

the largest outward displacement of atoms in the $1F_{1u}$ motion, resulting in attractive forces along the radial axes. The orbital overlapping partly occurs at contacting molecular faces and hence its contribution to the entire molecular vibration is thought to be small. However, the gradual decrease in the frequency of $1F_{1u}$ mode suggests that the intermolecular attractive force is strengthened through the increase in the π orbital overlapping

as the molecules approach under the application of pressure.

We expect that high-pressure Raman study will provide further insight into the vibrational and bonding properties in solid C_{60} . The pressure behavior of a "squashing" mode, a radial distortion from the spherical shape into an ellipsoid, is particularly interesting in comparison with the softening observed for the $1F_{1u}$ radial mode. A high-pressure Raman measurement is in progress.

Computational Study of the Imaging of a Molecular Crystal with the Atomic Force Microscope

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Constant force mode atomic force microscope images of the $\{100\}$ surface of DL-leucine are calculated. There are two principal cleavage planes at the $\{100\}$ crystal face exposing either methyl or amino groups. Topographs of both planes are calculated but found to be too similar to differentiate between on the basis of images calculated at a single force. This is especially true if the tip is modeled as a cluster of atoms. To distinguish between the two cleavage planes, it is proposed that the variation of a topograph as a function of force should be monitored in different scans of the surface.

Atomic force microscopy (AFM) has the capacity to probe the surface topography of a variety of materials with atomic scale resolution.¹⁻⁵ Unlike scanning tunneling microscopy AFM does not depend on the sample being an electrical conductor and therefore provides an ideal way to image the surfaces of non-conducting molecular crystals. Many studies have focused on characterizing the surfaces of metals or semiconductor crystals. An alternative and potentially important application of AFM is to the characterization of the surfaces of biochemical crystals, with a view to mapping out active sites in proteins. While AFM has been able to resolve the surface structure of crystals with atomic scale resolution, an important issue is the unique identification of individual surface atoms; for example, to use AFM to determine which cleavage plane of a molecular crystal is exposed. This letter reports a numerical simulation of a recent AFM study of the $\{100\}$ surface of a DL-leucine crystal performed by Hansma and co-workers using a shattered diamond tip.¹

The major point of the DL-leucine experiment was to demonstrate the atomic scale resolution possible using AFM even when imaging relatively soft organic materials. The crystal packing normal to the $\{100\}$ plane DL-leucine is shown in Figure 1. This figure reveals that two possible cleavage planes exist, exposing

either methyl or amino groups at the surface. The experiment was interpreted¹ as having imaged the methyl ends of the leucine molecules, although this relied on a qualitative judgement as to how the crystal actually cleaved. Clearly the nonpolar bonding at the methyl cleavage plane is expected to be weaker than the polar bonding across the amino plane. In a shattered sample of the crystal it would therefore be reasonable to expect that the methyl plane would most probably be exposed, although this would depend on the conditions under which the crystal was cleaved. Theoretical modeling has the potential to provide a firmer basis on which to interpret the experimental results. In other situations where competing cleavage planes exist, it might be less clear intuitively at which plane a crystal actually cleaved. Especially if the technique is to develop into an atomic resolution surface analytical tool, it is important to determine the ability of AFM to characterize individual features on the surface. It is therefore of considerable interest to understand to what extent theoretical simulations can be used in conjunction with AFM to identify individual atoms or groups at the surface of a crystal.

