nm. The image clearly reveals a distorted hexagonal 2D lattice consisting of ellipsoidal C_{70} molecules. The centre to centre spacing is typically 1·3 nm in one direction and 1·67 nm in another direction as can be seen from the line profiles in figures 4a and b respectively.


5.0
2.5
0
30
20
10
nm
0
10
20
30
(a)
6
4
2
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7.0
3.5
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80
60
40
20
nm
0
20
40
60
80
(b)

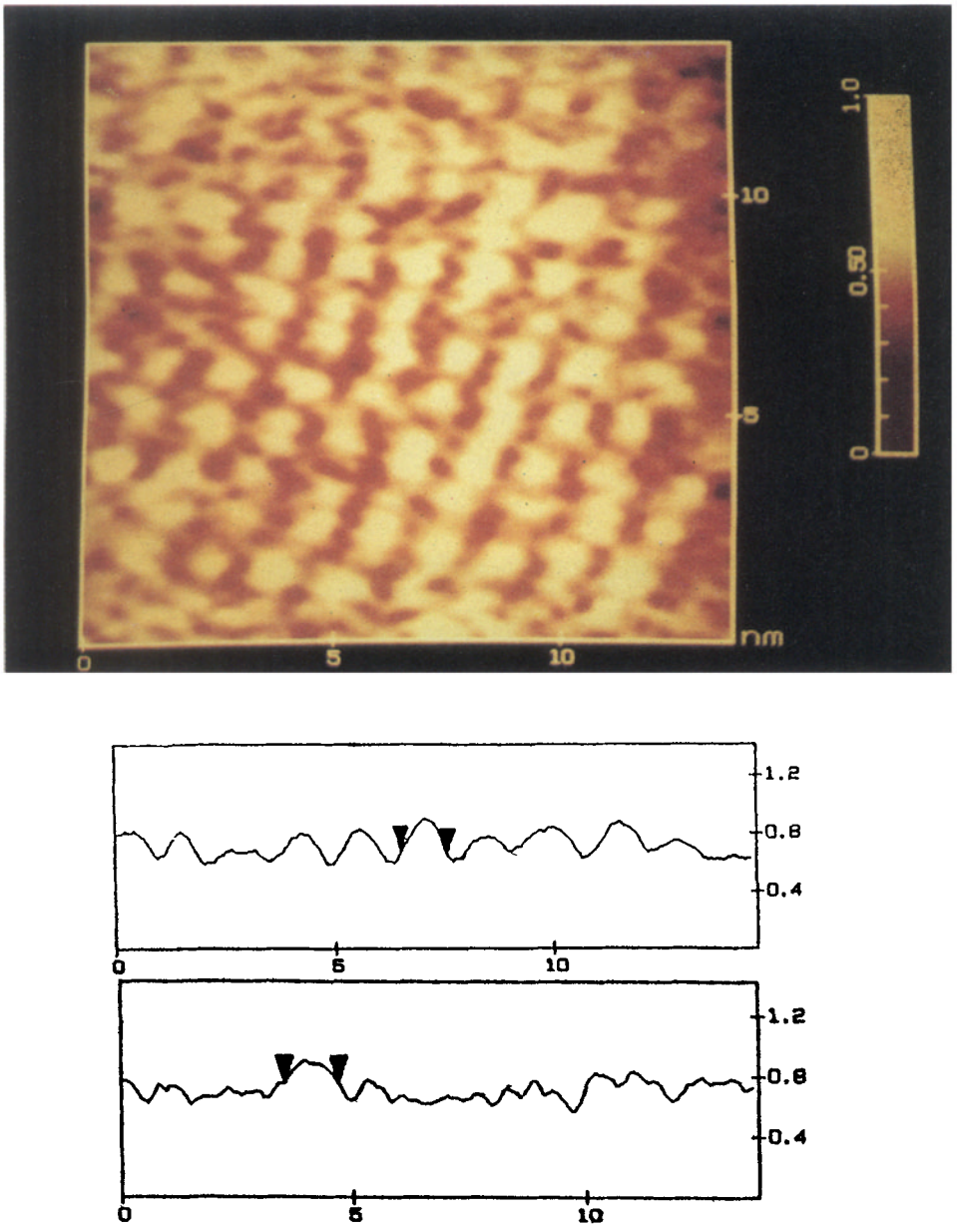
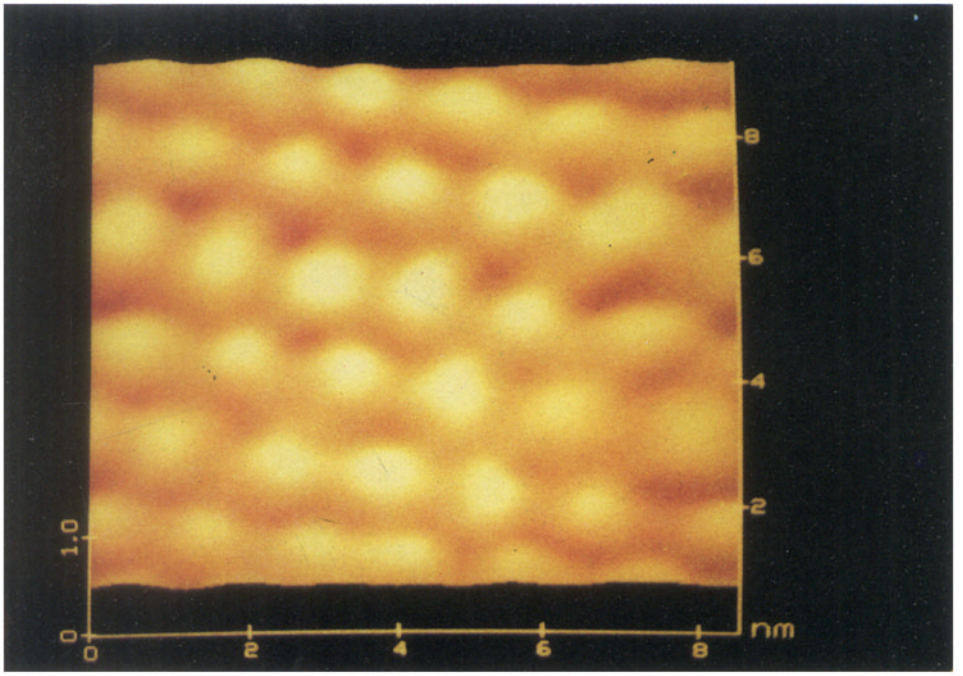


