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Modulations of valence-band photoemission spectrum from C_{60} monolayers on Ag(111)

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The photon-energy dependences of valence-band photoemission spectra have been investigated for monolayer, submonolayer, and multilayer C_{60} films on Ag(111). The intensity ratios of the highest and next-highest occupied molecular orbitals (the HOMO and NHOMO) of the films are found to oscillate with the same period as the incident photon energy is varied, but the amplitude of the oscillation is smaller with lower film coverage. Since the characteristics of the molecular orbitals of C_{60} in the monolayers are considerably different from those of the thick film due to the charge-transfer interaction between the metallic surface and the molecule the observation opposes the proposal in which the oscillation is entirely dependent on the nature of the empty and occupied states involved in the photoemission process. The results instead support the photoelectron interference model by Hasegawa *et al.* [Phys. Rev. B **58**, 4927 (1998)]. Variation of the oscillation amplitude with C_{60} coverage is explained in terms of hybridization of the HOMO and NHOMO with the surface. Depositing C_{60} onto Ag(111) held at a high temperature produces a single-phase $(2\sqrt{3}\times 2\sqrt{3})$ $R30°$ C_{60} monolayer. Angle-resolved photoemission experiments reveal changes in the relative intensities of the two bands with the azimuth-emission angle, measured with respect to the symmetry axes of the ordered monolayer. The intensity modulation is due to anisotropic scattering of photoelectrons along various molecular axes.

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I. INTRODUCTION

The electronic properties of fullerenes have been the subject of intensive research over the years since the discovery of C_{60}. One interesting phenomenon in the photoemission of fullerenes, which has not been observed for any other molecular solids, is that the intensities of the highest and next-highest occupied molecular orbitals (HOMO and NHOMO) show distinct oscillations as the incident photon energy is varied.[1–6] As the HOMO and NHOMO levels of C_{60} accommodate 10 and 18 electrons, respectively,[7] a ratio of 5:9 is expected for the photoemission intensities of the lines if the photoionization cross sections were identical. However, strong oscillations of the photoelectron intensities with photon energy are found in both the solid state as well as the gas phase of the fullerene.[2] The oscillations were initially attributed to the symmetry difference between the molecular orbitals (odd HOMO and even NHOMO);[1] however, detailed calculations based on this model showed inconsistency with experimental data.[3] A few different approaches have arisen to explain the phenomenon by considering effects of interaction between the photoelectrons originating from the molecule. Xu *et al.*[8] first calculated the energy positions of the cross-section minima based on two models of potential energy for the electron final state, and suggested the oscillation as being due to interference between the photoelectrons that leads to the formation of a spherical standing wave of the final state. However, Hasegawa *et al.*,[4] by using *ab initio* methods to determine the differential cross sections for the HOMO and NHOMO, showed that the intensity oscillation originates from the interference of the individual photoelectron waves emanating from each carbon atom of the C_{60} cage. Although the calculated results by Hasegawa *et al.* rely on the approximation of a simplified spherical-shell-like initial state, the intensity modulations of the HOMO and NHOMO were still obtained. This suggests that the oscillation is not genuinely related to the exact nature of the photoelectron initial and final states as in the proposed models by Xu *et al.*, but to the unique near-spherical structure of fullerenes. To date, the photon-energy dependences of photoemission intensities have been observed on thick C_{60} films[1,4] and single crystals.[3] In this paper, we present more detailed studies on monolayer and submonolayer films to confirm the origin of the intensity modulations. The issue is investigated by examining the valence-band photoemission spectra of the low-coverage and thick films as a function of photon energy. Adsorbed C_{60} molecules on the metal surfaces retain essentially their molecular structure, but the electronic states are modified by the substrate-adsorbate interaction. It is proposed that if the origin of the intensity oscillation is only the molecular characteristic, the same photon-energy dependence is expected for the monolayer and submonolayer films.

