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### Title

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# Determination of band curvatures by angle-resolved two-photon photoemission in thin films of C<sub>60</sub> on Ag(111)

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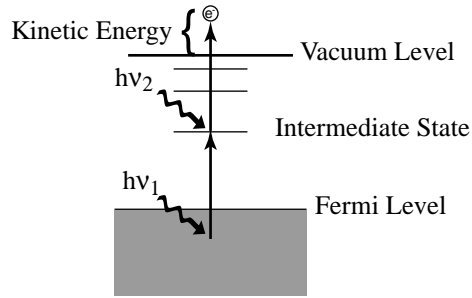
## Abstract

The thickness-dependent interfacial band structure was determined for thin films of C<sub>60</sub> on Ag(111) by angle-resolved two-photon photoemission spectroscopy. Dispersions of molecular-orbital derived bands (HOMO, LUMO+1, and LUMO+2) were acquired, and limits were placed on their possible effective masses. A group theoretic approach is also incorporated to further understand the properties of these states. The HOMO, LUMO+1, and LUMO+2 bands possess (best-fit) effective masses of  $-7 m_e$ ,  $-7 m_e$ , and  $-12 m_e$ , respectively. These values are consistent with theoretical calculations, averaged over the closely-spaced sub-bands for each state, and provide practical limits on the effective fundamental charge-transport properties of C<sub>60</sub> films.

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**Figure 1:** Schematic depiction of the two-photon photoemission process. A pump pulse,  $h\nu_1$ , excites an electron from below the Fermi level into an initially unoccupied intermediate state. A probe pulse,  $h\nu_2$ , arrives at some delay time later and excites the electron above the vacuum level. By measuring the kinetic energy of the photoemitted electron and knowing the energies of  $h\nu_1$  and  $h\nu_2$ , the energy of the intermediate state may be referenced to the vacuum level.

## 1 Introduction

Epitaxial thin films of  $C_{60}$  grown on metal substrates have received considerable attention in recent years as a model system for the study of molecular electronic devices.<sup>1-4</sup> This system is ideal for a number of reasons: among them are the ease of preparation of high-quality mono- and multi-layers, the rich electronic structure of the fullerenes, and the wealth of prior experimental and theoretical work on this system.

While a number of photoemission studies have been done on thin films of  $C_{60}$ ,<sup>5-17</sup> it has only been relatively recently that the technique of angle- and time-resolved two-photon photoemission (2PPE) has been applied to these films.<sup>18-21</sup> The advantage of a two-photon technique over other photoemission techniques (such as ultraviolet photoelectron spectroscopy or inverse photoelectron spectroscopy) lies in the fact that it can simultaneously probe both initially occupied as well as initially unoccupied electronic band structure, and that it can do so with an ultrafast temporal resolution.

Two-photon photoemission is a pump-probe technique for exploring the properties of interfacial electronic states. Initially unoccupied states as studied by 2PPE are illustrated in Fig. 1. Electrons from below the Fermi level ( $E_F$ ) of a metal substrate (or from an initially occupied surface<sup>22</sup> or

adsorbate<sup>23</sup> state) are excited into an intermediate state with a pump pulse,  $h\nu_1$ . This intermediate may be “virtual” in the case of an initially occupied state. The probe pulse  $h\nu_2$  then photoemits the excited-state electron by giving it energy greater than the vacuum level,  $E_{\text{vac}}$ . The binding energy of the unoccupied electronic states can be calculated by measuring the kinetic energy,  $E_{\text{kin}}$ , of the photoemitted electrons and then subtracting the energy of the probe pulse photon. This experiment may be performed in a time-resolved fashion, by delaying the probe pulse with respect to the pump pulse.

Two-photon photoemission can also be used as a probe of two-dimensional band structure by taking spectra as a function of the angle of the surface normal relative to the detector. In angle-resolved 2PPE, the objective is to determine the electronic band dispersion ( $E_{\text{kin}}$  vs the momentum  $\hbar k_{\parallel}$  parallel to the interface) of an interfacial state along a particular crystal direction. For an interface possessing long-range order, the parallel momentum of an electron is conserved during photoemission, and is related to  $E_{\text{kin}}$  via

$$k_{\parallel} = \sqrt{\frac{2m_e E_{\text{kin}}}{\hbar^2}} \sin \theta, \quad (1)$$

where  $m_e$  is the free electron mass and  $\theta$  is the detection angle from surface normal. The band dispersion is typically fit to a parabolic function

$$E_{\text{kin}} = E_0 + \frac{(\hbar k_{\parallel})^2}{2m^*}, \quad (2)$$

where  $E_0$  is the energy at the band minimum and  $m^*$  is an effective electron mass. Nearly free (delocalized) electronic states have values of  $|m^*| \approx m_e$ , while spatially-localized electronic states have apparent values of  $|m^*| \gg m_e$ .

A large value of  $m^*$  is necessary but not sufficient for an electronic state to be localized. In the

case of a localized electronic state, the measured large effective mass is a result of the fact that  $k_{\parallel}$  is not a good quantum number, and such states may be described as a superposition of plane waves with different values of  $k_{\parallel}$ . In this case, measurements as a function of  $\theta$  simply select the different  $k_{\parallel}$  components of the superposition, and  $E_{\text{kin}}$  is constant as a function of angle. It is possible, however, for a delocalized electron to have a large value of  $m^*$ . Note that the estimate of  $m^*$  is based on the assumption of a parabolic or cosine-like band structure. In general, such a function will not be a true representation for the band as a whole, however such estimates should be valid quantities in the vicinity of the  $\Gamma$  point ( $k_{\parallel} = 0$ ).

Angle-resolved 2PPE spectra were taken of thin films of  $\text{C}_{60}$  on  $\text{Ag}(111)$  in order to probe the fundamental charge-transport properties of these films. Dispersions of the molecular-orbital derived states were fit to values of  $m^*$ . These results are then compared to theoretical predictions of the electronic band structure.