Figure 3. Top-view image of C_{70} film deposited on gold/glass substrate. Ellipsoidal molecules can be seen. The line profiles along minor and major axes of a typical ellipsoidal C_{70} molecule are given below the image. The horizontal distances between the arrow are 1·07 nm and 1·17 nm respectively along the two axes.

Figure 2. (a) 36·93 nm × 36·93 nm STM image of C_{70} coverage on HOPG substrate. The line profile across a microcrystallite is also shown. The horizontal distance between the arrows is 13·91 nm, which is the typical size of microcrystallite and (b) STM image of C_{70} island formed at a step on HOPG surface.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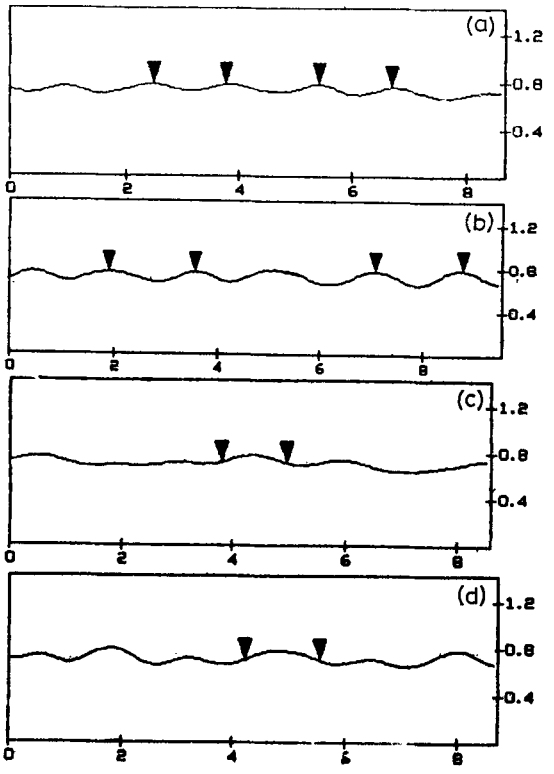
(a)
1.2
0.8
0.4
0
2
4
6
8
(b)
1.2
0.8
0.4
0
2
4
6
8
(c)
1.2
0.8
0.4
0
2
4
6
8
(d)
1.2
0.8
0.4
0
2
4
6
8