Ag(111) has been chosen as the substrate for the present study for two reasons. First, as for Cu(111) and Au(111) on which detailed studies of the electronic structures of adsorbed C_{60} have been carried out previously,[9,10] Ag(111) surface possesses low emission background around the Fermi level, and any peak due to charge transfer to C_{60} can be easily observed. Moreover, the advantage of Ag over other noble metals is that the *d* band lies at a higher binding energy than the Cu and Au *d* bands by about 2 eV, so that the HOMO and NHOMO peaks hardly overlap with the Ag 4*d* band, in contrast to the Cu and Au substrates. This allows more accurate determination of the HOMO and NHOMO intensities from low-coverage C_{60} films. Second, scanning tunneling microscopy (STM) studies reported two in-phase incommensurate structures with different growth orientations and a commensurate $(2\sqrt{3}\times 2\sqrt{3})$ $R30°$ structure for C_{60}

monolayers on Ag(111);[11,12] however, no low-energy electron-diffraction (LEED) patterns could be observed. Here, we report a LEED observation of ordered monolayers, which are produced by evaporating C_{60} while the Ag(111) substrate is held at a high temperature. The angular distribution of the valence-band photoemission for various photon energies has also been determined, the HOMO and NHOMO intensities are found to vary with the emission angle measured with respect to the close-packed directions of the underlying Ag(111) surface.

II. EXPERIMENT

The experiments were performed on BL4.1 of the synchrotron radiation source at the Daresbury Laboratory, using a standard UHV chamber equipped with a Scienta SES200 hemispherical electron analyzer (angular acceptance of ±5°). The Ag(111) crystal was prepared by argon-ion sputtering and annealing cycles at approximately 420 °C, until no impurities could be detected by photoemission, and sharp LEED patterns of the clean surface were observed. C_{60} (99.9% pure), purchased from MER corporation and thoroughly degassed in UHV, was deposited by sublimation from a quartz crucible heated at 370 °C in a Knudsen cell with the substrate kept at room temperature. X-ray photoelectron spectroscopy (XPS) was used to determine the C_{60} coverage by measuring the photoemission peak ratios of the overlayer (C $1s$) signal to the substrate (Ag $3d$) signal. We defined one monolayer (ML) as the saturation coverage produced by annealing a C_{60} sample to 350 °C, above the temperature required for desorption of the multilayer.[10] Sample heating was effected by electron-beam irradiation on the back of the sample. Ordered monolayers were produced by depositing C_{60} onto the Ag(111) substrate kept at 280 °C and characterized by LEED. The C/Ag intensity ratios of all the films deposited onto the hot Ag substrate were found to be approximately the same regardless of deposition time, and also identical to that of the annealed films. This confirms the films deposited onto the Ag substrate at 280 °C are monolayers. Ultraviolet photoelectron spectroscopy (UPS) spectra of the films were recorded in the photon energy range of $h\nu = 20-120$ eV at normal emission except for the angle-resolved photoemission measurements, in which the incidence angle of photons $\alpha = 20°$ and the take-off angle of photoelectrons $\theta = 30°$ measured from the surface normal. Binding energies for UPS spectra were referenced to the Fermi edge of the Ag surface.

III. RESULTS AND DISCUSSION

A. Oscillation in the valence-band photoemission spectrum

The valence-band spectra for clean Ag(111) surface, 0.5-ML, 1-ML, and multilayer films are presented in Fig. 1. The peak group between 4 and 7 eV bonding energies in the clean Ag spectrum is due to the Ag $4d$ band, while the featureless plateau below 4 eV is primarily due to the delocalized $5s$ states. As the C_{60} coverage increases, peaks due to its molecular orbitals grow, while the substrate features diminish. For the multilayer (>3 ML's) films, the Ag features are buried completely, and the spectrum represents the molecular orbitals of C_{60}. Since the deposition rate was kept at ~10 min per layer, well below the rate that causes significant non-layer-by-layer growth,[9] most C_{60} molecules in the 0.5- and 1-ML films are bound to the Ag surface. The spectra and peak positions of the films agree well with those published previously for C_{60} adsorbed on Ag(111).[13,14] The first three features are labeled in numbers. The strong peaks at 2.5 and 3.8 eV (labeled 1 and 2, respectively, in Fig. 1) are the HOMO and NHOMO, which are both derived almost entirely from the π-bonding states, whereas a mixture of σ and π states contributes to the peak 3.[7] In comparison to the multilayer, the HOMO and NHOMO peaks of 0.5- and 1-ML films shift towards the Fermi level by about 0.6 eV and locate at binding energies of 1.9 and 3.2 eV, respectively. This is characteristic of the first layer C_{60} adsorbed on the Ag surface due to partial filling of the lowest unoccupied molecular orbital (LUMO) of C_{60} by electronic charge transfer from the metallic substrate.[13,15]