The DL-leucine lattice was constructed from crystallographic data⁶ by transforming to orthogonal coordinates and taking a slab normal to the $\{100\}$ plane. (The cell constants of the triclinic $P\bar{1}$ structure of DL-leucine are $a = 14.12 \text{ \AA}$, $b = 5.39 \text{ \AA}$, and $c = 5.19 \text{ \AA}$, and angles $\alpha = 111.1^\circ$, $\beta = 97.00^\circ$, and $\gamma = 86.4^\circ$). In all calculations it was assumed that AFM was being performed in constant-force mode.¹ The forces between the tip and surface were calculated by summing the atom-atom forces between the tip atom(s) and each atom in the lattice using Lennard-Jones potential

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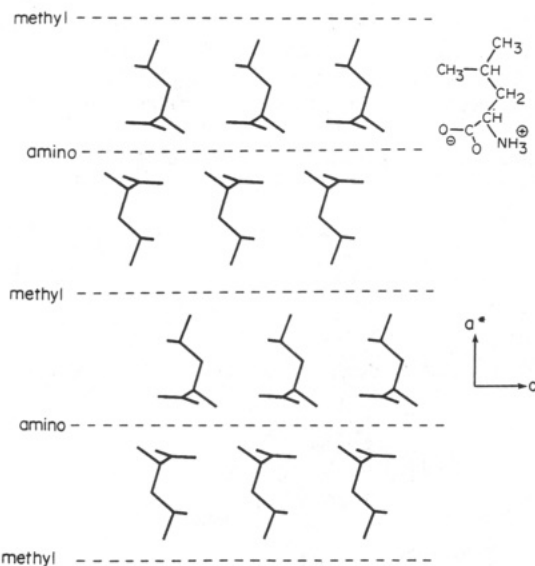


Figure 1. Crystal packing diagram illustrating the methyl and amino cleavage planes normal to the {100} surface of DL-leucine. The orientation of the crystallographic a^* and c axes in the plane of the figure are indicated.

energy functions and potential parameters given by Levitt.⁷ For comparison AFM topographs were also calculated using different potentials.^{8,9} Although the actual forces and tip-surface distances varied depending on the potential used, the results were qualitatively the same and quite insensitive to the particular choice of potential. The tip was first modeled as a single carbon atom and subsequently as a cluster of several carbon atoms. Surface relaxation in the presence of the tip was ignored in the present preliminary study which is the first simulation of AFM of a molecular crystal. Simulations of AFM of graphite and other nonmetallic materials have shown relaxation effects to be minimal¹⁰ although this is clearly not the case for metallic and certain semiconductor surfaces.^{11,12} This is also borne out by the DL-leucine experiment itself in that the cell constants obtained from the data are in good agreement with bulk values irrespective of which cleavage plane was assumed to have been imaged. The large cell constants in a molecular crystal such as DL-leucine suggest that surface relaxation effects might be *relatively* less important than for a metal surface for example. Convergence was obtained with one double layer of molecules and the unit cell enmeshed in a lattice with three rows of leucine molecules on each side (see Figure 1).⁶

Computed topographs for the methyl and amino cleavage planes using a single-atom tip are shown in Figure 2. Comparison with experimental images^{1,2} indicates that the amino image (Figure 2a) resembles the experimental results more closely than does the image of the methyl cleavage plane (Figure 2b). This conclusion ignores, however, a number of factors including multiple tip effects and possible surface relaxation. These effects are expected to reduce considerably the clear differentiation between the amino and methyl images apparent in Figure 2. Upon increasing the force, the image of the amino cleavage plane, shown in Figure 2c, reveals a pronounced asymmetry due to the carboxylic oxygen atoms adjacent and below the amino groups. By contrast the image of the methyl plane (not shown) was essentially unchanged from Figure 2b. The strong distance dependence of the repulsive

