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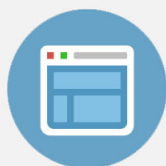
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Charge transfer between the Au(111) surface and adsorbed C₆₀: Resonant photoemission and new core-hole decay channels

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The interaction of C₆₀ with the Au(111) surface has been investigated using synchrotron radiation-based electron spectroscopy. Resonant photoelectron spectroscopy and autoionization spectroscopy have been used to probe the coupling between the molecule and the substrate. Three distinct high energy spectator Auger features were observed that are only evident for a monolayer of C₆₀ chemisorbed to the Au(111) surface and not a multilayer or the clean surface itself. Combined with C 1s x-ray absorption and valence band spectra, the data suggest a decay process not previously reported for this system. This is a spectator decay channel involving electrons transferred from the gold substrate to the adsorbed molecule, either in the ground state or during the timescale of the core-hole lifetime. Both possibilities are considered in the interpretation of the results, which support, on balance, a ground state charge transfer. © 2010 American Institute of Physics.

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I. INTRODUCTION

C₆₀ is a fascinating molecule from a nanoscience and molecular-electronics perspective. Since electrons can easily be donated to the fullerene cage from other molecules, atoms, and surfaces, C₆₀ is an ideal building block for molecular devices.¹ The ease with which electrons can be added to the cage is illustrated by the electronic properties of the alkali metal (A) fullerides A_nC₆₀ that range from insulating to metallic² and even high-temperature superconductivity.³ The charge transfer properties of fullerenes and their ability to act as electron acceptors have led to a number of applications in molecular photovoltaics when coupled with electron donors such as porphyrins.⁴ C₆₀ is known from scanning tunneling microscopy, among other techniques, to be strongly bound to gold surfaces,⁵ indicating chemisorption and therefore the possibility of charge transfer from the surface to the molecule. Indeed, in this paper C₆₀ monolayers were produced by annealing a thick film of C₆₀ to desorb the physisorbed multilayer and leave the more strongly bound monolayer chemisorbed to the surface. In this case of ionic bonding to the surface we might expect the fullerene lowest unoccupied molecular orbital (LUMO) to be partially filled by electrons from the surface. This has been shown to be the case for a C₆₀ monolayer on Au(111), where a weak feature around 0.1 eV below the Fermi level in angle resolved valence band photoemission of this surface was proposed to be the result of an estimated 0.8 electrons transferred to the fullerene cage.⁶ The weak LUMO-derived peak was not observed in earlier angle integrated valence band studies, although strong evidence of the formation of a chemisorption bond to the surface by modification of the occupied fullerene orbitals certainly was.⁷

In this paper we look at charge transfer in both direc-

tions: from lowest unoccupied molecular orbitals into the conduction band of the gold substrate, and from states near the Fermi level of the surface into the molecule. The former can be probed using the core-hole clock⁸ implementation of resonant photoemission (RPES) which has, in earlier work, led to the quantification of charge-transfer dynamics from adsorbed molecules to both semiconductor^{9,10} and metal surfaces.^{11,12} In the case of metallic surfaces, where there is the possibility for the core-excited LUMO to lie below the Fermi edge of the substrate, our previous RPES data have shown possible evidence for ultrafast back donation into a small chemisorbed aromatic molecule (bi-isonicotinic acid) on the timescale of the core-hole lifetime.^{11,12} The spectral features associated with this process are constant kinetic energy Auger-like electrons. Their energies are shifted higher than that normally accessible by the molecule with its usual complement of electrons, by an amount corresponding to the difference between the highest occupied molecular orbital and the lowest unoccupied molecular orbital (HOMO-LUMO). Here, we describe the results obtained for C₆₀ adsorbed on the Au(111) surface that show unambiguously that this process involves the charge transfer of electrons from the surface into the LUMO of the molecule, contributing new core-hole decay channels. However, the question concerning this and previous work still remains: does this happen in ground state or the core-hole excited state?