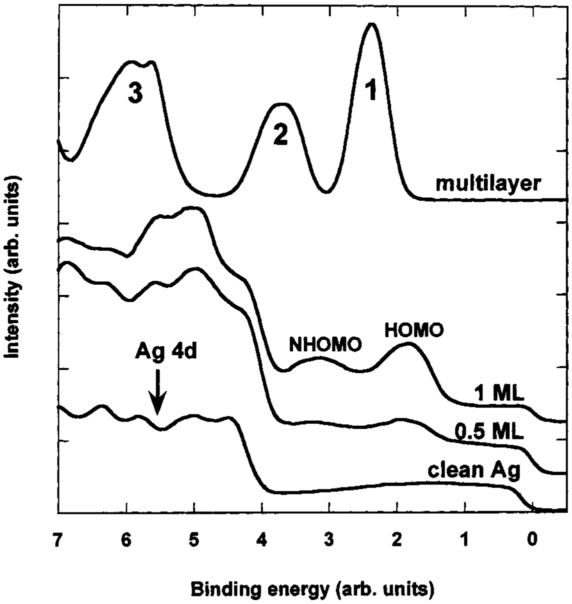

FIG. 1. Coverage dependence of normal-emission photoelectron spectra recorded from C_{60} films on Ag(111) using a photon energy $h\nu = 45$ eV. The first three peaks are labeled in numbers. Features 1 and 2 correspond to the HOMO and NHOMO of the C_{60} molecule, respectively.

Figure 2 shows the variations in the HOMO/NHOMO intensity ratio as a function of the photon energy in the range $h\nu = 20-120$ eV. The 0.5-ML, 1-ML and multilayer films show similar oscillating behavior with the maxima and minima occurring at the same energy positions, while the intensity ratios vary with the C_{60} coverage. Also presented in the figure are the arrows indicating the maxima and minima of the calculated HOMO/NHOMO intensity ratios of C_{60}, taken from Ref. 4. As seen in the figure, the spacing between the maxima and minima is not constant but increases with $h\nu$. The calculated energy positions are in good agreement with the experimental data for the three films, but the absolute values of the intensity ratios only match those of the multilayer film. The oscillation amplitude appears to be

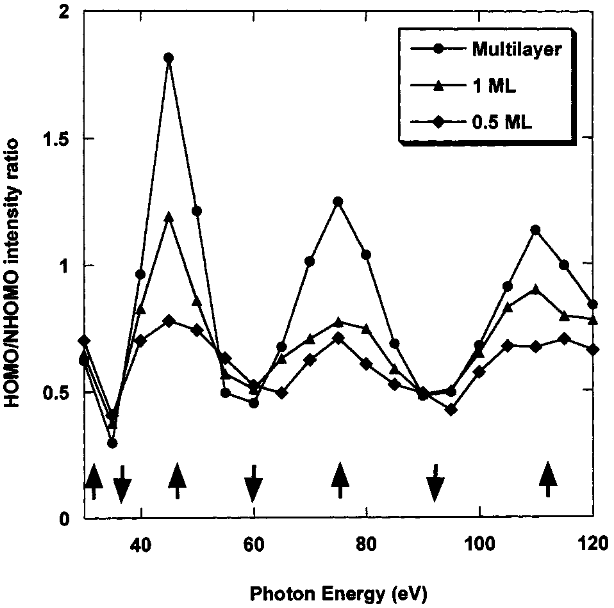

FIG. 2. Intensity ratio of HOMO and NHOMO peaks as a function of photon energy for different C_{60} coverages. The up and down arrows, respectively, indicate the maxima and minima of the calculated intensity ratio (extracted from Fig. 3 of Ref. 4).

smaller with lower C_{60} coverage; however, the effect of Ag substrate photoemission contributing to the measured HOMO and NHOMO intensities cannot be discounted. The main difficulty in determining the photoemission line intensities for low-coverage films is the selection of a suitable background for the peaks because of the signal contribution from the substrate. For the current results, the HOMO and NHOMO intensities of the 0.5- and 1-ML films have been obtained after subtraction of a background, which is proportional to the clean Ag spectrum recorded with the same photon energy.