## 2 Experimental

### 2.1 Ultrafast Laser System

Details of our laser system, constructed by Coherent, Inc., have been published elsewhere, and are only briefly described here.<sup>24</sup>

Our overall laser system is pumped by two Coherent Verdi<sup>TM</sup> pump lasers. The Verdis are diode-pumped, continuous-wave  $\text{Nd:YVO}_4$  lasers with intracavity lithium triborate doubling crystals producing 532 nm output. A Coherent Mira 900-F Ti:sapphire oscillator is pumped by a Verdi V-5 laser operating at 5.5 W, and a Coherent RegA 9000 regenerative amplifier is pumped by a Verdi V-10 laser operating at 10.5 W.

The Mira operates at 76 MHz and 800 nm and is optimized for mode-locked operation with a

bandwidth of 10–13 nm full width at half maximum, preferably 12 nm or higher. A small portion of the output, approximately 50 mW average power, is regeneratively amplified by the RegA, operating at 200 kHz. The RegA output is used to pump a Coherent OPA (optical parametric amplifier) unit, which generates white light continuum as well as the 400 nm second harmonic. Parametric amplification of a portion of the continuum allows for the generation of tunable visible light from 470 to 740 nm. The OPA output is compressed to a wavelength-dependent value of 70–120 fs via dispersion compensation (bluer wavelengths are closer to 120 fs), after which a portion of the beam is frequency doubled. The remainder of the OPA output is delayed in time (positively or negatively) with respect to the doubled beam via a Klinger translation stage.

## 2.2 Ultrahigh Vacuum Chamber

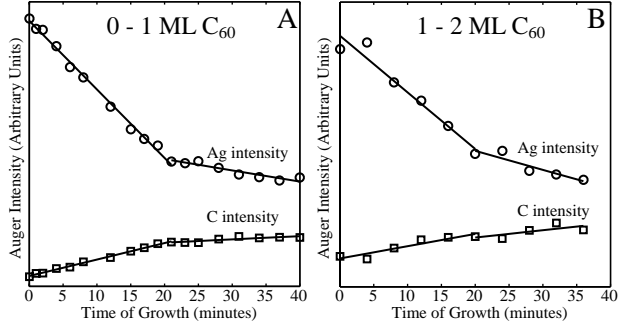
Our metal substrate is a single crystal of Ag(111), 99.999% pure, obtained from MaTecK GmbH. The crystal is mounted on a manipulator arm which allows for the rotation of the surface normal of the crystal about a fixed point, in addition to the standard whole-crystal translations and rotations to face various viewports and instruments in the chamber. The crystal is wedged, adding to the maximum angular range provided by the surface-normal goniometer. The wedge angle was determined to be  $6.0^\circ$  from the minimum energy in the dispersion of the image states on the clean surface, allowing for the surface normal to be rotated from  $-3.5^\circ$  to  $+26.0^\circ$ . The Ag(111) crystal is oriented such that dispersion measurements are taken along the  $\Gamma$ -X direction, although LEED indicates that the crystal is slightly misaligned by approximately  $9^\circ$ .

The Ag(111) crystal is kept in a UHV chamber with a base pressure on the order of  $1 \times 10^{-10}$  torr. The crystal is connected to a Janis ST-400 continuous flow cryostat capable of using liquid nitrogen or helium, achieving a base temperature of approximately 125 K with nitrogen and 50 K with helium. Photoelectrons are captured by a time-of-flight detector. Additionally, the chamber

is outfitted with an SRS RGA300 quadrupole mass spectrometer for residual gas analysis, a LEED and Auger system (Omicron SPECTALEED) for assessing the quality and composition of thin films on the substrate, a precision leak valve for introducing various gases into the chamber, and an ion gun for  $\text{Ar}^+$  sputter cleaning of the surface. Auger spectra are recorded using software provided by Omicron, and LEED images are captured via an EHD KAMPro02 CCD camera (EHD Imaging GmbH). The vacuum chamber is also connected via a gate valve to a smaller chamber, referred to as the molecular beam epitaxy (MBE) chamber.

The MBE chamber has a base pressure on the order of  $1 \times 10^{-9}$  torr and is equipped with a small furnace (Applied EPI Low Temp K-cell with PBN crucible) capable of heating source material up to  $1000^\circ\text{C}$  with  $\pm 0.1^\circ\text{C}$  stability. The crucible-to-substrate distance is  $\sim 34$  cm and a pinhole of 1 cm diameter is located immediately before the gate valve (21 cm before the sample) to minimize contamination of the 2PPE chamber.

The  $\text{C}_{60}$  used in this study was obtained from Strem at a purity of 99.9%, and was placed into the MBE chamber without further purification, where it was thoroughly degassed prior to use. Similar to what was observed on  $\text{Cu}(111)$ ,<sup>18</sup> multilayers of  $\text{C}_{60}$  on  $\text{Ag}(111)$  may be removed from the surface by simply heating the crystal above 450 K, but  $\text{C}_{60}$  monolayers on  $\text{Ag}(111)$  resist our “standard”  $\text{Ar}^+$  sputter and anneal cycle (a 0.5 keV  $\text{Ar}^+$  sputter for 20 minutes at 500 K, followed by annealing the substrate for 20 minutes at 725 K), requiring instead an initial higher-energy sputter cycle for 10 minutes at 1.5 keV and 500 K, followed by a normal sputter and anneal cycle. After this procedure, LEED, Auger, and 2PPE indicate that the  $\text{Ag}(111)$  surface is clean.



**Figure 2:** (a) Monitoring the growth of a 0–1 ML C<sub>60</sub> film by Auger. Preparation conditions are a substrate temperature of 613 K and an MBE cell temperature of 410°C. (b) Monitoring the growth of a 1–2 ML C<sub>60</sub> film by Auger. Preparation conditions are a substrate temperature of 400 K and an MBE cell temperature of 400°C.