II. METHOD

Experiments were carried out at beamline I311 of the Swedish synchrotron facility MAX-laboratory in Lund. The beamline has a photon energy range of 30–1500 eV and is equipped with a Scienta SES200 hemispherical electron analyzer.¹³ The radiation has a high degree of elliptical polarization and may be considered as linearly polarized for the purposes of this study. The base pressure, in the analysis

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chamber, was in the mid- 10^{-11} mbar range and, in the preparation chamber, it was in the low 10^{-10} mbar range.

The substrate was a single crystal of dimensions 10 mm diameter \times 2.5 mm. It was mounted on a loop of tungsten wire (0.5 mm) that passed tightly through the body of the crystal, ensuring that a good electrical and thermal contact. A thermocouple was attached within the body of the crystal in order to accurately monitor the temperature. The crystal was cleaned along the lines of Barth *et al.*¹⁴ by cycles of sputtering using 1 kV Ar ions and then annealing at 900 K by passing a current through the tungsten wire mount. Surface contamination was checked by monitoring the C 1s core-level photoemission peak.

C₆₀ was evaporated from a Knudsen cell type evaporator at a temperature of ~ 425 °C onto the sample held at room temperature and a distance of ~ 20 cm. A multilayer of C₆₀ was produced by depositing for sufficient time so as to suppress the substrate Au 4f photoemission signal and to produce the characteristic symmetric lineshape and shake-up features in the C 1s spectrum.¹⁵ To obtain a monolayer coverage, the sample was then annealed to 300 °C to desorb the physisorbed multilayer so as to leave the chemisorbed monolayer. Again, the monolayer coverage was checked by monitoring the C 1s and Au 4f core-level peaks and the emergence of the characteristic asymmetric lineshape of the C 1s peak,¹⁵ and the C 1s:Au 4f peak ratio.

The monochromator exit slits of the beamline were set to give a resolution of ~ 50 meV for photons of energy $h\nu = 340$ eV. The photon energy was calibrated from the separation between the Au 4f peaks measured with first and second order radiation. For measuring x-ray absorption and resonant photoemission spectra, a taper (+4 mm) was applied to the undulator to reduce the intensity variation of the radiation as the photon energy was scanned. For x-ray absorption spectroscopy (XAS) and RPES measurements, the analyzer pass energy and entrance slits were set to give an analyzer resolution of ~ 500 meV with respect to binding energy. The analyzer was also set to record spectra in fixed mode for these measurements to give the best compromise between energy resolution and the large number of counts required for two-dimensional resonant spectra. For core-level spectra, the analyzer was set to record in swept mode.

III. RESULTS AND DISCUSSION

The valence band photoemission spectrum for a C₆₀ multilayer adsorbed on the Au(111) surface is presented in Fig. 1. The HOMO, HOMO-1, and HOMO-2 peaks are located at 1.45, 2.75, and 4.75 eV, respectively, leading to relative energy positions of 0, 1.3, and 3.3 eV.

Two-dimensional resonant photoemission data sets were measured for the clean Au(111) surface, a multilayer of C₆₀ and a C₆₀ monolayer. The monolayer and multilayer data sets are shown in Fig. 2 and were obtained by measuring the valence band photoemission up to 16 eV binding energy for a range of photon energies covering the C 1s absorption edge in 0.1 eV steps. The clean surface spectrum (not shown)

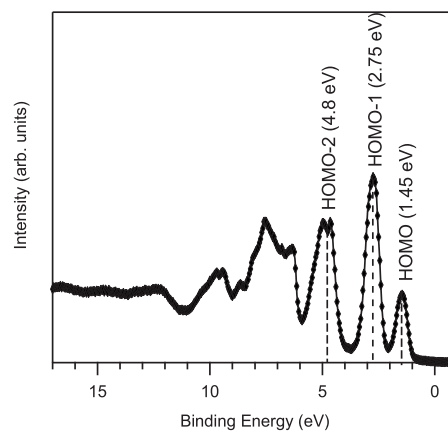


FIG. 1. Valence band photoemission spectrum ($h\nu=60$ eV) for a multilayer of C₆₀ on Au(111). The three highest molecular orbital peaks have similar spacings as the spectator bands in the RPES spectra for the monolayer [Fig. 2(b)].

exhibits simply an intense band due simply to the direct valence band photoemission of the clean Au(111), as we would expect.