These spacings are only slightly different from the expected values of 1·01 nm and 1·68 nm along the two directions. This can arise from orientational differences of individual molecules or due to C_{70}–HOPG interaction (Liu *et al* 1992). The line profiles along the minor and major axis of a typical ellipsoidal unit in the image shown in figures 4c and d however indicate the aspect ratio to be $1{\cdot}3 + 1{\cdot}15 \approx 1{\cdot}1$ exactly confirming the D_{5h} structure of the C_{70} molecule when viewed perpendicular to its five-fold symmetry axis.

Orientational disorder of C_{70} has been reported by several workers (see for example Ramasesha *et al* 1994, Rao and Seshadri 1994). The room-temperature phase of C_{70} is orientationally disordered as confirmed by solid state NMR measurements which show the molecules to be rotating anisotropically near room temperature (Fischer and Heiney 1993). Because the C_{70} molecule has the shape of rugby-ball, we can readily see disorder in terms of the orientation of the major axis. STM images of C_{70} films/HOPG show the presence of such orientational disorder. In figure 5, we show a zoomed lattice image of a C_{70} film showing the ellipsoidal molecules with an aspect ratio of 1·1. This image vividly demonstrates the presence of orientational disorder, i.e. differences in the orientation of individual molecules with respect to one another. This can be clearly seen from the drawing corresponding to the image given in figure 5. We also see the standing-up configuration (i.e. the long axis perpendicular to interface) of the C_{70} molecules. This configuration of C_{70} is expected for an hcp arrangement. In figure 6 we show a lattice-resolved image from a different area of the C_{70} film. The ellipsoidal molecules are orientationally different from one another as can be seen distinctly in the marked portion in the lower half of the image.

The STM image of the C_{70} film in figure 7 shows the presence of grain-boundary between two different regions of the C_{70} lattice. The arrow drawn through the image indicates the location of the grain boundary. High-resolution lattice images of C_{70} films generally showed a disordered hcp lattice arrangement free from any other apparent defects. However, on scanning different areas extensively on the atomic scale, the sample showed some regions containing certain lattice defects. In figure 8, we show an area with a defect which is also given in the drawing below (figure 8b). The defect somewhat resembles an edge dislocation in some way. The height difference between the two incomplete rows characterizing the defect is only around 0·2 nm and is not sufficient to attribute it to the growth of one row of molecules over the other.

We have obtained high-resolution images of individual C_{70} molecules from the films deposited on gold/glass substrates, by changing the imaging conditions appropriately. The internal structure of C_{70} cage can be realized only when the rotational motion of the molecule is frozen. This has been possible probably because of the change in the electronic structure of the films caused by the interaction with the gold film and the consequent pinning of the molecule by the electric field