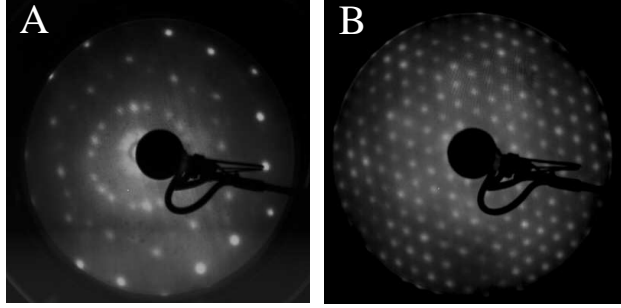
### 3 Results

#### 3.1 C<sub>60</sub> Layer Growth: Calibration and Characterization

According to previous reports,<sup>18</sup> highly ordered C<sub>60</sub> thin films are a prerequisite for observing sharp image states and narrow photoemission peaks. Consequently, before investigating the ultrafast electron dynamics of these films, some time was spent perfecting their growth. Thin films of C<sub>60</sub> on Ag(111) are more like those on Au(111) rather than those on Cu(111) — the equilibrium film structure on Ag(111) and Au(111) is a  $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$  structure, rather than the  $4 \times 4$  structure seen on Cu(111).<sup>25</sup> Consequently, the dosing parameters were adjusted to find the conditions reported by Tzeng et al.<sup>25</sup> as resulting in high-quality thin films (elevated substrate temperature during deposition and a slow growth rate of 0.05 monolayers/min).

The C<sub>60</sub> coverage was calibrated via Auger spectroscopy, by examining the intensities of the C peak<sup>26</sup> at 272 eV and the Ag primary peaks at 351–356 eV as a function of dosing time. When a slope change is observed in both features, this is interpreted as the completion of a layer.<sup>27</sup> For the monolayer, favorable conditions for growth were an MBE cell temperature of 410°C and a substrate temperature of 613 K. These conditions give a completed monolayer at approximately 23 minutes of dosing (Fig. 2a). LEED of this layer (Fig. 3a) shows that the  $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$  structure is the

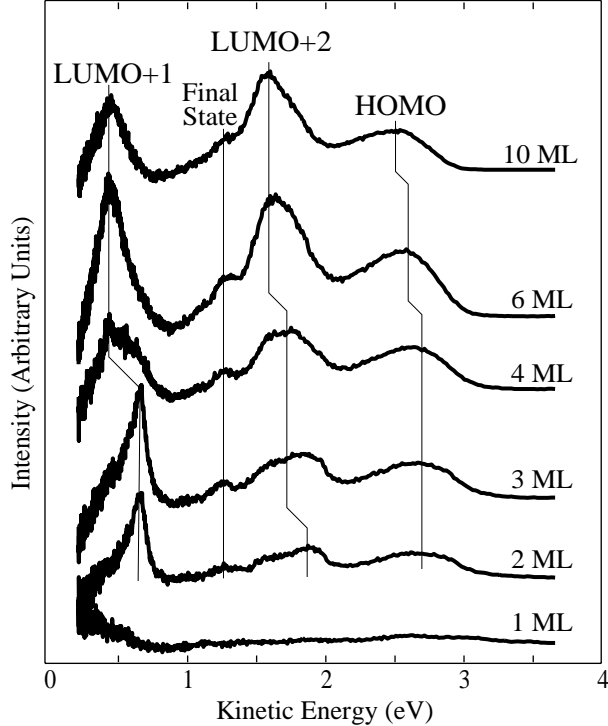




**Figure 3:** (a) LEED pattern taken at 32.0 eV of a 1 monolayer  $C_{60}$  film. The  $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$  phase is the majority phase, but spots corresponding to the minority  $R \pm 14^\circ$  phases are present as well. (b) LEED pattern taken at 54.0 eV of a 10 monolayer  $C_{60}$  film.

majority phase, although there are small amounts of the  $R \pm 14^\circ$  phases present. These minority phases could unfortunately never be completely quenched by varying the dosing conditions.

The growth of the second monolayer was also calibrated via Auger (Fig. 2b), with the objective of determining conditions for multilayer growth that enable highly crystalline films of the thermodynamic (rather than kinetic) domains to predominate. Unfortunately, it is very difficult to observe the slope change in the C peak for these coverages, and so the layer completion time was determined by the slope change observed in the Ag signal. The substrate temperature for multilayer growth was chosen to be 400 K, as it was observed that the second and higher monolayers slowly desorb at temperatures above 450 K. Auger indicated that the MBE cell temperature of  $410^\circ\text{C}$  used for the monolayer was slightly too high (slope change in approximately 18 minutes), and so the MBE cell temperature was lowered to  $400^\circ\text{C}$  for multilayer growth, yielding a slope change at approximately 20 minutes. A 20-minute dose at  $400^\circ\text{C}$  MBE cell temperature at a substrate temperature of 400 K was therefore determined to be the unit of multilayer dosing, and higher coverages were assigned based on this dosing time. LEED of the 10 monolayer coverage (Fig. 3b) indicates that the multilayer films are highly crystalline and possess the expected structure.