The multilayer spectrum, shown in Fig. 2(a), presents a number of features associated with the resonant photoemission of the molecules isolated from the surface in a thick film. The binding energy scale of the multilayer spectrum was calibrated to Fermi level of the substrate via the second order C 1s peak (visible in the top left hand corner of the image) to take account of steady state charging in the thick film. When the photon energy reaches the LUMO resonance (and then again at the energies of the LUMO+1 and LUMO+2 resonances), there is a strong resonant enhancement of the HOMO at 1.5 eV and the HOMO-1 at 2.8 eV. This is known as *participator* decay, arising from the originally excited electron (in this case to the LUMO) being involved in the nonradiative decay of the C 1s core-hole, leading to a final state identical to that of direct photoemission.⁸ This is entirely expected in the case of the multilayer because electrons excited to the LUMOs in molecules which are isolated from the surface cannot tunnel away into the substrate conduction band on the timescale of the core-hole lifetime (a few femtoseconds) but can instead *participate* in an Auger-like core-hole decay process.

Since the participator final state [referred to as P_{LUMO} in Fig. 3(b)] is identical to that of direct photoemission of the valence orbital involved, these electrons exhibit a constant binding energy with increasing photon energy and appear as enhancements of the relevant occupied states at those photon energies corresponding to excitation to the various LUMO states. In addition to these participator electrons, there are features that track with constant kinetic energy which arise from *spectator* decay of the core-hole. In this case, the originally excited electron is not involved in the decay process, but merely spectates as an otherwise normal Auger process occurs, inducing little more than a small and upward spectator energy shift due to its presence in the unoccupied state in question. Spectator electrons, along with normal Auger electrons, account for the high intensity region observed in the RPES spectra on the right hand side—slowly drifting out of