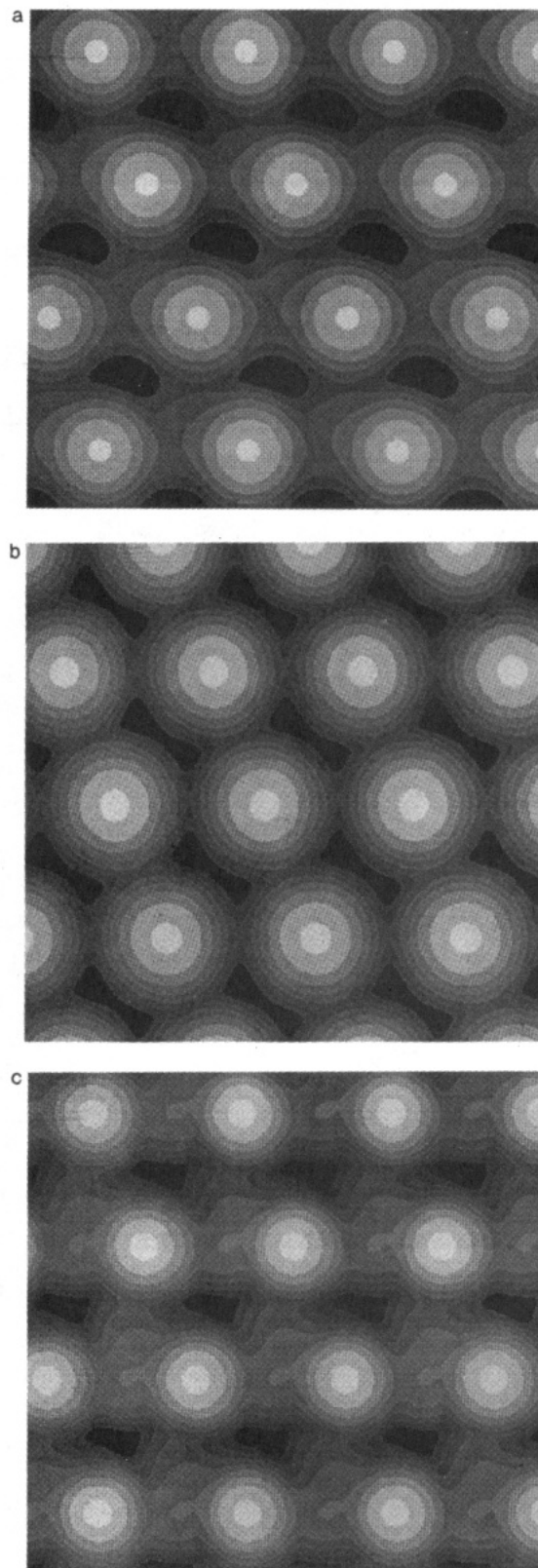


Figure 2. Calculated topographs of the {100} surface of a DL-leucine crystal using a single atom carbon tip: (a) amino cleavage plane; (b) methyl cleavage plane. In both cases the force, $F = 6 \times 10^{-12}$ N. In (c) $F = 6 \times 10^{-9}$ N, and the image is of the amino cleavage plane. At this force the methyl image remains essentially unchanged. The gray scale, showing the height of the tip normal to the surface goes from black (minimum) to white (maximum). The dimension of each image is $14.5 \text{ \AA} \times 14.5 \text{ \AA}$.

forces between tip and surface suggests that it might be possible to distinguish between competing cleavage planes experimentally by collecting data at several different forces, thus probing the force profile at the surface. Use of AFM in this kind of "spectroscopic"