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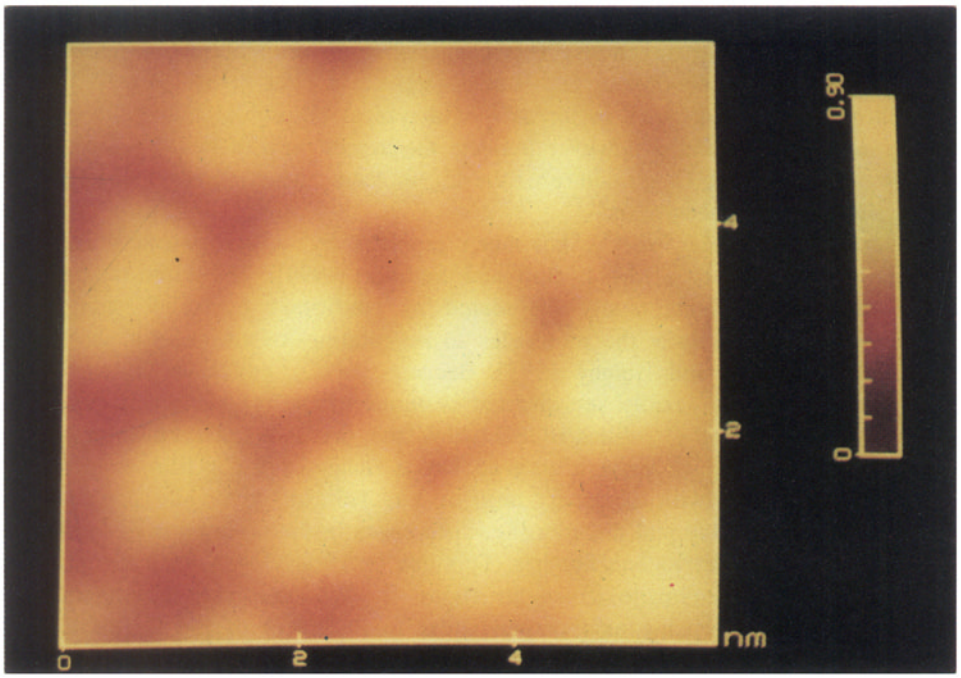
Figure 4. Typical lattice-resolved STM image of C_{70} film deposited on HOPG in 3D perspective at 60° pitch (scan size 8·47 nm × 8·47 nm). The line profiles along two directions of the lattice give the centre to centre spacing between the molecules as 1·30 nm in (a) and 1·67 nm in (b) respectively. The line profiles along the (c) minor and (d) major axes of a typical C_{70} molecule give the size of molecule to be 1·15 nm × 1·30 nm with an aspect ratio of ~ 1·1.



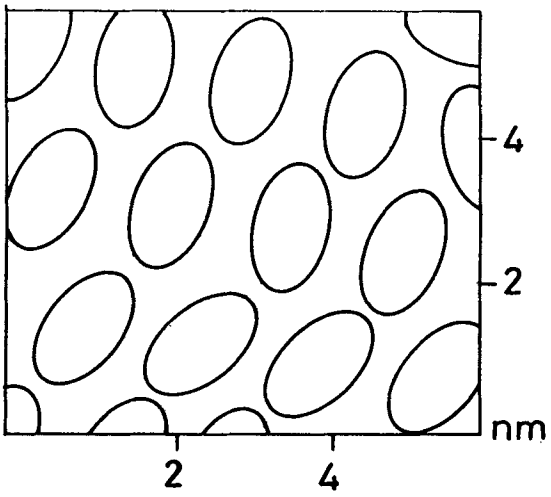


Figure 5. Zoomed lattice image of a C_{70} film on HOPG. Scan size (5·79 nm × 5·79 nm). Drawing corresponding to the STM image shows the orientational disorder.

between the STM tip and the surface of the film. In figure 9, we show a high resolution image of an individual C_{70} molecule. The arrangement of hexagons (H) and pentagons (P) has been sketched in the drawing given below the image in figure 9. The bond lengths are in the range of 0·14 nm. The size and shape of molecule are also clearly revealed. A pentagon is attached to hexagons as expected

