

Local electronic properties of a molecular monolayer: C₆₀ on Ag(001)

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We have spatially resolved the local electronic structure of a C₆₀ monolayer on Ag(001) using scanning tunneling spectroscopy at $T=7$ K. Our measurements resolve four band states derived from C₆₀ highest occupied molecular orbital, lowest unoccupied molecular orbital (LUMO), and LUMO+1. We observe spatial inhomogeneity in the energy-resolved local density of states, which reflects C₆₀ internal structure. In addition, we are able to resolve the molecular orientation of coexisting bright and dim C₆₀ molecules in the monolayer. This combination of topographic and spectroscopic measurements provides further evidence that the appearance of bright and dim molecules originates from a Ag surface reconstruction.

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Fullerene-based thin films provide a unique scaffold for future technological applications.¹ C₆₀ films, for example, have been shown to superconduct when doped with alkali metals,² and provide a foundation for transistor device functionality.³ In studies of C₆₀/metal interfaces, the C₆₀/Ag(001) monolayer in particular has received significant attention in recent years. This system has been shown to exhibit a strong C₆₀ charge transfer⁴ and a C₆₀-C₆₀ separation even larger than that seen in the alkali-doped fullerene superconductors (where the intermolecular spacing correlates with T_c).^{5,6} Though C₆₀/Ag(001) has not been predicted to superconduct, recent photoemission measurements on this system showed the opening of an energy gap as temperature was lowered below 250 K.⁷ This gap has been speculated to originate from either superconductivity or a Jahn-Teller distortion,⁷ but has yet to be observed using other techniques.

Previous scanning tunneling microscopy (STM) studies of the C₆₀/Ag(001) monolayer have focused on its unusual geometric structure. These studies show that C₆₀ forms a complex overlayer featuring coexisting “bright” and “dim” C₆₀ molecules in a near 2:3 ratio.⁵ The bright and dim molecules organize into three distinct coexisting phases and display a difference in height, which is nearly equal to the Ag(001) lattice-plane spacing.⁵ The origin of the bright and dim molecules is still unclear, but one possible mechanism is an underlying Ag surface reconstruction.⁸ C₆₀-induced surface reconstructions have been observed on several surfaces such as Al(111),⁹ Au(110),¹⁰ Ni(110),¹¹ and Pd(110).¹² Another suggested mechanism involves large variations in electronic structure between monolayer molecules in the absence of a Ag reconstruction.^{5,8,13} Such an effect might be caused by different bonding geometries^{8,14,15} for bright and dim molecules, leading to the apparent height differences observed for C₆₀/Ag(001).

In order to better understand the electronic and geometric structures of C₆₀ monolayers, we have conducted a scanning tunneling spectroscopy study of the C₆₀/Ag(001) monolayer at 7 K. We have performed energy-resolved spatial mapping of the electronic density distribution for monolayer states derived from the HOMO (highest occupied molecular orbital), LUMO (lowest unoccupied molecular orbital), and LUMO+1 of C₆₀. These spectroscopic images show localized structures that reflect the electronic density distribution

of individual C₆₀ molecules. Spectroscopic measurements of the C₆₀ monolayer do not show an energy gap near the Fermi energy E_F as observed in photoemission experiments.⁷ The density of states near E_F is similar to that observed for an isolated C₆₀ monomer,¹⁶ with small differences due to the additional C₆₀-C₆₀ interaction and modified C₆₀-Ag environment. Comparison of the properties of a C₆₀ monolayer and an isolated C₆₀ monomer leads us to conclude that a Ag surface reconstruction is the most probable cause for the appearance of bright and dim molecules in the monolayer.

We performed our measurements using a homebuilt UHV STM, cooled by a liquid-He bath via exchange gas. The single-crystal Ag(001) substrate was cleaned in UHV by repeated cycles of Ar-ion sputtering and annealing. C₆₀ was deposited onto the clean Ag surface using a calibrated thermal boat evaporator. The total deposition was slightly less than a monolayer, which allowed areas of bare Ag surface to be used as a spectroscopic reference. Large, well-ordered C₆₀ domains (containing both bright and dim molecules)^{5,8} were obtained by annealing the sample at ~ 500 °C after deposition. The sample was then transferred in vacuum to the STM and cooled to 7 K. dI/dV spectra were measured through lock-in detection of the ac tunnel current driven by a 450 Hz, 10 mV (rms) signal added to the junction bias under “open-loop” conditions. dI/dV images were acquired both through closed-loop (constant current) scanning and through open-loop ramping to the desired voltage at each data-acquisition point.