The common feature of fullerene absorption on noble-metal surfaces is the ionic character of the bonding with the substrate. Such charge-transfer interaction obviously has significant effects on the density of states such as the position and width of the photoemission lines as well as the degeneracy of the states (e.g., fivefold degeneracy in HOMO and ninefold degeneracy in NHOMO). It is probable that the nature of the empty states is affected in a similar manner. An example is when C_{60} is adsorbed on Ag(111) both the occupied and unoccupied states are shifted towards the Fermi level.[11] The amount of charge transfer has been estimated about 1.7 electrons per C_{60} molecule adsorbed on the Ag(111) surface.[15] In addition to the filling of the LUMO, the HOMO and NHOMO bands of the monolayers are thought to exhibit some degree of hybridization with the valence bands of the noble metals.[15,16] This is evident from the broadened HOMO and NHOMO peaks in comparison to those of the thick film, as seen in Fig. 1. Nevertheless, the molecular orbitals retain much of the photoemission oscillation character. The observation that the relative intensities of the two strongest low-binding energy features oscillate with identical period over the entire photon energy range employed suggests that the oscillations are *not* dependent on the exact nature of the initial and final states of the photoelectrons. This clearly indicates that the model based on a spherical standing wave of the final state is incorrect since the overlap of the standing wave with the initial states would be different for the low-coverage and thick films, and intensity maxima and minima would occur at different photon energies. Instead, the results support the photoelectron interference model of Hasegawa *et al.*,[4] in which the intensity variation arises from the interference of photoelectron waves originating from each carbon atom in the spherical C_{60} cage. It is clear that this model does not contradict the current observation since adsorption on Ag(111) would have little effect on the shape and radius of the molecular cage.

The reduced oscillation amplitudes for the monolayers compared to the thick film could be due to interaction of the molecular orbitals with the substrate. Since the HOMO and NHOMO both have nearly pure π character and are formed from atomic orbitals pointing in the radial direction,[17] adsorption of C_{60} on the Ag(111) could cause inhomogeneous charge distribution within the molecule and changes in the state density of the HOMO and NHOMO. The smaller HOMO/NHOMO intensity ratios observed for the ML films are due to higher strength of the hybridization of the NHOMO. In quantum perturbation treatment of chemical bonds between an adsorbate and a metal substrate, mixing would occur between electron states with similar binding energies. As the NHOMO band has the binding energy closer to that of the Ag *d* band, one should expect the NHOMO hybridizes considerably more than the HOMO. This effect has been observed for C_{60} on Au(110),[16] and it was suggested that due to symmetry-breaking interaction with the substrate the NHOMO is split into two components, the $6g_g$ and $10h_g$, one of which (the $10h_g$) interacts strongly with the surface.[16,17] The low-density Ag 5*s* band is known to play a negligible role in the hybridization because of its weak interaction with C_{60}.[13] The fullerene-surface interaction also has effects on the symmetry of the molecules. In the monolayers the molecules interact with the surface through ionic bond, and the molecular symmetry is distorted from I_h point-group symmetry. The reduced symmetry of the monolayer molecules relaxes the spectroscopic selection rules, leading to availability of final states which are forbidden for the symmetries in the I_h point group. This results in a reduction in the oscillation amplitudes for the monolayers. It should be noted here that the UPS escape depth of photoelectrons has been estimated to be about one molecular layer,[18] thus UPS probes all carbon atoms in the monolayer including the atoms at the interface.

B. Angle-resolved valence-band photoemission of the ordered ML

Upon deposition of C_{60} onto Ag(111) substrate held at 280 °C, a $(2\sqrt{3}\times2\sqrt{3})$ $R30°$ LEED pattern is observed. Figure 3 shows the patterns for clean Ag(111) substrate and one ordered ML of C_{60} coverage. The pattern of Fig. 3(b) corresponds to a hexagonal overlayer with an intermolecular separation of 10.3 Å, about 3% more than the bulk separation in the fullerite crystal (10.004 Å).[19] No LEED patterns were