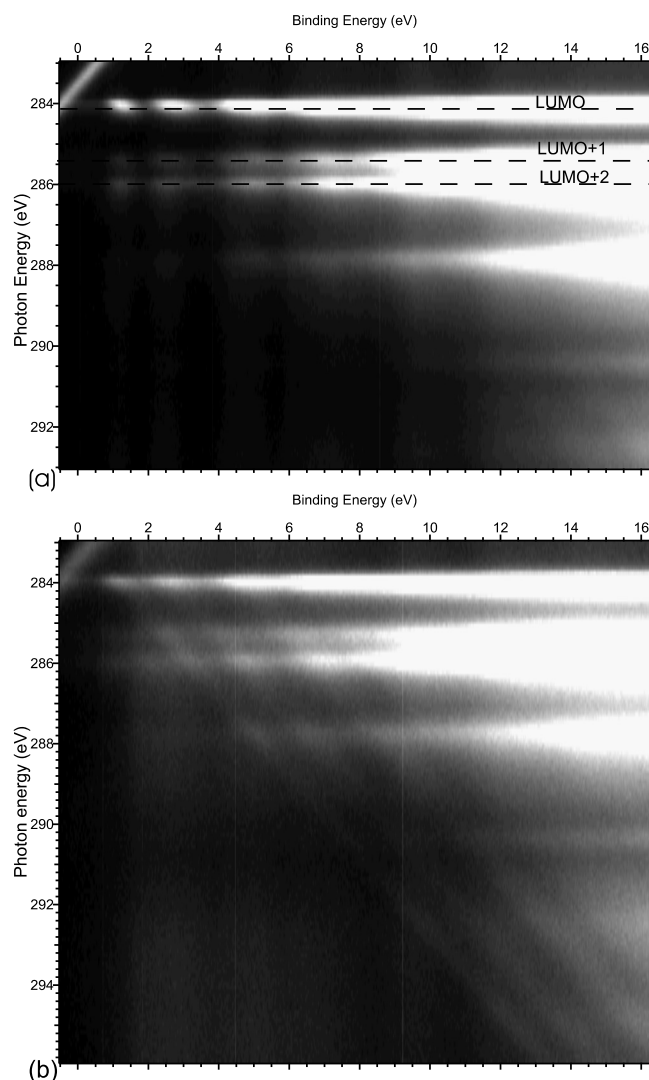


FIG. 2. Resonant photoemission spectra for (a) a multilayer of C_{60} and (b) a monolayer of C_{60} . The horizontal axis represents the binding energy and the vertical axis is the photon energy. The monolayer spectrum was calibrated to the Fermi level of the underlying substrate and the multilayer spectrum was calibrated to the monolayer using the second order $C\ 1s$ peak visible in the top right hand corner to take account of steady state charging in the thick film.

the energy window due to their constant kinetic energy. By a consideration of the electronic levels involved, as outlined in Fig. 3, it becomes clear that the highest kinetic energy Auger-like electrons that can be emitted—in the absence of charge transfer—will occur via a process in which two electrons from the HOMO are involved in the decay, spectated by an electron in a previously unoccupied molecular orbital. This is the autoionization decay process referred to as S_{LUMO} in Fig. 3(c). The minimum possible energy separation between participator and spectator electrons will occur at the LUMO absorption photon energy and will be equal to the HOMO-LUMO binding energy separation of the molecule.

Turning to the RPES spectrum for the C_{60} monolayer shown in Fig. 2(b), we now observe three new low binding energy (high kinetic energy) features as diagonal bands to the low binding energy side of the spectator and Auger electrons. These are absent from both the clean surface spectrum (not shown) and the multilayer spectrum [Fig. 2(a)]. These three

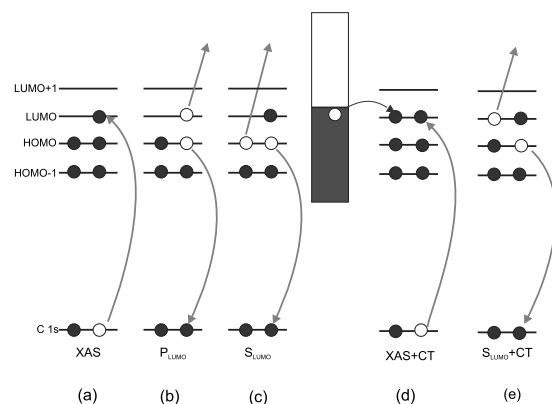


FIG. 3. Electron excitation and deexcitation processes: (a) resonant core-level excitation into unoccupied bound states (x-ray absorption); (b) participator decay following x-ray absorption induced core-hole; (c) spectator core-hole decay; (d) x-ray absorption in the presence of charge transfer from states near the Fermi level of the metal substrate; and (e) spectator core-hole decay in the presence of charge transfer.

features track with constant kinetic energy and must, therefore, arise from a new Auger-like decay channel available only to those molecules directly coupled to the metal surface. The kinetic energies of the three lines are calculated as 282.3, 281.0, and 278.8 eV, respectively (± 0.2 eV), leading to relative energy positions of the three Auger lines of 0, 1.3, and 3.5 eV. The spacings and profile of the constant kinetic energy (KE) features closely match those of the peaks at the top of the valence band spectrum, as shown for the C_{60} multilayer in Fig. 1.