Figure 1 shows a typical STM image of a C₆₀ monolayer on Ag(001) at 7 K. As seen in previous studies,⁵ we observe bright and dim molecules with a frequency ratio of 37:63 and apparent heights of 5.6 ± 0.2 and 4.0 ± 0.2 Å, respectively (measured relative to a bare Ag terrace with $V = +2.0$ V, $I = 1$ nA). Unlike previous STM studies, however, we are able to resolve the internal structure and orientations of the C₆₀ molecules in the C₆₀/Ag(001) monolayer. Since the locations of lobes in positive bias images correspond to the locations of pentagons in the C₆₀ cage structure,^{16,17} we observe that bright and dim molecules differ in their predominant orientation. 99% of all bright molecules are oriented with a 5-6 bond facing up, while 84% of all dim molecules are oriented with a 6-6 bond facing up. 16% of dim

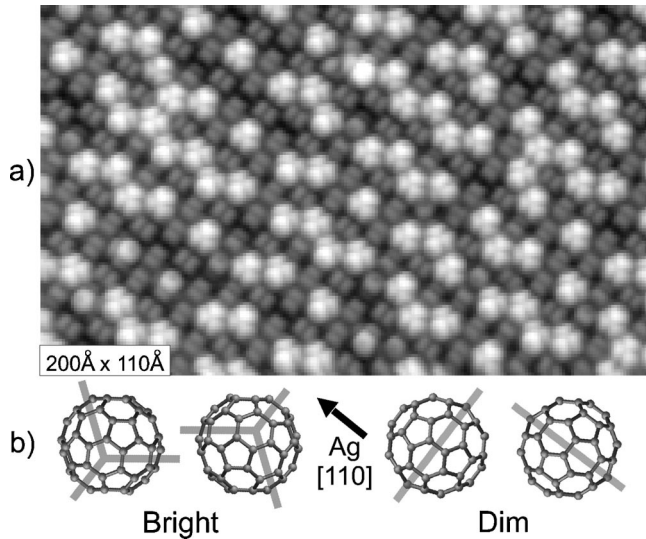


FIG. 1. (a) $200 \times 110 \text{ \AA}$ topograph of a $C_{60}/Ag(001)$ monolayer ($T=7 \text{ K}, V=+2.0 \text{ V}, I=1 \text{ nA}$). (b) Schematic diagram of the most commonly observed orientations for bright and dim C_{60} molecules in the $C_{60}/Ag(001)$ monolayer (nodal lines are highlighted).

molecules are oriented with an apex atom facing up. As schematically shown in Fig. 1(b), the topmost 6-6 and 5-6 bonds for bright and dim molecules, respectively, are always directed along either the $[110]$ or $[\bar{1}\bar{1}0]$ Ag(001) crystallographic directions.

We performed dI/dV spectroscopic measurements on the C_{60} monolayer in order to probe the electronic structure of this molecular film. Figure 2 shows a set of spectra taken at nine different points (as indicated in the inset) on a 5-6 bright molecule (i.e., one with the 5-6 bond facing up). These spectra contain four main features: a shoulder at $-1.8 \pm 0.3 \text{ V}$ and peaks at 0.15 ± 0.03 , 0.55 ± 0.03 , and $1.75 \pm 0.10 \text{ V}$. The