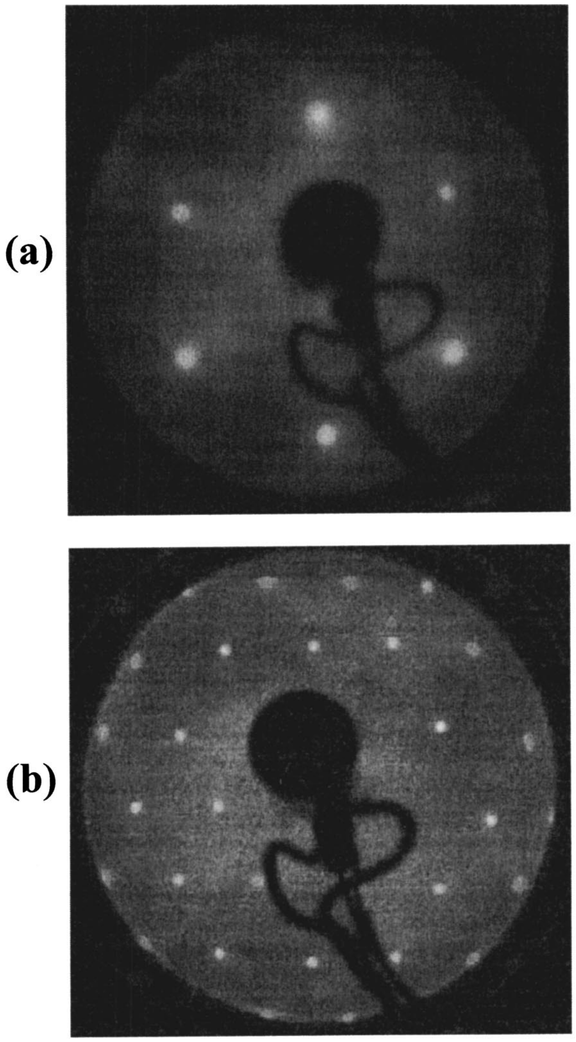

FIG. 3. LEED patterns: (a) clean Ag(111) surface (electron energy$=$118 eV); and (b) one ordered ML $(2\sqrt{3}\times2\sqrt{3})$ $R30°$ C_{60}/Ag(111) (electron energy$=$32 eV).

found for the C_{60} monolayers, which were deposited onto Ag(111) at room temperature and annealed for various durations. This is in accord with the previous finding that the $(2\sqrt{3}\times2\sqrt{3})$ $R30°$ structure coexists with some incommensurate structures over a large temperature range and that annealing increases the proportion of the incommensurate phases.[20] Despite almost perfect geometrical match in $R30°$ phase between the inter-molecular spacing and Ag(111) surface lattice constant, C_{60} monolayers grown on Ag(111) at room temperature contain a large proportion of domains with other orientations ($R12°$ and $R46°$),[12] which are poorly lattice-matched with the surface. It is thought that the growth of these domains is strongly affected by substrate step edges, where the molecules preferentially adsorb and form islands at low coverages. At high temperatures, the Ag atoms at step edges and hence adsorbed molecules have significant mobility, leading to growth of islands with the only one favorable orientation and formation of the commensurate structure in the ordered ML.

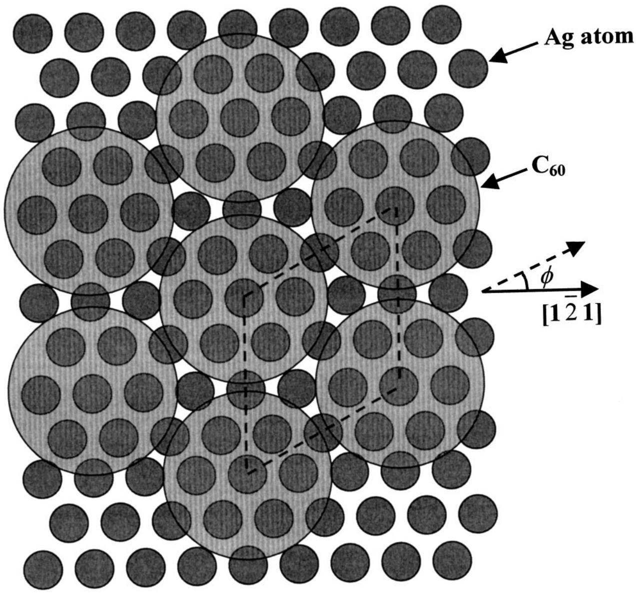

FIG. 4. Schematic showing the $(2\sqrt{3}\times2\sqrt{3})$ $R30°$ C_{60}/Ag(111) reconstruction. The dashed rhomboid represents the unit cell. Angle ϕ, measured with respect to the $[1\bar{2}1]$ direction of the overlayer, is used in the angle-resolved photoemission experiment.

