

The position of Loki-B in March is constrained in one dimension by its occultation egress time: the constraint in the other dimension is based on its position in the images relative to Kanehekili and the assumption that Kanehekili was fixed. The resulting error box includes Loki Patera, a prominent dark lake-like feature seen by Voyager, lending some support to this reasoning.

A bright hotspot, presumably Loki-A, was also seen in speckle observations by Howell (personal communication), polarization measurements made by some of us in November and December (Goguen and Sinton), and in eclipse observations on 8 November 1989 (Spencer and Sinton). If Loki-A was actually in the same location as Loki-B, at or near Loki Patera, its 3.8- μm flux dropped by a factor of 10 between December 1989 and March 1990. But if our tentative position for Loki-A is correct, it faded below detectability by March 1990. Our tentative location places it close to Amaterasu Patera, identified as a hotspot by Voyager in 1979⁴. In December it may have masked the much fainter lower-latitude emission from Loki-B. Loki-A's 3.8- μm December flux is comparable with previous observations of Loki at its brightest⁵. A similar dramatic fading of a hotspot in the Loki region occurred between December 1985 and September 1986¹⁰.

In contrast, Kanehekili's 3.8- μm flux was virtually the same in December and March, indicating a different type of volcanic activity. The December error box, but not the position assuming no motion between December and March, includes a conspicuous unnamed dark rectangular area of flows imaged (but not scanned in the infrared) by Voyager.

The third, very faint, hotspot seen in the March occultation egress is farther west, in a region seen only at low resolution by Voyager (Fig. 3). Because its position is only constrained in one dimension it is not yet possible to correlate it with any specific feature seen by Voyager. Its error 'box' just excludes the location of the short-lived source Poliahu seen on 10 July 1985^{11,12}.

The 24 December 1989 temperature of Loki-A is constrained to be ≥ 370 K by its 3.8- μm flux and the fact that its radius is ≤ 120 km, if circular. Because all occultation observations are at 3.8 μm , the only direct temperature measurements come from post-occultation images taken in March in which Loki and Kanehekili are resolved at both 3.8 μm (Fig. 1d) and 4.8 μm . Colour temperatures (Table 1) are within the normal range for Io hotspots⁵, and Kanehekili is probably somewhat hotter than Loki-B. The 2.2- μm eclipse images taken in March do not resolve individual hotspots but indicate small areas with temperatures over 600 K somewhere on the disk, as did disk-integrated eclipse measurements at this wavelength in 1979²¹. □

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Imaging C₆₀ clusters on a surface using a scanning tunnelling microscope

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RECENT developments in the synthesis of macroscopic amounts of the C₆₀ and C₇₀ carbon clusters¹⁻³ have made possible spectroscopic^{1,2,4-7} studies of these species. Infrared^{1,2} and vibrational Raman⁴ spectra strongly support the proposed 'soccer ball' structure for the C₆₀ cluster⁸, and NMR spectroscopy directly confirms its icosahedral symmetry^{5,6}. Here we present images of C₆₀ clusters obtained with the scanning tunnelling microscope. These species are roughly spherical and form mobile hexagonal arrays on a Au(111) surface with an intercluster spacing of 11.0 Å. Brighter features evident in the arrays are tentatively identified as C₇₀ clusters.

We prepared samples of C₆₀ with some C₇₀ by resistively heating graphite in 100 torr of helium and subliming these clusters out of the resulting soot onto a gold foil. Mass spectrometry, vibrational Raman and NMR spectroscopy indicate that this method produces clean mixtures of C₆₀ and C₇₀ clusters^{4,5}. The C₇₀ NMR spectrum had five lines with intensity ratios 1:2:1:2:1 and chemical shifts 130.8, 145.3, 147.3, 148.1 and 150.6 p.p.m. (internally referenced to the C1 resonance of fully deuterated toluene at 137.5 p.p.m.), in agreement with measurements of Taylor *et al.*⁶. This five-line spectrum supports a proposed elongated 'rugby ball' shape for C₇₀ (ref. 9). The scanning tunnelling microscopy (STM) measurements were made in a ultra-high-vacuum system which has been described previously¹⁰. The gold foil with the fullerene deposit was transferred into this system through an airlock and left for several hours. A gold(111) single-crystal face was prepared by cycles of sputtering and annealing at 600 °C, as in previous studies¹¹⁻¹³. The clusters were transferred onto the crystal by placing the fullerene-coated foil 3 cm away and flashing it to 800 °C. The coated crystal had roughly equal Auger intensities for the 272-eV carbon peak and the 255-eV Au peak, indicating submonolayer fullerene coverage.

The crystal was then transferred (under ultra-high-vacuum conditions) to the STM chamber and slow-scan (1 line per second) images were recorded at a tunnel current of 0.3 nA. Figure 1 shows a series of images recorded a few minutes apart at a tip bias of -0.1 V. In Fig. 1a the slow upward scan sweeps the tip across an ordered array of numerous similar dots which we believe are C₆₀ ('fullerene') molecules. As the tip moves into the upper region of the frame, the surface steps down and the image becomes unstable. Some of the clusters appear distinctly brighter. In Fig. 1b, the initial tip position was translated away from this unstable region, but now instability and a large asperity appear in the right portion of the frame. A triad of brighter dots in the centre of this frame serves as a landmark. Figure 1c shows that the instabilities reappear if we translate back toward the top of the image. In Fig. 1d instrumental drift has subsided and the hexagonal character of the cluster arrays is apparent. In these arrays we find an intercluster spacing of 11.0 ± 0.5 Å (calibrated using the Au(111) atomic spacing¹¹), in reasonable agreement with an estimate obtained by adding the 7.1-Å diameter calculated for fullerene^{14,15} to the 3.35-Å layer separation of graphite. The straight rows of clusters are nearly parallel to the