As a consequence, it is reasonable to assume that the origin of the three constant kinetic energy features lies in an Auger-like core-hole decay process involving the HOMO, HOMO-1, and HOMO-2 of the fullerene molecule. Furthermore, it is clear that the resulting decay process must involve an interaction with the gold substrate since these features are absent from the multilayer or the clean Au(111) spectra. In most cases we might expect the transition probability and therefore the intensity of the resulting Auger-like features to get weaker going from HOMO to HOMO-1 and HOMO-2 due to the diminishing spatial overlap with the LUMO. Here, however, the effect is suppressed due to the LUMO and HOMO levels being largely delocalized over the whole C_{60} cage.¹⁶

If we focus our discussion—for the moment—on the highest kinetic energy feature, assigned to a core-hole decay channel involving an electron from the HOMO, we see that the kinetic energy is too high for it to be a simple spectator process. Indeed, if we extrapolate the path of this feature back to the LUMO absorption energy, we find that it intersects with the binding energy of the HOMO itself. So, when the originally excited electron is excited to the LUMO, the resulting final state of the decay process is one that is indistinguishable from direct photoemission of the HOMO, and therefore from a participator decay process involving an electron from the HOMO. As illustrated schematically in Fig. 3, this can only occur if an additional electron is transferred from the gold substrate into the LUMO prior to the core-hole decay process. The process referred to in Fig. 3(e) as $S_{LUMO+CT}$ is a spectator decay channel involving an

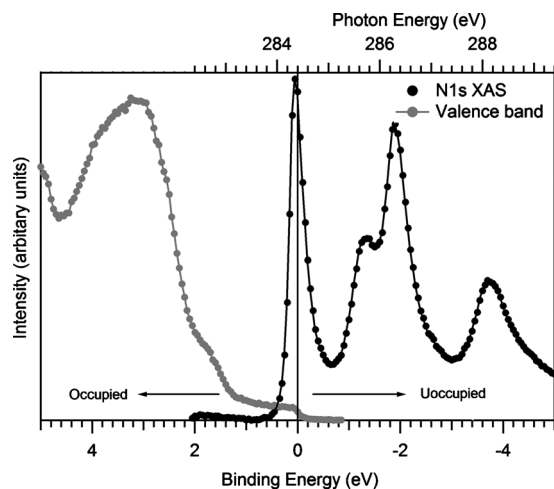


FIG. 4. Energy level alignment of the substrate valence band and the unoccupied molecular orbitals of the molecule placed a common binding energy scale. Created by combining the photon calibrated x-ray absorption spectrum (top photon energy axis), the measured C 1s photoemission core-level binding energy of 284.4 eV, and the valence band photoemission spectrum for the C_{60} monolayer calibrated to the Fermi level of the Au(111) surface (Ref. 18).

electron from the HOMO [or HOMO-1, HOMO-2 for the other two bands in Fig. 2(b)] and a charge-transfer process into the LUMO from states near the Fermi level of the Au(111) substrate. This results in a final state which is identical to direct photoemission of the adsorbed molecule following a charge-transfer event (from the surface to the molecule). It is easier to understand this process when we consider that it is always the electron transferred from the surface into the LUMO that is emitted in the Auger process that gives rise to the diagonal features in Fig. 2 even when the initial core-excitation is to the LUMO+1, LUMO+2, etc. As such, we will use the term *superspectator* to refer to all such processes involving an electron transferred from the substrate, and to distinguish them from normal spectator decay.

In the case of probing charge transfer *from* an adsorbed molecule to the conduction band of the surface to which it is bound, monitoring the participator channel can actually elucidate the dynamics of that process.⁸⁻¹⁰ When examining charge transfer in the other direction, however, the presence of a superspectator decay channel does not, on its own, tell us anything about *when* the electron was transferred to the molecule. Charge transfer between the molecule and the substrate in either direction depends on the energetics of the lowest unoccupied molecular orbitals with respect to the substrate density of states. If the LUMO lies beneath the Fermi level of the gold surface then charge transfer is possible. In the core-excited state, the presence of the core-hole can lead to the LUMO state being excitonically pulled down so that it crosses the Fermi level of the gold surface.¹⁷ We can measure the position of the core-excited LUMO with respect to the Fermi level by placing the calibrated C 1s XAS and valence band photoemission for the C_{60} monolayer on a common binding energy scale,¹⁸ as in Fig. 4. The data show the LUMO of the molecule to lie mostly below the Fermi level of the Au(111) surface. This would theoretically allow