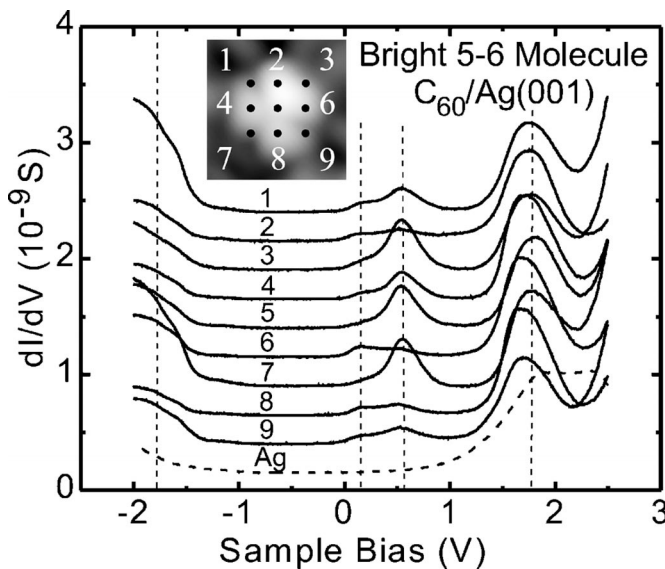


FIG. 2. Spatially dependent dI/dV spectra measured for a single bright 5-6 molecule in a $C_{60}/Ag(001)$ monolayer. Spectra were obtained at the grid points shown in the inset. All spectra, except for the bare Ag spectrum, are shifted for clarity.

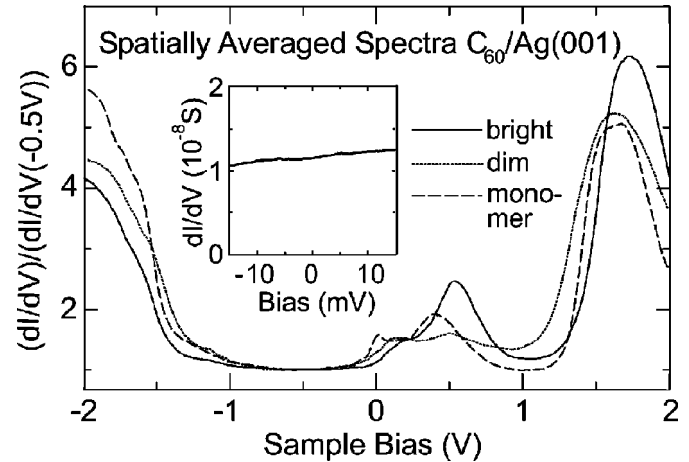


FIG. 3. Spatially averaged spectra for bright and dim C_{60} molecules in the $C_{60}/Ag(100)$ monolayer, as well as for an isolated C_{60} molecule on the Ag(001) surface (all spectra are normalized at $V = -0.5 \text{ V}$). Inset: low bias spectrum of $C_{60}/Ag(001)$ monolayer shows no features near E_F at $T=7 \text{ K}$ (this spectrum was taken over a bright molecule).

relative amplitudes of these features reveal a strong spatial dependence not previously reported in spectroscopic characterizations of C_{60} monolayer systems.^{14,18} All bright 5-6 molecules show nearly identical behavior, independent of their local geometry. Changing the STM tip height from an average junction resistance of $2 \text{ G}\Omega$ to one of $2 \text{ M}\Omega$ had little effect on the observed spectral features other than slightly increasing the relative amplitude of the 0.15 V peak.

The spectroscopic behavior of dim molecules is qualitatively very similar to the bright molecule behavior, as seen in the spatially averaged spectra of Fig. 3. Some differences exist, however, such as a slight shift in peak locations and a broadening of resonance widths. The dim molecule spectrum shows a shoulder at $-1.7 \pm 0.3 \text{ V}$ and peaks at 0.11 ± 0.03 , 0.49 ± 0.03 , and $1.62 \pm 0.10 \text{ V}$. These spectral features are broadened by 20–50% relative to the bright molecule spectrum. In addition, the dim molecule spectrum shows a marked reduction in the 0.5 and 1.6 V peaks, and a slight enhancement of the 0.1 V peak relative to the corresponding bright molecule features.

We performed low bias spectroscopic measurements on the C_{60} monolayer in order to look for signs of a Fermi-level energy gap. A typical result can be seen in the inset of Fig. 3, and shows no sign of a gap opening. Extensive spectroscopic mapping of the C_{60} monolayer showed no significant deviations from this behavior.