A model of the C_{60} phase showing the unit cells of the substrate and the ordered C_{60} overlayer is presented in Fig. 4. Also shown in the figure is the azimuthal angle ϕ, measured with respect to the $[1\bar{2}1]$ direction of the C_{60} monolayer [or $[10\bar{1}]$ axis of the Ag(111) surface]. Given significant mobility of C_{60} on noble-metal surfaces,[12] one might expect the molecules in the ordered ML to uniformly adsorb in the orientation that yields the strongest bond to the surface. For ordered C_{60} ML's on Al(111) and Cu(111) the photoelectron diffraction patterns display a sixfold symmetry, indicating that the molecule adsorbs on one of its hexagons.[21] This is in accord with the STM study of C_{60}/Cu(111) where threefold internal molecular contrast has been observed.[22] By analogy to these adsorbate structures it is also expected that the molecules adsorb on Ag(111) with one hexagonal ring facing towards the surface. There are two reasonable adsorption sites, namely atop and threefold hollow, for C_{60} on the Ag(111) surface. The model in Fig. 4, which shows the molecules occupy atop sites, is only arbitrary.

Figure 5 illustrates the variation in the valence-band photoemission spectrum of the ordered ML measured with $\theta=30°$ for the emission angle $\phi=-30°-+30°$, using photon energy $h\nu=45$ eV. In this figure, the spectra have all been normalized to the maximum of the NHOMO peak at $\sim$3.3 eV binding energy. The variation in the intensity of the HOMO peak is clearly discernible as ϕ is increased from 0 to 30°. It is noted that the spectra of the ordered ML measured at normal emission give identical HOMO/NHOMO intensity ratios to those of the disordered ML. The spectra of the ordered ML are found to be identical at $+\phi$ and $-\phi$ emission angles for each photon energy used, an example is shown in the figure for $\phi=\pm30°$. This indicates sixfold symmetry in the photoemission of the ordered ML. The

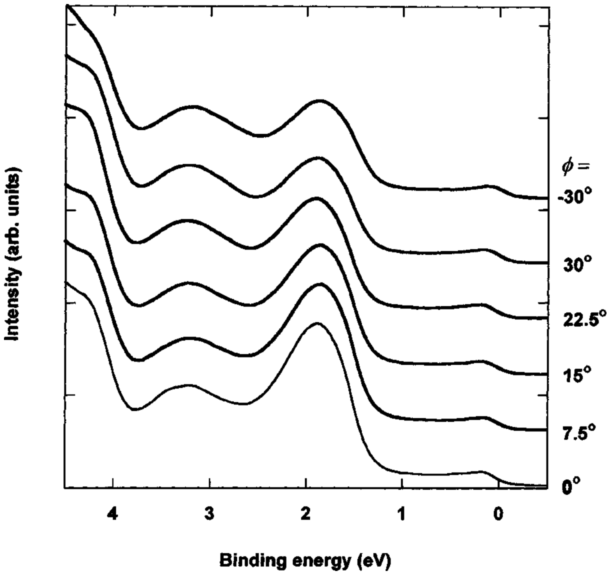

FIG. 5. Photoemission spectra from the $(2\sqrt{3}\times2\sqrt{3})$ $R30°$ C_{60} monolayer on Ag(111), recorded with $h\nu=45$ eV at various photoemission angle ϕ (see Fig. 4). These spectra have been normalized to the intensity of the NHOMO peak at 3.3 eV. The spectra of $\phi=30°$ and $-30°$ are identical.

HOMO/NHOMO intensity ratio is plotted in Fig. 6 as a function of ϕ for various photon energies between $h\nu=30$ and 110 eV. The most significant change in the HOMO/NHOMO intensity ratio occurs at $h\nu=45$ eV, the ratio gradually decreases from 1.7 to 1.1 as ϕ goes from 0° to 30°. Less distinct decreases can also been seen around $h\nu=75$ and 110 eV, while the intensity ratio remains almost constant at about 0.5 with other photon energies. It is interesting to realize that $h\nu$ of 45, 75, and 110 eV correspond to the energy positions of the HOMO/NHOMO intensity maxima recorded at normal emission (see Fig. 2). This clearly indicates a photoelectron interference effect that gives rise to shifts in relative phases of the photoelectrons, and again supports the model of Hasegawa *et al.*[4] It is noted that the intensity variation with azimuth-emission angle was not observed for the multilayer and disordered ML films due to lack of an ordered structure.