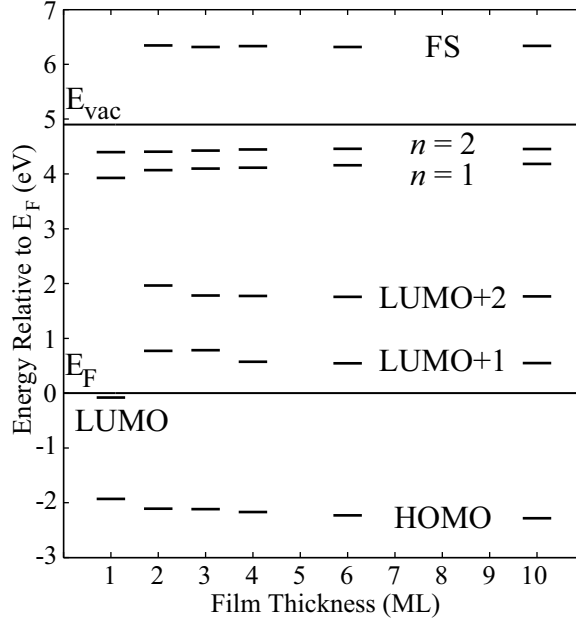


**Figure 4:** One-color 2PPE spectra of  $C_{60}$  layers of varying thickness, taken with both  $h\nu_1$  and  $h\nu_2$  equal to 4.78 eV energy. The molecular orbital-derived states are labelled as such, and the feature labelled “Final State” corresponds to a final state resonance energetically located above the vacuum level. The lines indicate how the peak positions shift as a function of layer thickness.

### 3.2 2PPE Spectra

Films 1, 2, 3, 4, 6, and 10 monolayers (ML) thick of  $C_{60}$  were grown on a Ag(111) substrate. Substantial charge transfer from the metal substrate to the film occurs for the 1-ML coverage (on the order of 0.75 electrons per molecule<sup>28</sup>), but subsequent layers remain electrically neutral. As such, spectra of the 1-ML film are substantially different from those of thicker films, which appear relatively similar regardless of coverage. Note that, in order to eliminate complications relating to possible glass transitions or polymerization in multilayer  $C_{60}$  films,<sup>16,29</sup> all 2PPE was performed at temperatures of 80 K or below, and the sample was shielded from the femtosecond laser pulses until these temperatures were reached.

One-color 2PPE spectra of each  $C_{60}$  coverage (Fig. 4) exhibit several different peaks after background subtraction. The background function accounts for contributions from inelastically



**Figure 5:** Position of the various observed energy levels as a function of  $C_{60}$  film thickness.

scattered electrons, which can dominate the signal at low kinetic energies. The background function used was first described by Shirley<sup>30</sup> for photoemission from a gold substrate, and has also been applied in a study of photoemission from the  $sp$  band of  $Ag(111)$ .<sup>31</sup>

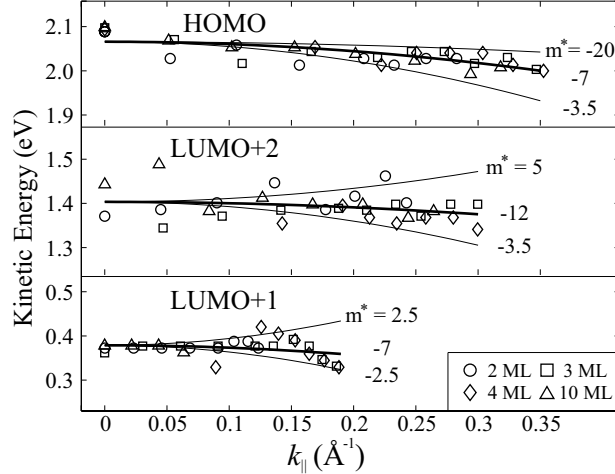
In order to ascertain the identities of these peaks, wavelength surveys were undertaken, in which the peak positions are examined as a function of the pump and probe photon energies. Systematic peak shifts with changes in photon energy give information about the number and time ordering of the system's interactions with the pump and probe photons, which can then be used to reference the different peaks to the Fermi or vacuum level. The energy level diagram resulting from these studies is given in Fig. 5.

The identities of the observed peaks are fairly clear from both reference to the existing  $C_{60}$  photoemission studies of Dutton and co-workers on  $Cu(111)$ <sup>18-20</sup> and  $Au(111)$ <sup>21</sup> as well as the electronic structure of isolated  $C_{60}$  molecules.<sup>32-34</sup> Observed features include image potential states, final state resonances above the vacuum level, and states derived from  $C_{60}$  molecular orbitals. (Note that the LUMO and  $n = 1$  and  $n = 2$  image potential states in Fig. 5 are not visible in the one-color

2PPE spectra shown in Fig. 4; however, they are seen in the two-color 2PPE data, available in the Supporting Information.) The properties of the molecular orbital-derived states will be the focus of the remainder of this manuscript; details of the other features will appear in a forthcoming paper. Once the molecular-orbital derived states (HOMO, LUMO+1, and LUMO+2) were assigned, their dispersions were examined in the  $\bar{\Gamma}$ - $\bar{M}$  direction (a  $30^\circ$  rotation from the Ag(111) direction due to the  $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$  structure of the  $C_{60}$  overlayers). The overbars indicate that the dispersions being examined are those along a two-dimensional surface. Previous studies on fullerenes<sup>35</sup> indicate that the escape depth for photoelectrons is roughly the size of a single  $C_{60}$  molecule. In other words, the detected photoelectrons originate primarily from the topmost layer, a result corroborated by the work of Dutton and co-workers.<sup>20</sup> So, throughout the rest of this manuscript, we will be interpreting our dispersions as due to the dispersions of the electrons in the topmost  $C_{60}$  layer, which considerably simplifies the analysis as compared to the full three-dimensional case.

The positions of the molecular-orbital derived states are difficult to ascertain in the 1-ML film, and so dispersions from this coverage are not used in the estimates of  $m^*$  for these bands. For thicker films, the energetic positions of the bands change slightly as a function of coverage, but the effective masses of the bands appear to be independent of film thickness. It should be noted that these measured effective masses correspond to an average over the energetically degenerate or nearly degenerate sub-bands; we are unfortunately unable to resolve separate peaks for the 5-fold degenerate HOMO, 3-fold degenerate LUMO+1, or the 5-fold degenerate LUMO+2.