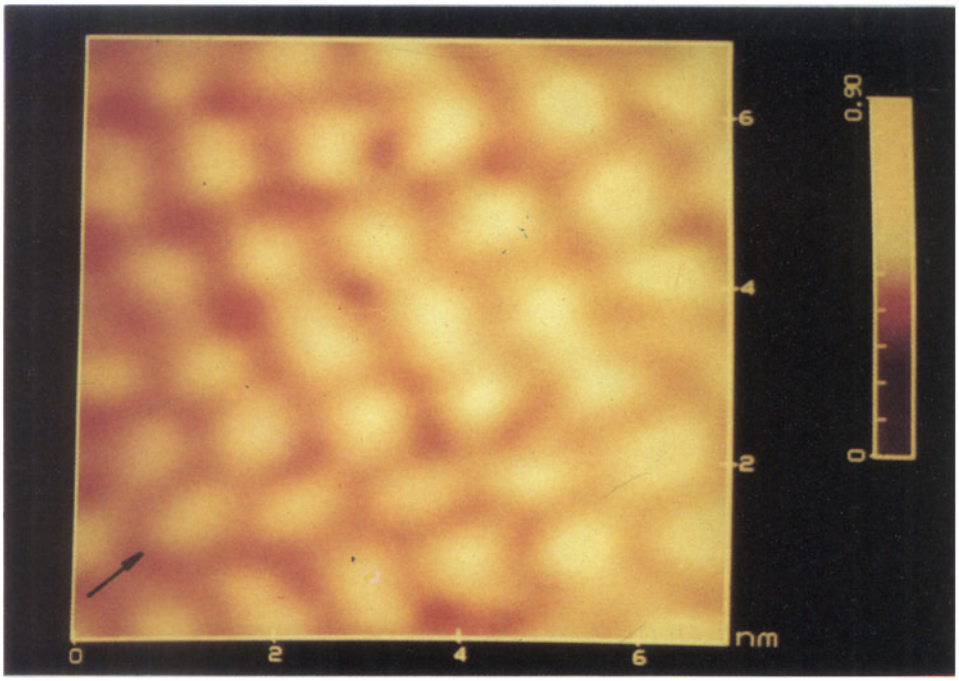


Figure 6. STM image (6·89 nm × 6·89 nm) of C_{70} lattice of HOPG from the area marked by an arrow shows orientational disorder.