In order to probe the spatial dependence of the observed spectral features, we performed energy-resolved dI/dV mapping of the C_{60} monolayer. Figure 4(a) shows a constant current topograph ($+2.0 \text{ V}, 1 \text{ nA}$) of a typical $60 \times 60 \text{ \AA}$ patch of C_{60} monolayer. Figures 4(b)–4(e) show dI/dV maps taken over this same region at energies corresponding to bright molecule resonances. The spatial dependence of the molecular band at 1.65 V [Fig. 4(b)] shows filamentary electronic structure linking the different molecules. As bias voltage is decreased to 0.55 V [Fig. 4(c)], the filamentary density pattern in nearly inverted, and intensity shifts to previously

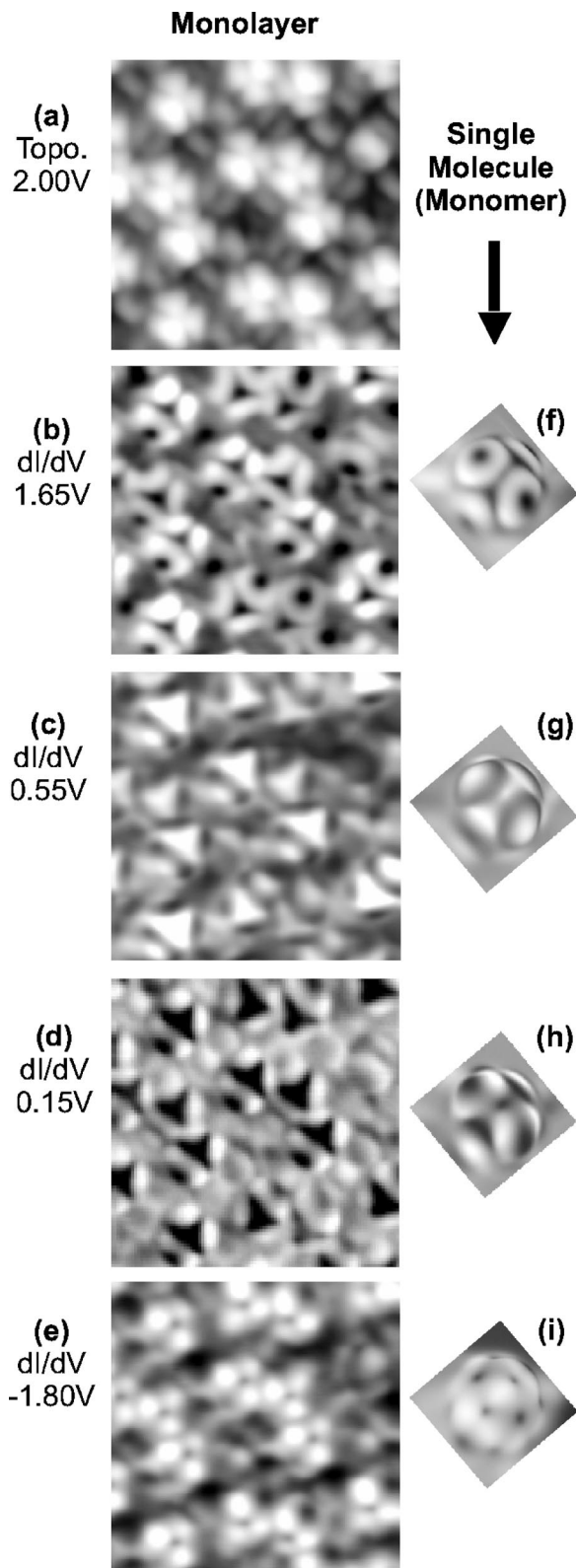


FIG. 4. Left panels show the same $60 \times 60 \text{ \AA}$ region of a $C_{60}/\text{Ag}(001)$ monolayer. (a) Constant current topograph (+2.0 V, 1 nA); (b) dI/dV map at 1.65 V; (c) dI/dV map at 0.55 V; (d) dI/dV map at 0.15 V; (e) dI/dV map at -1.8 V. Right panels show $25 \times 25 \text{ \AA}$ dI/dV maps of an isolated C_{60} monomer on $\text{Ag}(001)$ (from Ref. 16). (f) dI/dV map at 1.55 V; (g) dI/dV map at 0.42 V; (h) dI/dV map at 0.00 V; and (i) dI/dV map at -1.70 V.

unoccupied regions. At 0.15 V [Fig. 4(d)], the electron density is mostly shifted back to the filamentary structures observed at 1.65 V. At -1.80 V [Fig. 4(e)], we see localized charge-density buildup in regions different from those observed in the other spectral maps. dI/dV maps taken at energies corresponding to dim molecule resonances show similar behavior, but with heightened spectral intensity at dim molecule locations.