the transfer of electrons from the valence band of the metal to the majority of the vibrational states of the LUMO that now lie below the Fermi level. A similar energy alignment was found for bi-isonicotinic acid on Au(111) in which a charge-transfer spectator process was first detected.¹¹

While we can directly measure the energy alignment of the LUMO in the core-excited state with respect to the substrate, as shown in Fig. 4, x-ray absorption cannot tell us where the LUMO is located in the ground state. But there are timescale consequences to this question. If the LUMO lies partially below the Fermi edge already in the ground state, then charge transfer could occur from the surface at any time. However, if the LUMO lies below the Fermi edge only in the core-excited state, then the charge transfer of electrons from the surface to the C_{60} molecule must occur during the core-hole lifetime in order for it to be involved in the core-hole decay process. This would place the charge-transfer dynamics on the low femtosecond timescale. The key consideration in addressing this question is the extent to which the core-hole pulls down the LUMO in the core-excited state¹⁷ compared to the ground state.

A. Charge transfer in the core-excited state: To and from the molecule

While the superspectator lines are evidence for the presence of charge transfer in the *reverse* direction (from the surface into the molecule), we can actually get a measure of the charge transfer dynamics in the *forward* direction (from the molecule to the surface) from the participator channel in the RPES spectrum as mentioned above. In Fig. 2 participator peaks are observed for both the multilayer and monolayer, appearing as resonant enhancements of the HOMO, HOMO-1, and HOMO-2 peaks at the absorption energies corresponding to excitation to the LUMO, LUMO+1, and LUMO+2. An integration of the intensity over the HOMO peak as a function of photon energy is shown for both the multilayer and monolayer in Fig. 5, and compared to the associated x-ray absorption spectrum (normalized to the intensity of the LUMO) in both cases.

A large proportion of participator electrons are expected in the case of the multilayer as the molecules are effectively isolated from the substrate so that no charge transfer can take place. Electrons excited to the LUMOs therefore remain on the molecule long enough to participate in the core-hole decay, leading to a final state identical to direct photoemission of the HOMO state involved [Fig. 3(b)]. In fact, the multilayer is taken as the benchmark in the core-hole clock analysis to determine the anticipated participator intensity for each LUMO state in the absence of charge transfer.⁸⁻¹⁰ In the case of the C_{60} monolayer on Au(111), an exact quantitative analysis is not possible since the RPES and XAS need to be normalized to the intensity of the LUMO. Because the LUMO of C_{60} in the core-excited state lies, in part, both above and below the Fermi level of the substrate, the possibility of charge transfer into and out of this state renders the normalization quantitatively unreliable. However, qualitatively there is clearly a very strong participator intensity for the LUMO+1 and +2, indicating a very slow rate of charge

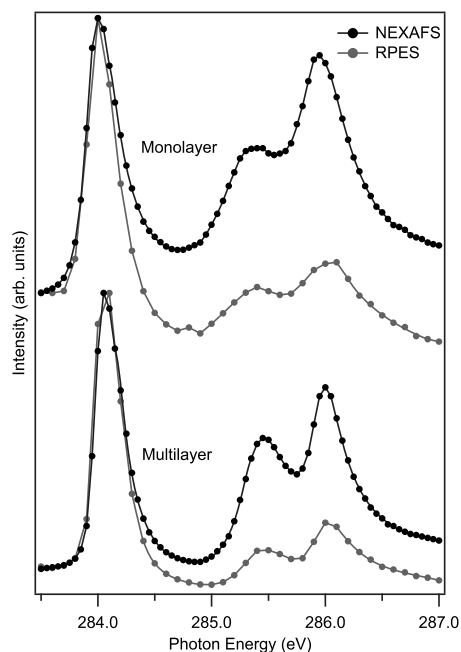


FIG. 5. C 1s RPES and C 1s XAS spectra of the C₆₀ multilayer and monolayer on Au(111). The RPES spectra shown here are binding energy integrations from 0 to 2 eV over for the data sets shown in Fig. 2.