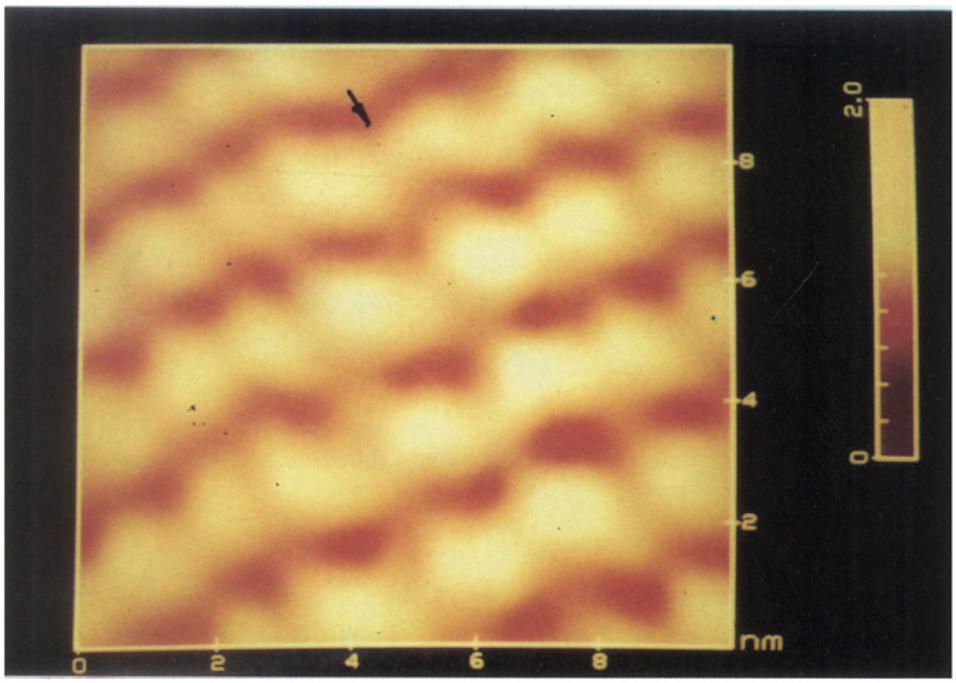
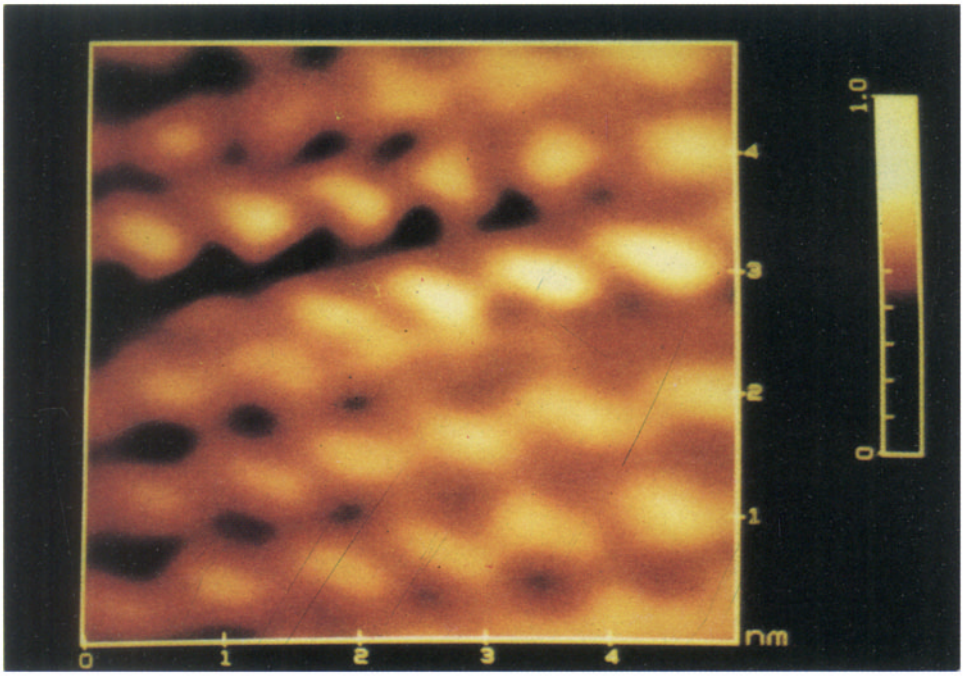


Figure 7. STM image of C_{70} film/HOPG showing a grain-boundary (GB) in the marked portion of the image.