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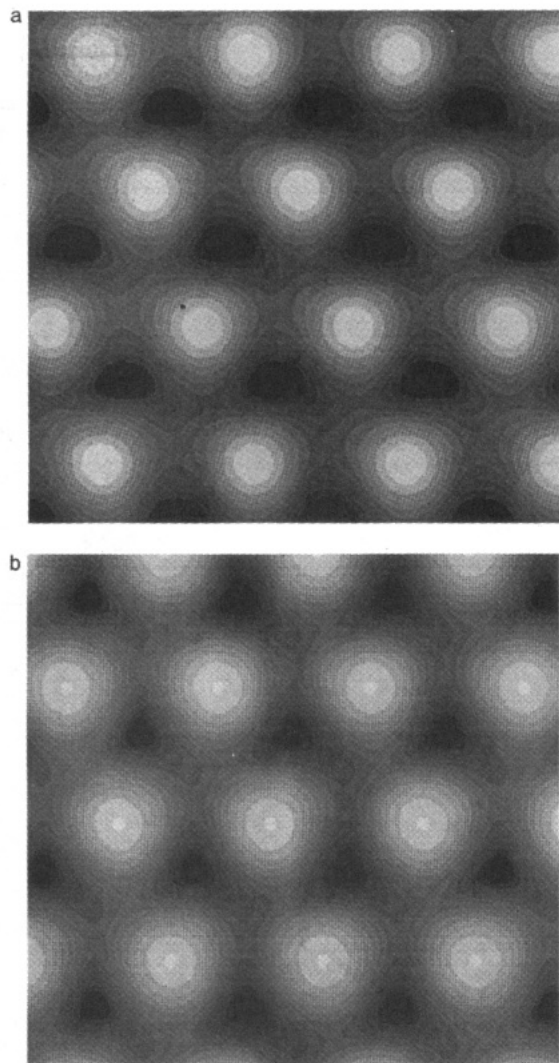


Figure 3. Calculated topographs of the {100} surface of a DL-leucine crystal using a tetraatomic tetrahedral atom carbon tip with the apex of the tetrahedron toward the surface: (a) amino cleavage plane; (b) methyl cleavage plane. In both cases the force, $F = 6 \times 10^{-12}$ N. The dimensions and the gray scale are as in Figure 2.

mode is encouraged to provide a practical way of pinning down the precise atomic structure of the surface, particularly if used in conjunction with bulk crystallographic data.

As noted, it is important to determine how multiple atom tips affect the images. In particular, it is necessary to understand if multiple or asymmetric tips can wash out or mask the asymmetry observed in the amino images obtained using a single atom tip. To study this, multiple atom tips were used containing two, three, and four (tetrahedrally arranged) carbon atoms with the C-C bond distances appropriate to diamond. The effect of multiple atom tips depends on the relative size of the cell constants of the crystal and the interatom spacing in the tip and its projection onto the surface. This conclusion is consistent with a theoretical study of AFM imaging of graphite in which the projection of the interatom tip distance was commensurate with the lattice spacing.¹⁰ In this case multiple tips led to *apparent* corrugation of the surface in the computed images.

A large number of simulations of the DL-leucine experiment were carried out using multiple atom tips in which the vertical and lateral orientation of each tip were varied with respect to the surface. The results of these studies gave rise to a greater or lesser degree to simple distortions (i.e., stretched or compressed versions) of Figure 2. Although most reduced the clear distinction between the amino and methyl images shown in Figure 2, in no case did the tip introduce asymmetries on a length scale comparable to the cell constants. Most significantly, the asymmetry between