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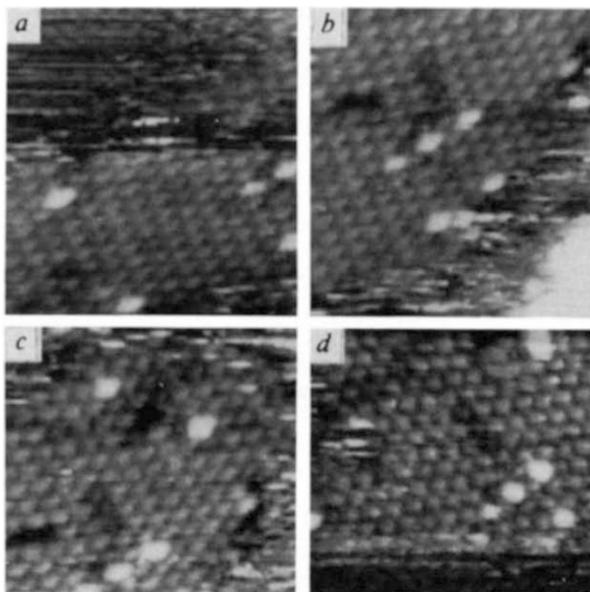


FIG. 1 Sequence of four STM images taken several minutes apart showing ordered arrangements of C_{60} clusters on a Au(111) surface. The brighter dots are believed to be due to C_{70} clusters. Bilinear interpolation has been used in rendering the raw data. The fast scan width (horizontal axis) is $\sim 150 \text{ \AA}$ and the slow scan width varies owing to piezoelectric creep following translation of the tip to a new area.

Au atomic rows, so the array may be commensurate. In Fig. 1d, the vacancy above and to the left of the three bright dots has been filled in, and the bright dot at the lower right has moved.

Our data show ordered arrays of equivalent mobile species on the Au(111) surface with a spacing consistent with fullerene diameter. It is highly unlikely that the chemically unreactive gold surface can dissociate fullerene, especially if the fragments must be equivalent subunits that form an array with the proper spacing. We therefore conclude that these images represent intact fullerene clusters on the gold surface.

The observation of distinctly brighter dots in the ordered arrays (with an apparent height 2 \AA greater than for the C_{60} clusters) demands an explanation. Conceivably the taller features are second-layer fullerene clusters. We would not, however, expect on-top registration for van der Waals' spheres, particularly as the STM tip would probably dislodge molecules in thicker layers^{16,17}. Here the taller features seem to be quite stable, even at the island edges. The most likely explanation is that the brighter dots are C_{70} clusters. The elongation of the C_{70} molecule, together with differences in its electronic structure relative to C_{60} (ref. 18), could easily account for the brighter clusters. Systematic work on samples with varying proportions of C_{60} and C_{70} is required to substantiate this assignment.

It may seem surprising that STM can image such a thick molecule which, by virtue of the 1.5–2.0 eV gap between its highest occupied molecular orbital (HOMO) and lowest unfilled molecular orbital (LUMO)¹⁸, might be thought of as insulating. But the C_{60} ionization potential is in the range 7.5–7.72 eV (ref. 19), so the LUMO is not far from the metal Fermi level (E_F). Furthermore, interactions with the Au surface and neighbouring clusters will shift, split and broaden the cluster orbitals thus giving some density of states at E_F , $\rho(E_F)$ (ref. 16). STM is quite sensitive to $\rho(E_F)$ on the topmost atoms in the cluster, because the tunnel current varies roughly exponentially as $\rho(E_F) 10^{\sqrt{\phi z}/2}$, where ϕ is the tunnel barrier in electron volts and z is the elevation of the top of the cluster in angstroms²⁰. For STM on metal surfaces in vacuum, ϕ is typically 1 eV, so a reduction of $\rho(E_F)$ by a factor of 10 relative to the metal only reduces the apparent height of the molecule by 2 \AA . Experimentally the molecules are easily detected, as the corrugation in close-packed regions is $\sim 1.5 \text{ \AA}$ and the peak-to-vacancy corrugation, or apparent height, is $\sim 4 \text{ \AA}$ for fullerene and 6 \AA for the taller clusters. The same ordered arrays and two heights of peaks are

observed at bias voltages between -1 and 1 V , so orbitals with sharply defined energies do not seem to be involved.

A potential difficulty for STM is the fact that the tip, which moves roughly 10 \AA above the bare metal surface, withdraws only another 4 \AA when traversing the molecules. Given the cluster diameter of $\sim 10 \text{ \AA}$, the tip approaches them very closely and may cause them to move. Indeed, in this system the observed image noise in areas bordering close-packed islands may indicate the presence of STM-induced²¹ or thermal motion of molecules not constrained by their neighbours. This behaviour may be relevant to earlier unsuccessful attempts to image these clusters using STM²².

We have not yet observed internal structure of individual fullerenes. These nearly spherical C_{60} clusters, which interact with the surface and each other only through van der Waals' interactions, may occupy rotational states which might smear out the atomic detail. Reducing the temperature or using a more reactive substrate could hinder such rotations¹⁷. The ease with which images of these carbon clusters can be made suggests that STM studies of these species and their derivatives²³ should be interesting and revealing. \square

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