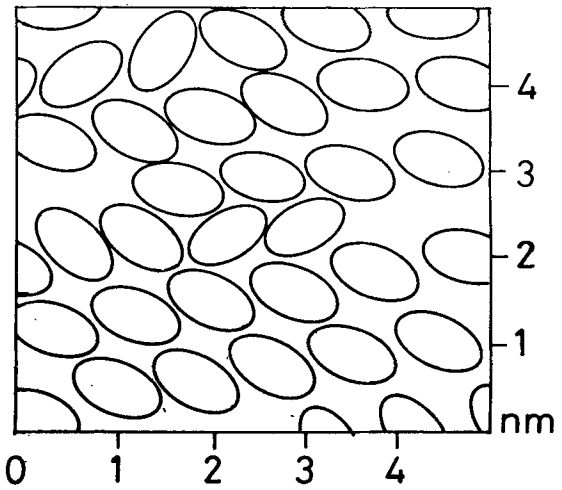
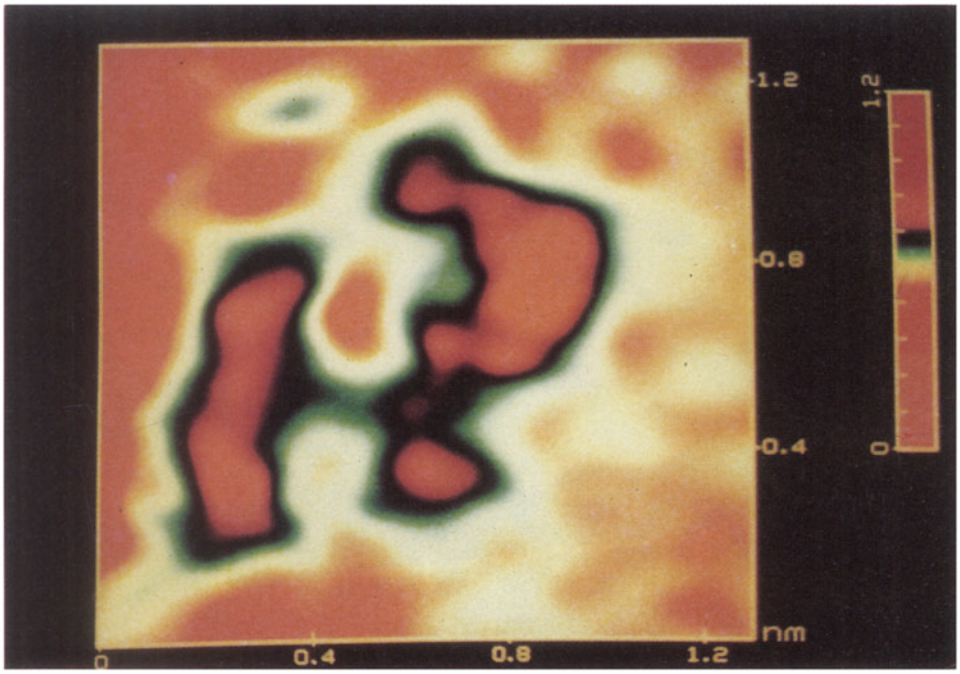


Figure 8. STM (top-view) image of a C_{70} film on HOPG showing the presence of defect. The drawing corresponding to the image is also shown.

from the structure of the molecule.

We have also studied the STM images of films comprising solid solutions of C_{70} and C_{60}. In figure 10, we show a typical STM surface plot of a solid solution. The image shows the presence of the smaller C_{60} molecules along with the larger C_{70} molecules. The distance between two C_{60} molecules is 1·47 nm, while the distance between two C_{70} (in the absence of C_{60} in the vicinity) is 1·19 nm. The



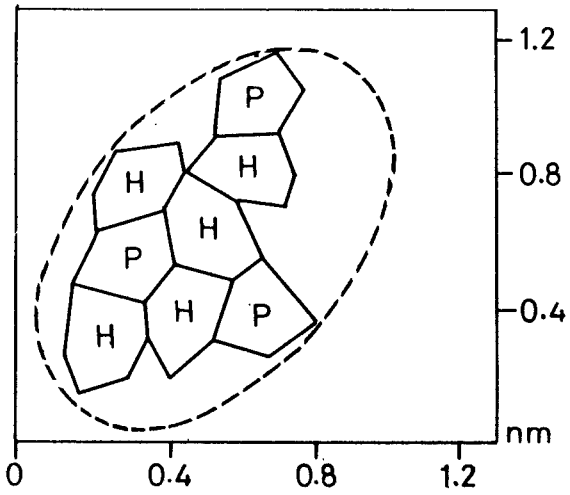


Figure 9. Typical high-resolution image of individual C_{70} molecule on gold/glass substrate (scan size $1{\cdot}25 \times 1{\cdot}25$ nm^2) showing the internal cage structure. The drawing corresponding to the image is shown below depicting the characteristic arrangement of hexagons (H) and pentagons (P).

C_{70}–C_{70} distance in the region where C_{60} is present is around 1·8 nm, the C_{60}–C_{70} distance also being ~ 1·8 nm. These results indicate that addition of C_{60} to C_{70} generates a strain field in the C_{70} lattice causing the C_{70}–C_{70} distance to increase further.