As it is experimentally difficult to distinguish between large values of  $m^*$  (the experimental observable,  $E_{\text{kin}}$ , varies as  $1/m^*$ , which changes slowly for large values of  $m^*$ ), we report a range of effective masses for the HOMO, LUMO+1, and LUMO+2 bands, corresponding to our estimates from the data of the most likely values of  $m^*$ . Figure 6 shows this graphically. In order to plot data from multiple coverages on the same axes, the  $k_{\parallel}$  values were first determined from the measured



**Figure 6:** Dispersion data for the HOMO, LUMO+1, and LUMO+2 states in  $C_{60}$  films 2, 3, 4, and 10 ML thick. The lines are possible fits to the effective mass of the band. For the HOMO level, the effective mass (in units of  $m_e$ ) is expected to lie between  $-3.5$  and  $-20$  with a best fit value of  $-7$ . For the LUMO+1 level, the effective mass is expected to lie between  $+2.5$  and  $-2.5$  with a best fit value of  $-7$ , and for the LUMO+2 level, the effective mass is expected to lie between  $-3.5$  and  $+5$  with a best fit value of  $-12$ .

kinetic energies, using Eq. 1. After the parallel momenta (and consequently the curvatures of the states) were determined, the data from each coverage were then offset by a constant energy in order to fit values of  $m^*$  to the full data set at once. These constant energy shifts essentially just account for the shift in band positions with film thickness seen in Fig. 5.

As seen in Fig. 6, the HOMO-derived band has a negative effective mass but the signs of the LUMO+1- and LUMO+2-derived masses are difficult to unambiguously determine, although the best fit values are negative in both cases. Table 1 shows the effective masses (ranges and best fit value) for the HOMO, LUMO+1, and LUMO+2 bands, using equation 2.

Identity	$m^*$ bounds	$m^*$ best fit
HOMO	$-3.5 - -20$	$-7$
LUMO+1	$-2.5 - +2.5$	$-7$
LUMO+2	$-3.5 - +5$	$-12$

**Table 1:** Upper and lower bounds and best fit values of the effective mass (units of  $m_e$ ) for the HOMO, LUMO+1, and LUMO+2 states.

We should note that previous work has indicated that the presence of random orientational disorder can lead to an anomalously flat dispersion,<sup>36</sup> but this is not expected to be an issue at the

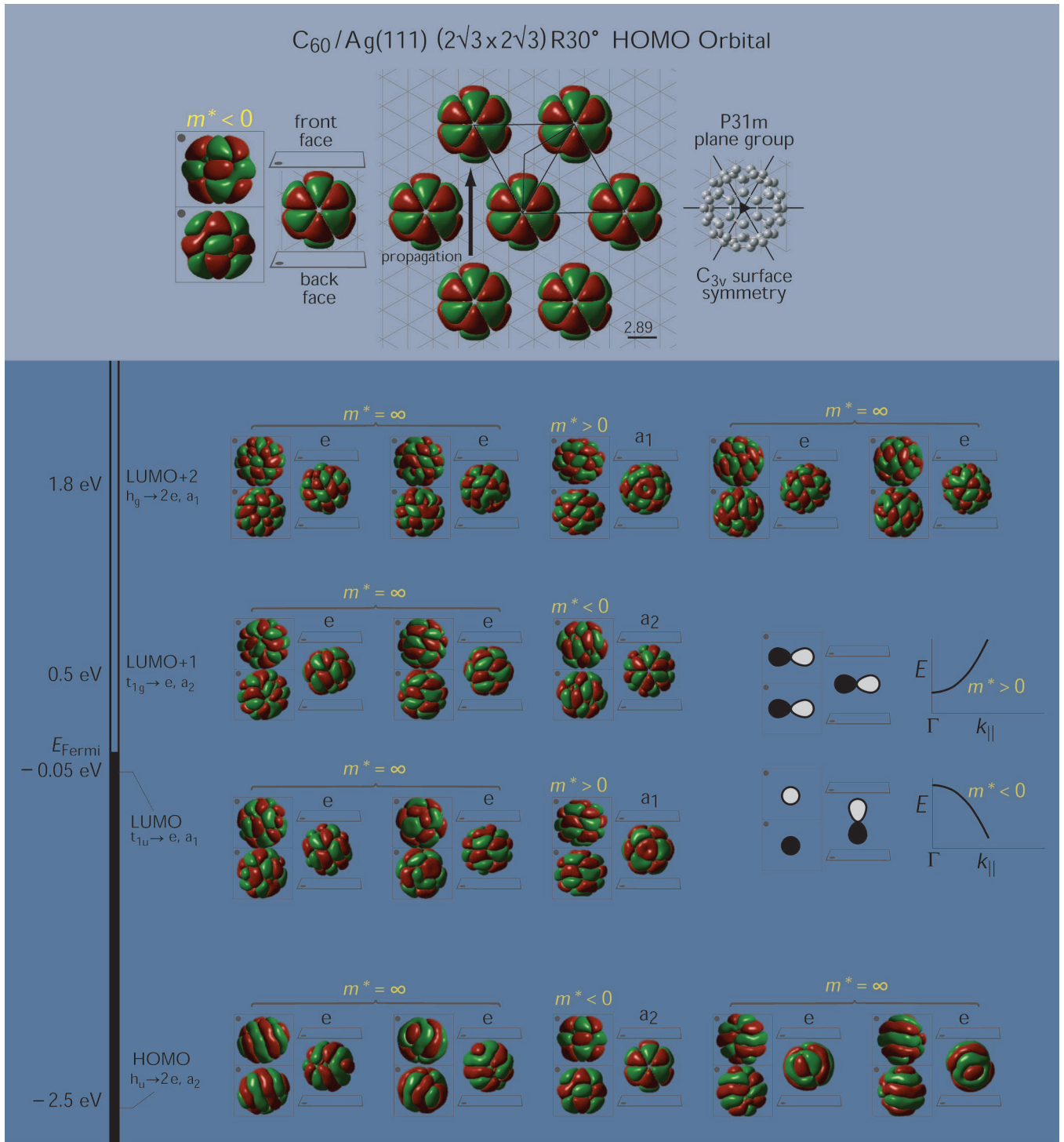
temperatures used here, as  $C_{60}$  molecules below the rotational phase transition at approximately 90 K are expected to be predominately in one rotational orientation.<sup>37,38</sup>

