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Imaging C_{60} clusters on a surface using a scanning tunnelling microscope


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Recent developments in the synthesis of macroscopic amounts of the C_{60} and C_{70} carbon clusters have made possible spectroscopic studies of these species. Infrared and vibrational Raman spectra strongly support the proposed 'soccer ball' structure for the C_{60} clusters, and NMR spectroscopy directly confirms its icosahedral symmetry. Here we present images of C_{60} clusters obtained with the scanning tunnelling microscope. These species are roughly spherical and form mobile hexagonal arrays on an Au(111) surface with an intercluster spacing of 11.0 Å. Brighter features evident in the arrays are tentatively identified as C_{70} clusters.

We prepared samples of C_{60} with some C_{70} 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 C_{60} and C_{70} clusters. The C_{70} 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. This five-line spectrum supports a proposed elongated 'soccer ball' shape for C_{70} (ref. 9). The scanning tunnelling microscopy (STM) measurements were made in a ultra-high-vacuum system which has been described previously. 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 studies. 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 C_{60} ('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 spacing), in reasonable agreement with an estimate obtained by adding the 7.1-Å diameter calculated for fullerene to the 3.35-Å separation of graphite. The straight rows of clusters are nearly parallel to the **Acknowledgements.** The NASA Infrared Telescope Facility is operated by the University of Hawaii under contract with NASA.

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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 Å greater than for the C₆₀ clusters) demands an explanation. Conceivably the taller features seem to be quite stable, even at the island edges. The most likely explanation is that the brighter dots are C₇₀ clusters. The elongation of the C₆₀ molecule, together with differences in its electronic structure relative to C₆₀ (ref. 18), could easily account for the brighter clusters. Systematic work on samples with varying proportions of C₆₀ and C₇₀ 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 unoccupied molecular orbital (LUMO)¹⁹, might be thought of as insulating. But the C₆₀ ionization potential is in the range 7.5–7.72 eV (ref. 19), so the LUMO is not far from the metal Fermi level (Eₚ). Furthermore, interactions with the Au surface and neighboring clusters will shift, split and broaden the cluster orbitals thus giving some density of states at Eₚ, ρ(Eₚ) (ref. 16). STM is quite sensitive to ρ(Eₚ) on the topmost atoms in the cluster, because the tunnel current varies roughly exponentially as ρ(Eₚ) 10⁻⁶Z², where Z is the tunnel barrier in electron volts and the cluster height, is ~2 Å.

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