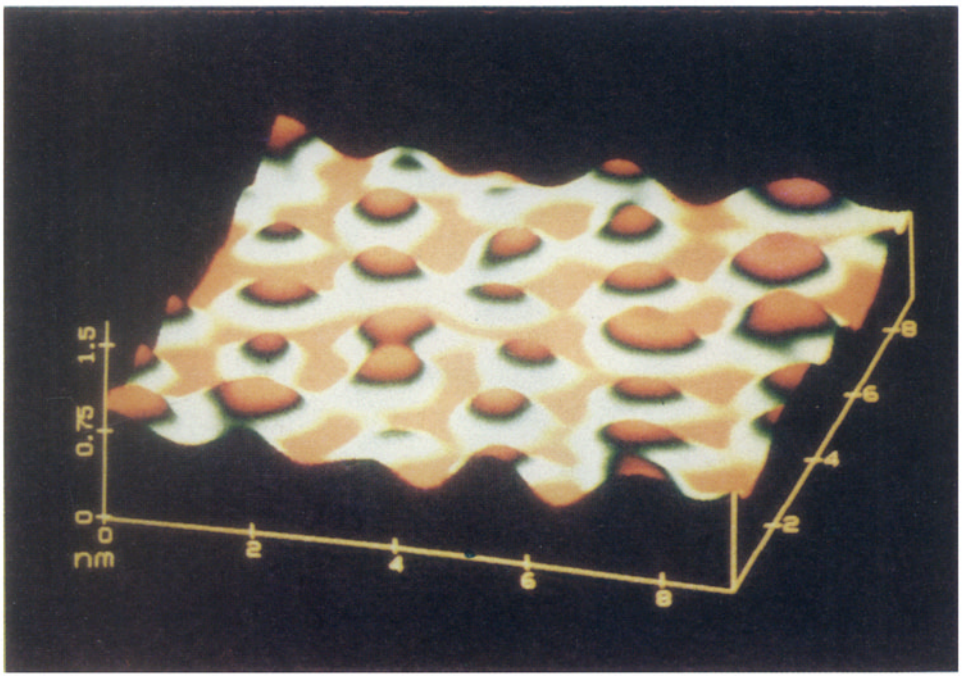


Figure 10. Typical STM surface plot (in 30° pitch) of film of a C_{60}–C_{70} solid solution on HOPG.

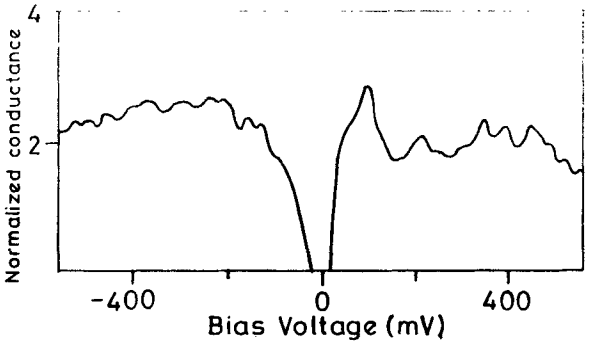


Figure 11. Typical variation of normalized tunneling conductance ($d \ln I / d \ln V$) vs bias voltage (mV) measured for a C_{70} film on HOPG.

Tunneling conductance measurements on C_{70} films reveal the presence of a small energy gap of 0·275 eV in contrast to the energy gap of 1·6 eV for ideal C_{70} samples (see the normalized tunneling conductance curve in figure 11). The decrease in the gap is attributed to the charge transfer between HOPG and the C_{70} film which changes the electronic structure making the film quite conducting. There is indeed considerable evidence to show that C_{60} and C_{70} acquire a negative charge on interaction with the metals (Santra *et al* 1993). This is also in agreement with

the observation that STM images were acquired at a bias voltage well below the HOMO-LUMO gap of 1·6 eV for C_{70}.

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