The effective mass ( $m^*$ ) values estimated above for the HOMO, LUMO+1, and LUMO+2 bands in thin film  $C_{60}$  are important parameters for understanding charge transport in these bands. The band width, the magnitude of the energy difference between the top and bottom of the bands (proportional to  $|1/m^*|$ ), is related to the extent of orbital overlap, and the sign of  $m^*$  indicates the presence or absence of nodes between nearest neighbors.<sup>39</sup> The nodal structure is dictated by the symmetry of the lattice and of the molecular orbital basis. If there is no node between identical replicas of the molecular orbital, then the effective mass will be positive; conversely, if there is a node, the effective mass will be negative.<sup>23,39</sup>

As the signs of the dispersions for the LUMO+1 and LUMO+2 derived states are uncertain from the experimental data, a theoretical approach is desired in order to attempt to resolve this ambiguity. Two methods are taken. The first method is a “brute force” approach, involving a direct calculation of the wavefunctions. The second method utilizes group theory to understand the symmetries of the orbitals along the  $\bar{\Gamma}$ - $\bar{M}$  direction.

In order to directly examine the orbitals, the HOMO, LUMO, LUMO+1, and LUMO+2 orbitals for isolated  $C_{60}$  molecules were calculated with Gaussian<sup>40</sup> at the RHF/STO-3G level of theory and visualized using Gaussview. The  $C_{60}$  molecules were then placed with hexagonal faces down on hcp sites of the Ag(111) lattice, in accord with recent calculations of the  $C_{60}$  orientation in the  $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$  phase on Ag(111).<sup>41</sup> Figure 7 shows the different HOMO, LUMO, LUMO+1, and LUMO+2 sub-bands, in addition to detailing how these orbitals are arranged on the Ag(111) lattice.

In Figure 7, the different colors of the orbitals represent the sign of the wavefunction. The direction of propagation ( $\bar{\Gamma}$ - $\bar{M}$ ) connects the front face of one orbital with the back face of another.



**Figure 7:** Top panel: One sub-band of the five-fold degenerate HOMO is tiled on a Ag(111) lattice. This structure corresponds to the P31m plane group, and the symmetry of the  $C_{60}$  is lowered from  $I_h$  to  $C_{3v}$ . The colors of the orbital indicate the sign of the wavefunction. The arrow indicates the  $\bar{\Gamma}$ - $\bar{M}$  direction, which connects the front face of one orbital with the back face of another. For the sub-band shown, the signs of the wavefunction are opposite over the entire face, corresponding to a node between the molecules at  $k_{\parallel} = 0$ , and consequently a negative effective mass. Bottom panel: Wavefunction visualizations for the HOMO, LUMO, LUMO+1, and LUMO+2 orbitals, along with expected curvatures of the states. The  $e$ ,  $a_1$ , and  $a_2$  labels correspond to the symmetries of these wavefunctions in the  $C_{3v}$  point group. Inset: a schematic of the nodal structure for two simple cases, along with sketches of the dispersion for these cases.

Therefore, if the front and back faces have opposite colors in the same spatial region, there is a node in between them, and  $m^*$  is expected to be negative, as in the case of the orbital represented in the top panel. The pairs of orbitals in Fig. 7 connected with curly braces transform as a pair, and have a net flat curvature ( $m^* = \infty$ ). To summarize this figure, the HOMO and LUMO+1 orbitals should have net negative effective masses (averaged over the sub-bands which are not experimentally resolvable), and the LUMO and LUMO+2 orbitals should have net positive effective masses.

These results may also be understood in a more formal way with the aid of group theory. Specifically, examining the nodal symmetry of the front face of one orbital with the back face of another is identical to examining the character of the orbitals under a reflection through a plane which is perpendicular to the  $\bar{\Gamma}$ - $\bar{M}$  direction and which bisects the molecules. With this in mind, all that remains is to determine the symmetries of these states and examine how they transform under reflection.

Isolated  $C_{60}$  molecules are highly symmetric, belonging to the icosahedral point group,  $I_h$ . This group has 120 symmetry elements and a formidable character table. However, when  $C_{60}$  is placed on a surface, its overall symmetry is dramatically lowered due to the difference between the surface below and the vacuum above. In the following analysis, we consider a  $C_{60}$  molecule with a hexagonal face down on an hcp site of the Ag(111) lattice, as in Fig. 7. A layer of  $C_{60}$  molecules in this orientation belongs to the P31m plane group, and the symmetry of each molecule is reduced to  $C_{3v}$ . The dispersion direction probed in our experiments corresponds to a high-symmetry direction, and the energetic curvature of the bands may be understood by considering their characters with respect to a reflection under  $C_{3v}$  symmetry. A character of +1 under this operation corresponds to the wavefunctions on the front and back faces possessing the same sign and a positive effective mass, while a character of -1 under this operation corresponds to the wavefunctions differing by a phase of  $180^\circ$ , and thereby having opposite signs and a negative effective mass.