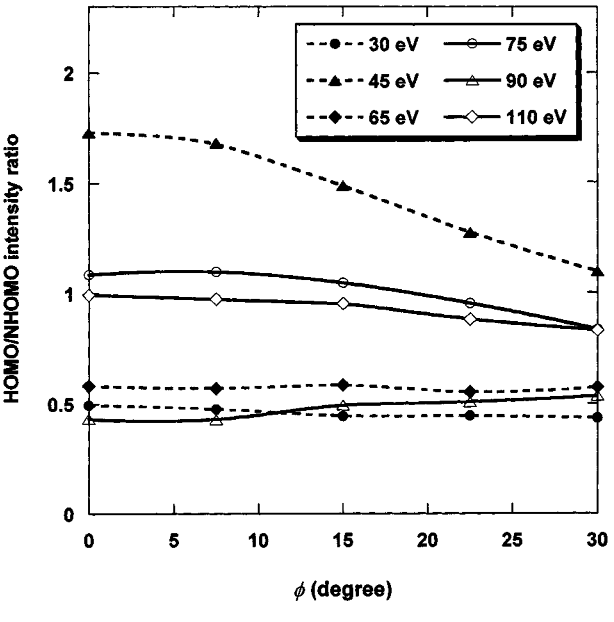

FIG. 6. Intensity ratio of HOMO and NHOMO peaks as a function of emission angle ϕ. The decreases in the intensity ratio at $h\nu=45$, 75, and 110 eV as ϕ increases are clear, while the ratio remains almost constant at about 0.5 for other photon energies (only three typical data sets are shown for $h\nu=30$, 65, and 90 eV).

The variations of the HOMO/NHOMO intensity ratios with emission angle ϕ are attributed to anisotropic scattering along various molecular axes. Since all the 60 carbon atoms of the molecules act as photoemitters, the photoelectrons emitted from one atom are scattered by other surrounding ion cores. Previous angle-resolved photoemission studies of the fullerite crystal have failed to reveal any significant changes in the intensities of the HOMO and NHOMO.[3,23] One important factor contributing to the absence of intensity modulation might be the rotational disorder: individual C_{60} molecules in the solid state spin with rotational correlation times of the order of ps.[24] In contrast, the molecules in ordered C_{60} ML's adsorbed on some single-crystal surfaces are known to be immobile and have one fixed molecular orientation. In the C_{60}/Cu(111) and C_{60}/Al(111) ordered ML systems, the molecules adsorb on a hexagon, which aligns with the substrate surface such that its sides are perpendicular and parallel to the $[10\bar{1}]$ axes of the underlying Cu(111) and Al(111), respectively[21] (the bonding configurations were thought to be strongly influenced by the molecule-surface interaction[25]). STM images of occupied states for an $(2\sqrt{3}\times2\sqrt{3})$ $R30°$ C_{60} domain on Ag(111) have also shown hexagonal shape of the internal molecular structure, the edges of the hexagon were observed to align with the $[10\bar{1}]$ directions of the Ag(111) surface.[11] The angular symmetry in valence-band photoemission is thus consistent with the adsorption symmetry of the molecules in the ordered ML. Although the HOMO and NHOMO display strong intensity modulations, we did not observe any sizable changes in the relative intensity of the LUMO with ϕ. This is most likely due to the fact that the photoelectrons, which are responsible for the LUMO peak, originate from the charge transferred from the substrate and are localized in the region close to the substrate.[10] The orbital therefore does not have the spherical character of the C_{60} molecule, which is the essential factor in causing the photoelectron interference. However, analysis of the behavior of the LUMO peak is difficult due to its weak intensity and changes in the spectral background. It therefore cannot rule out the possibility that there are small changes in the LUMO intensity.

In conclusion, the photon energy dependences of photoemission intensities have been investigated for monolayer, submonolayer and thick C_{60} films. The intensity ratios of the HOMO and NHOMO peaks oscillate with the same period, while the amplitude of the oscillation varies with C_{60} coverage. The results indicate that the oscillations are independent of the nature of the initial and final states, and support the model, in which the oscillation arises from the interference of photoelectrons. Depositing C_{60} onto Ag(111) kept at a high temperature produces a single phase of $(2\sqrt{3}\times2\sqrt{3})R30°$ C_{60} monolayers. The relative intensities of the HOMO and NHOMO from the ordered ML are found to vary with azimuth-emission angle. The observation is due to anisotropic scattering of photoelectrons along molecular axes as the molecules in the ordered ML all have the same adsorption orientation. This also confirms the origin of the intensity oscillation phenomenon as being due to interference of photoelectrons emitting from the molecule.

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