transfer (far outside the timescale of the core-hole lifetime) from those states, despite overlapping energetically with the substrate conduction band.

In a general sense, it need not automatically follow that slow charge transfer in the forward direction implies a similarly slow charge transfer in the reverse direction. However, charge transfer requires two conditions to be met: there must be energetic overlap so that filled state in the molecule overlaps with empty states in the substrate, and there should be sufficient chemical coupling between to provide a charge transfer pathway. The first condition is met for the LUMO +1 and +2 of C₆₀ on Au(111), as shown in Fig. 4, thus the strong participator channel in this case suggests insufficient coupling to the substrate to facilitate charge transfer on a timescale comparable to core-hole lifetime. Added to this, we have the fact that charge transfer from a surface to an adsorbed molecule should in principle be an altogether slower process than the other way around. If we consider an electron passing from molecular states to Au states, this electron will delocalize, existing in a mixed state where it will coherently sample all coupled states. The enormous number of conduction band states reduces the likelihood of the electron returning to the molecular state. Coherence with the initial state is lost on a timescale of the order of 10 fs through electron relaxation processes^{19,20} so the continuum of states is sufficient to localize the electron in the substrate. In contrast if we consider an electron tunneling from a continuum of states into a discrete molecular state, charge localization on the molecule should require the breaking of the energy level alignment by nuclear degrees of freedom. The time this takes is of order 100 fs for most molecular species.^{19,20} These conditions may be relaxed to some extent for C₆₀ and there is evidence from RPES and x-ray emission spectroscopy for ultrafast vibronic coupling in C₆₀ on the timescale of the

core-hole decay.²¹ However, the absence of charge transfer on the low femtosecond timescale in the forward direction should be a strong indicator that a similar timescale cannot be achieved in the reverse direction.

B. Charge transfer in the ground state: To the molecule

A consideration of charge transfer in the core-excited state suggests that the electrons responsible for the super-spectator decay channels in C₆₀/Au(111) are more likely to be transferred from states near the Fermi level of the surface into the LUMO of the molecule already in the ground state. For this to occur, the LUMO would need to lie partially below the Fermi level before the core-excitation. In Fig. 4 the peak of the LUMO state lies just 0.1 eV below the Fermi level in the core-excited state. In order for the LUMO to lie below the Fermi level in the ground state the effect of the C 1s core-exciton on the position of the LUMO in the XAS must be negligible.

For solid C₆₀, the difference between the energy of the LUMO in the core-excited state and the ground state, determined using valence photoemission and inverse photoemission, respectively, is around 1.8 eV.¹⁷ This shift is dominated by the Coulomb interaction, estimated to be around 1.5 eV.⁸ A similar shift adsorbed C₆₀ would place the ground state LUMO around 1.75 eV above the Fermi level of the Au(111) surface, and no surface-to-molecule charge transfer would be possible. However, the screening effect of the metallic surface and the pinning of the LUMO to the Fermi level by virtue of the formation of an ionic bond to the surface might negate the excitonic shift such that the XAS spectrum measured for the monolayer more closely matches the true ground state picture. Low temperature scanning tunneling spectroscopy (STS) and density functional theory calculations have recently shown the ground state LUMO of C₆₀ adsorbed on the Au(111) surface to sit just 0.5 eV above the Fermi level and to be a relatively broad resonance due to symmetry breaking and the lifting of the LUMO's threefold degeneracy.²²