The  $h_u$  HOMO,  $t_{1u}$  LUMO,  $t_{1g}$  LUMO+1, and  $h_g$  LUMO+2 orbitals of the  $I_h$  point group transform into combinations of  $a_1$ ,  $a_2$ , and  $e$  states in the  $C_{3v}$  point group (Table 2). The  $a_1$ ,  $a_2$ , and  $e$  states each have a different character under reflection, corresponding in our experiment to differing signs of  $m^*$ . The  $a_1$  states have a +1 character (positive  $m^*$ ) and the  $a_2$  states have a -1 character (negative  $m^*$ ) under reflection. But what of the  $e$  states, which possess a character of 0? The character of 0 implies that these states have neither a positive nor a negative dispersion, but instead have a rigorously flat dispersion, corresponding to  $m^* = \infty$ . While it may appear from Fig. 7 that one of a pair has a positive dispersion and the other has a negative dispersion (see the  $e$  states of the HOMO), these states must be taken as pairs to fully span their two-dimensional representations, and, when proper linear combinations of them are taken, they must have a curvature of 0.

Identity	$I_h$	$C_{3v}$	$\sigma$	net curvature
HOMO	$h_u$	$e, e, a_2$	0, 0, -1	negative
LUMO	$t_{1u}$	$e, a_1$	0, +1	positive
LUMO+1	$t_{1g}$	$e, a_2$	0, -1	negative
LUMO+2	$h_g$	$e, e, a_1$	0, 0, +1	positive

**Table 2:** Symmetries of the HOMO, LUMO, LUMO+1, and LUMO+2 orbitals under the  $I_h$  and  $C_{3v}$  point groups, their characters under reflection, and the net curvature of the bands. Positive and negative curvatures correspond to positive and negative signs of  $m^*$ , respectively.

The type of analysis shown in Table 2 indicates that, from a symmetry standpoint, the HOMO and LUMO+1 orbitals are expected to have a net negative curvature, and the LUMO and LUMO+2 orbitals are expected to have a net positive curvature. However, for the initially unoccupied orbitals, this analysis may be too simplistic. It has been suggested<sup>21</sup> that the states assigned here as LUMO+1 and LUMO+2 may not be populated by charge transfer from the metal substrate (anions), but instead might be due to excitations on the molecules themselves (excitons). The dispersions of excitonic states would then entail the movement of a correlated electron-hole pair, rather than the movement of a single particle, which is an implicit assumption of the above analysis.

Fortunately, the group theoretic approach is readily extended to consider on-molecule excitons. These types of states can be represented by a direct product of the electron orbital and the hole orbital on a given  $C_{60}$ , and the symmetries of the resulting states can be analyzed as above. At the photon energies used in these experiments, the relevant excitons to consider are the HOMO–LUMO+1 and the HOMO–LUMO+2 excitons. (The HOMO-1–LUMO+1 exciton is not considered, as this is a dipole-forbidden transition.) The direct products corresponding to these excitons are

$$h_u \otimes t_{1g} = t_{1u} + t_{2u} + g_u + h_u \quad (3)$$

for the HOMO–LUMO+1 exciton, and

$$h_u \otimes h_g = a_u + [t_{1u}] + [t_{2u}] + [g_u] + g_u + 2h_u \quad (4)$$

for the HOMO–LUMO+2 excitons, where the braces indicate the antisymmetric product (triplet states). The different split states resulting from these direct products may then be considered as above, by examining how they behave under a lowering of the symmetry from  $I_h$  to  $C_{3v}$ , and, finally, using their characters under reflection to predict their effective masses.

The  $h_u$  and  $t_{1u}$  states should transform like the HOMO and LUMO levels in Table 2, respectively, while the  $g_u$  and  $t_{2u}$  states have to be manually decomposed with the aid of character tables. When the full analysis is performed on the singlet states of these two excitons, it is seen that the HOMO–LUMO+1 exciton should have a net positive effective mass, and the HOMO–LUMO+2 exciton should have a net negative effective mass (Table 3).

Unfortunately, a certain determination of whether the LUMO+1 and LUMO+2-derived features are due to molecular excitations (excitons) or charge transfer from the metal (anions) is not possible from the theory and experimental data presented here, particularly as the group theory says nothing

Identity	$I_h$	$C_{3v}$	$\sigma$	net curvature
HOMO-LUMO+1	$t_{1u}$	$e, a_1$	0, +1	positive
	$t_{2u}$	$e, a_1$	0, +1	positive
	$g_u$	$e, a_1, a_2$	0, +1, -1	flat
	$h_u$	$e, e, a_2$	0, 0, -1	negative
Net	$t_{1u} + t_{2u} + g_u + h_u$	$5e + 3a_1 + 2a_2$	$5(0) + 3(+1) + 2(-1)$	positive (+1)
HOMO-LUMO+2	$a_u$	$a_2$	-1	negative
	$g_u$	$e, a_1, a_2$	0, +1, -1	flat
	$2 h_u$	$2 \times e, e, a_2$	$2 \times 0, 0, -1$	negative
Net	$a_u + g_u + 2h_u$	$5e + 1a_1 + 4a_2$	$5(0) + 1(+1) + 4(-1)$	negative (-3)

**Table 3:** Symmetries of singlet components of the HOMO-LUMO+1 and the HOMO-LUMO+2 excitons under the  $I_h$  and  $C_{3v}$  point groups, their characters under reflection, and the net curvature of the bands. Positive and negative curvatures correspond to positive and negative signs of  $m^*$ , respectively. The numbers in the net curvature column do not correspond to predicted effective masses; they simply correspond to the number of remaining states if positive and negatively dispersing states are allowed to cancel.

about the relative energies of the excitonic sub-states. For instance, it is possible that not all 15 of the singlet HOMO-LUMO+1 combinations will be populated, and as such, the observed dispersion will only be due to the average over the populated states. Further calculations of these excited states, such as by a configuration interaction approach, would be needed to clarify this issue. Experimentally, the approach to determine if these states are excitonic or anionic in nature would be a wavelength-dependent study in which one can tune on or off molecular resonances; such resonances should not be present if the excitations are from the relatively flat density of states residing in the metallic substrate. The relatively congested nature of the  $C_{60}$  electronic levels may hinder this determination, but systems with a simpler electronic structure should be amenable to this approach.