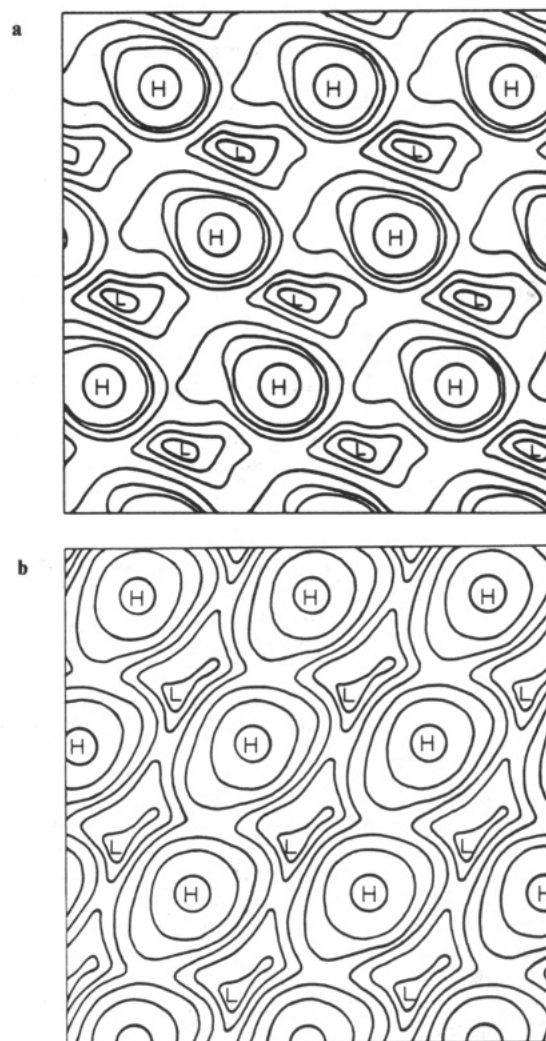


Figure 4. Contour plots of tip height at a constant force, $F = 6 \times 10^{-9}$ N using a two-atom tip in which one tip atom was $0.5 \text{ \AA}$ farther from the surface than the other. The dimensions are as in Figure 2 with the contours equally spaced: (a) amino cleavage plane, $L = 1.46 \text{ \AA}$ and $H = 2.76 \text{ \AA}$; (b) methyl cleavage plane, $L = 1.20 \text{ \AA}$ and $H = 2.70 \text{ \AA}$.

the methyl and amino images due to the underlying carboxyl groups could be observed with any reasonable tip geometry by varying the force applied. Figure 3 compares amino and methyl images calculated using a tetraatomic tip. To allow more detailed comparison, contour maps of both the amino and methyl cleavage planes are presented in Figure 4 for a typical example using an asymmetric two atom tip. The spacing between the primary and secondary maxima in Figure 2c is larger than the spacing between the atoms of the tip, and so the two-atom tip does not wash out the asymmetry between the amino and methyl images. The projection of the distance between any two tip atoms onto the surface is significantly shorter than the crystal cell constants, and therefore multiple atom tip effects are expected to be readily distinguishable from real structural details of the surface. Also the response of atoms lying below the surface plane to changes in force is different from those at the surface because of the different distances involved, e.g., in some images the subsurface atoms are barely visible. This provides a further way to characterize the surface and near-surface structure.

The relatively large cell constants in a typical molecular crystal compared to those of the tip mean that AFM imaging of molecular crystals is likely to be less plagued by tip-induced artifacts than imaging metallic or semimetallic surfaces. Surface reconstruction in the presence of the tip is also expected to be less important for molecular crystals, although further study is required in this area. Particularly will this be necessary if AFM is to be extended to the study of the surfaces of biochemical crystals such as proteins.

From a practical point of view, the present study suggests that monitoring the change in an image as the force is varied will enhance the ability of AFM to characterize surfaces of molecular crystals. Combined with bulk crystallographic data and numerical simulations AFM has the capacity to become an important surface

crystallographic tool.

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Electrochemical Preparation of Ultrathin Polypyrrole Film at Microarray Electrodes

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Electrosynthesized polypyrrole grows effectively at a hydrophobic substrate. Hydrophobic pretreatment of interdigitated microarray electrodes with silanization reagents prompts the lateral growth of polypyrrole film, resulting in the interconnection of arrays with a thin, uniform film. On the basis of this phenomenon, the micropatterning with polypyrrole can successfully be carried out by electropolymerization at a substrate with a silanized pattern.

Introduction

Electrosynthesized conducting polymers such as polypyrrole and polyaniline have been studied extensively because of the fundamental interests and the potentiality in practical applications.¹ The conductivity characteristics of electrosynthesized conducting polymers have recently been investigated by in situ measurements using microarray electrodes coated with the polymers.²⁻⁵ Such array electrodes also serve as electrochemical devices responsive to chemicals influencing the polymer conductivities.^{6,7} We recently reported the characterization of the copolymer of pyrrole and *N*-methylpyrrole by in situ conductivity measurements⁸ and the fabrication of an enzyme-based switching device⁹ showing the on → off response upon addition of NADH. Through these researches, we found that formation of thin polymer films at the arrays is essential to improve the sensitivities and reproducibilities of the devices. The thin film can be formed by promoting the lateral growth of the polymer along to the substrate upon polymerization. So far, there are a few report¹⁰⁻¹² on the control of growing direction of electrosynthesized polymers.