The electronic structure of the $C_{60}/\text{Ag}(001)$ monolayer is best understood in light of the properties of an individual C_{60} molecule. In the energy range of our experiments, a C_{60} molecule exhibits a fivefold degenerate HOMO and threefold degenerate LUMO and LUMO+1.¹⁹ These states broaden and split when a C_{60} molecule is adsorbed to the $\text{Ag}(001)$ surface. This can be seen in the dashed curve of Fig. 3, which shows a spatially averaged STS spectrum for an isolated C_{60} molecule residing on $\text{Ag}(001)$. This spectrum has all the main features observed in the monolayer spectrum, as seen by the shoulder at -1.7 ± 0.3 V, and peaks at 0.02 ± 0.02 , 0.41 ± 0.03 , and 1.62 ± 0.10 V. These monomer features correspond to the C_{60} HOMO manifold, a split LUMO manifold, and the LUMO+1 manifold, respectively.¹⁶ Comparing the single-molecule spectrum to the monolayer spectra in Fig. 3, we identify the -1.8 V monolayer feature as a HOMO band, the 0.15 and the 0.55 V monolayer resonances as split LUMO bands, and the 1.65 V monolayer resonance as a LUMO+1 band. These spectra show that C_{60} monolayer formation causes the unoccupied monomer states to shift up in energy by ~ 130 mV and broaden by 20–50%. Slight differences between the bright and dim molecular spectra likely arise from small differences in the C_{60} -Ag environment of these species. Overall, the observed electronic structure shows that C_{60} - C_{60} interaction plays only a small role in monolayer behavior compared to the dominant C_{60} -Ag interaction.

This is further seen by comparing dI/dV spectral maps of the $C_{60}/\text{Ag}(001)$ monolayer and an isolated C_{60} monomer. The right column of Fig. 4 shows dI/dV maps obtained at resonance energies for an isolated monomer oriented with a 6-6 bond facing up (taken from Ref. 16). Although the monomer has a slightly rotated orientation relative to bright monolayer molecules, it is clear from the figure that the monolayer and monomer states have similar electronic density distributions. The filamentary monolayer structures at 1.65 and 0.15 V thus reflect the locations of carbon pentagons [i.e., the bright rings in Fig. 4(f)], while the localized high-density regions observed in the monolayer HOMO band (-1.80 V) can be identified with carbon double bonds (i.e., 6-6 bonds).

Comparison of the C_{60} monolayer to individual C_{60} monomers provides new insight into the origin of bright and dim molecules in the $C_{60}/\text{Ag}(001)$ monolayer. First we consider the height of C_{60} monomers. Isolated C_{60} on $\text{Ag}(001)$ is observed to have an apparent height of $\sim 5.7 \text{ \AA}$, irrespective of orientation.¹⁶ This insensitivity to surface orientation implies that differences in electronic structure due to C_{60} -Ag orientation are an unlikely cause for bright-dim apparent height differences in the monolayer. Second, we consider spectroscopic behavior. The fact that bright monolayer, dim mono-

layer, and isolated monomer spectra are all nearly identical implies that there is no significant difference in C_{60} -Ag bonding character between the three molecule types [in contrast to what is observed for $C_{60}/\text{Si}(111)$ (Ref. 15)]. Strong differences in the C_{60} -Ag chemical bond^{5,8} are thus unlikely to be the source of bright/dim formation. C_{60} -induced modification of the underlying Ag surface (i.e., Ag surface reconstruction) remains as the most plausible mechanism for bright/dim formation in $C_{60}/\text{Ag}(001)$ monolayers. The broadening of dim molecule spectral features relative to bright molecule spectral features is consistent with the interpretation that dim molecules are imbedded further into the Ag surface.

In conclusion, we have spatially resolved the local electronic structure and molecular orientation of a C_{60} monolayer on Ag(001). Our STS measurements show no evidence of anomalous Fermi-level gaps such as those observed in recent photoemission experiments.⁷ We believe that this rules out

the possibility of superconductivity in the $C_{60}/\text{Ag}(001)$ monolayer. Our monolayer measurements are best understood by starting with the behavior of a C_{60} monomer and considering the effects of additional C_{60} - C_{60} interactions and a modified C_{60} -Ag environment. Comparison of C_{60} monomer and monolayer behavior shows that these effects lead to a nearly rigid shift of the single-molecule electronic structure and a slight broadening of spectral features. Such comparisons allow us to further conclude that the coexistence of bright and dim C_{60} molecules most likely originates from an underlying Ag surface reconstruction.

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