Regardless of the excitonic or anionic qualities of the unoccupied orbitals probed in these experiments, it is clear that in studying the photoemission from the HOMO orbital that the dispersions should map exactly onto the above group theory and direct visualization routes, and this state does indeed have an unambiguously negative value of  $m^*$ .

Additionally, the LUMO level is actually partially occupied in the monolayer, and it does indeed have a positive dispersion (as predicted by its symmetry properties in  $C_{3v}$ ) when examined in two-

color 2PPE experiments (not presented here). However, this state lies close enough to the Fermi level that it quickly disperses above the high-energy cutoff, precluding any quantitative analysis.

As such, while the values of  $m^*$  presented for the LUMO+1 and LUMO+2 may not correspond to the motion of a single particle in a band, the estimated range of  $m^*$  for the HOMO ( $-3.5$ – $-20 m_e$ ) should be correct, as this state is initially occupied and there are no questions of the exciton vs. anion variety.

For all orbitals observed experimentally, it appears as if the different sub-bands do not disperse by more than the measured peak-width of approximately 500 meV for the HOMO level and 100 meV for the LUMO+1 and LUMO+2 orbitals. This is unfortunate, as otherwise we might be able to extract values of  $m^*$  for the different sub-bands. Instead, our measured dispersions correspond to movement of the center-of-energy of the band. The exact source of these relatively large peak widths is uncertain, but it has been suggested that they may be due to vibronic or phononic broadening.<sup>42,43</sup> The small splitting between sub-bands is not just an issue for 2PPE; the overall coupling between orbitals on adjacent molecules will likely involve an average over the closely-spaced levels unless chemical substitution or externally-applied fields enhance the splitting. The measurements from 2PPE are thus appropriate for describing the ensemble-averaged properties of thin films, which are relevant to their performance in device applications.

## 4 Conclusions

Angle-resolved 2PPE spectra were taken of  $C_{60}$  thin films on Ag(111), and the resulting dispersions for the HOMO, LUMO+1, and LUMO+2 states were fit to an effective mass  $m^*$ . To evaluate the experimental data, both direct and group theoretic considerations of nodal structure along the  $\bar{\Gamma}$ – $\bar{M}$  dispersion direction were made. For the HOMO, the sub-band nodal structure is consistent with our measured dispersion, and for the LUMO+1 and LUMO+2 levels, the bands have an appar-

ent nearly flat dispersion, and theoretical considerations are not sufficient to determine whether these features are due to states involving molecular excitations or charge transfer from the metal substrate. Nevertheless, these results indicate that angle-resolved 2PPE can be used as a direct experimental probe of band structure in systems with quite complicated electronic energy levels. The ability to measure the dispersions of both initially occupied and initially unoccupied states as functions of layer thickness and preparation will likely be a valuable asset in understanding the performance of model molecular-electronic devices.

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**Supporting Information Available:** Two-color 2PPE spectra of 1–10 ML C<sub>60</sub>/Ag(111) showing the presence of image potential states, LUMO and LUMO+1-derived features, and a peak due to an sp-band transition from the bulk substrate. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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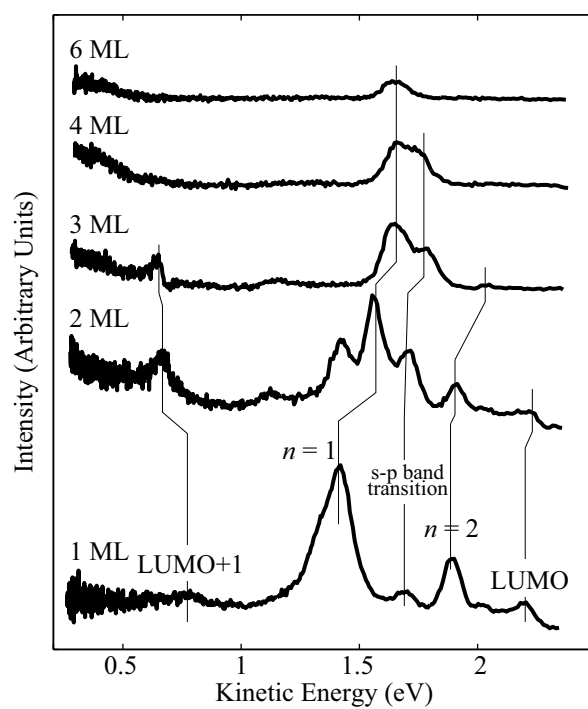
Supporting information for: Determination of band curvatures by  
angle-resolved two-photon photoemission in thin films of C<sub>60</sub> on  
Ag(111)

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## 1 Supporting Information

In addition to the one-color 2PPE spectra shown in Fig. 4 of the main text, two-color 2PPE spectra were taken as well (Figure S1). These spectra show the image potential states ( $n = 1$  and  $n = 2$ ) of the C<sub>60</sub>/Ag(111) interface, a state assigned to the partially occupied LUMO (populated via charge transfer from the metal to the first monolayer), and a feature arising from a bulk sp-band transition in the substrate. These states are indicated in the full energy-level diagram presented in Fig. 5 of the manuscript (except for the bulk transition), but as their properties are not relevant to the primary discussion, the two-color 2PPE spectra which show them are located here.



**Figure S1:** Two-color 2PPE spectra of C<sub>60</sub> layers of varying thickness, taken with a pump energy of 4.78 eV and a probe energy of 2.39 eV. The LUMO and LUMO+1 derived states from C<sub>60</sub> and the sp bulk-band transition are labelled as such. The features labelled  $n = 1$  and  $n = 2$  correspond to image potential states. The lines indicate how peak positions shift as a function of coverage.