In this paper, we report the promotion of the lateral growth of polypyrrole by hydrophobic pretreatment of the substrate. The pretreatment of the glass area of the microarray electrodes is effective for the interconnection of the arrays with thin polymers. Since the polymerization selectively proceeds on the hydrophobically pretreated area, the patterned pretreatment results in a micropatterning of a glass substrate with polypyrrole.

Thin Polypyrrole Film Connecting the Array Electrodes

The microarray electrode used in this study was interdigitated type with two sets of Pt arrays separated by 10 μm from the adjacent elements (see Figure 1). The array electrode was fabricated on a glass substrate by photolithography. The hydrophobic pretreatment of the microelectrode was carried out by silanization¹³ in a 20 mM octadecyltriethoxysilane/benzene solution for 12 h, followed by a through rinse with pure benzene and drying. Judging from the wettability of the treated electrode, the silanization proceeds mainly at the glass area. The array electrode was placed at a bottom hole of the electrochemical cell with an O-ring (4-mm diameter); the total electrode area exposed to the solution was ca. $5 \times 10^{-3} \text{ cm}^2$.

The electropolymerization at the hydrophobically pretreated electrode was conducted in an aqueous solution containing 0.1

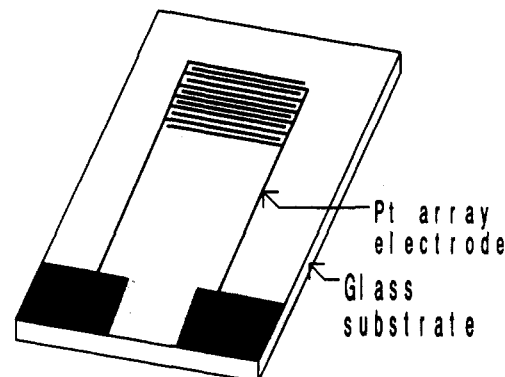


Figure 1. Schematic drawing of microarray electrode used in the present study. Electrode length: 3 mm. Electrode width: 10 μm . Gap width: 10 μm .

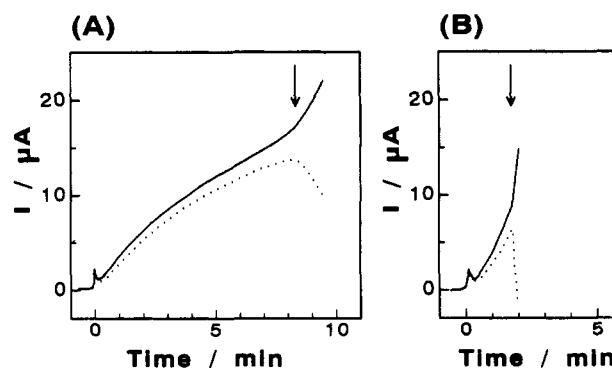


Figure 2. Variation of currents during the controlled potential polymerization at the microarray electrodes in 0.1 M pyrrole/0.1 M KNO_3 aqueous solution. (A) Untreated electrode. (B) Hydrophobically pretreated electrode. (—) Current at the array held at 670 mV vs SCE. (---) Current at the array held at 650 mV vs SCE. Arrow indicates the moment of interconnection between the arrays.

M KNO_3 and 0.1 M pyrrole under potentiostatic conditions. Pyrrole was used immediately after being purified by distillation under a reduced pressure. The polymerization potential for one of the two arrays was set at 650 mV and the other at 670 mV vs SCE by means of a bipotentiostat. Since the potential of the two arrays are slightly different, the ohmic current is superposed

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