A consideration of the energy gain afforded by the image potential, due to the highly polarizable metal surface, and the distortion of the adsorbed fullerene molecule has also previously been shown to drastically reduce the HOMO-LUMO gap and therefore feasibly allow the overlap of at least a small portion of the LUMO with the Fermi level of the gold surface in the ground state.⁷ It is therefore theoretically possible for charge to be transferred from the gold surface to C₆₀, and thus the formation of an ionic chemisorption bond. The partial occupation of the LUMO in the ground state though should, in principle, be measurable in valence band photoemission. The valence band spectrum ($h\nu=60$ eV) for the C₆₀ monolayer on the Au(111) surface, shown in Fig. 4, is insufficient to demonstrate this. However, high-resolution angle resolved valence band photoemission measured at lower photon energies has indeed detected a LUMO-derived peak at a binding energy of 0.1 eV below the Fermi level of the substrate for an annealed monolayer of C₆₀ on the Au(111) surface.⁶ This peak arises from electrons transferred

to those vibrational states within the LUMO that lie just below the Fermi level of the surface, while the LUMO itself may be centered 0.5 eV above the Fermi level, as shown by STS.²² From the photoemission LUMO-derived intensity, the amount of charge transferred from the surface to the molecules was estimated at around $0.8e$ per C_{60} molecule. This supported the earlier surface-enhanced Raman experiments that suggest that the bonding interaction between gold and C_{60} is largely ionic in nature, albeit less so than on other noble metal surfaces.²³ The lower amount of charge transferred to gold than to other metal surfaces may be due to an interface dipole layer caused by the gold's asymmetric 6 *sp*-band orbitals at the gold-vacuum interface. So the HOMO and HOMO-1 orbitals will be shifted slightly higher in energy (~ 0.2 eV).²⁴ This would cause a reduction in the energy gain due to the image potential, although not large enough to prevent charge transfer from the surface.

IV. CONCLUSIONS

Our resonant photoemission measurements of a C_{60} monolayer on the Au(111) surface show three distinctive constant kinetic energy features. Their absence from multilayers of C_{60} and from the clean gold surface shows that the features are due directly to the interaction between the molecule and the substrate. The kinetic energies of these features closely match the separation of the three highest occupied molecular orbitals of C_{60} , indicative of a core-hole decay channel involving electrons from these three orbitals. However, the kinetic energy is higher than can be achieved by the molecule with its ground state complement of electrons, requiring an additional electron to be transferred from states near the Fermi level of the Au(111) substrate into the LUMO, which can then take part in the autoionization core-hole decay process. Moreover, the highest kinetic energy feature of the three tracks back to the binding energy of the HOMO at the LUMO position, and hence results in a final state indistinguishable from both direct photoemission of the charge-transferred molecule HOMO and participator decay in resonant photoemission. The additional electron is most likely transferred from the substrate in the ground state rather than within the core-hole lifetime in the core-excited state. This assertion is based on the observation of very slow charge transfer in the forward direction from the molecule into the conduction band of the substrate, certainly outside the core-hole lifetime. This agrees with evidence from angle resolved photoemission in which LUMO-derived intensity was found just below the Fermi level arising from electrons transferred to those vibrational states in the low energy tail of the LUMO, which has been shown previously by STS to lie 0.5 eV above the Fermi level.²² Our x-ray absorption data place the core-excited LUMO at 0.1 eV below the Fermi level, which would suggest core-excitonic shift of just 0.6 eV to lower binding energy, further suggesting that such effects do not play such a significant role where the molecule is chemisorbed to a metallic surface in a bonding mechanism largely characterized by charge transfer. We are currently exploring this through a similar study of small aromatic molecules on the Au(111) surface. Since the intensity of the su-

perspectator features in the RPES spectra of the monolayer should be directly related to the amount of charge transferred to the molecule from the surface, the next step in this investigation will be to study C_{60} monolayers on the Cu(111) surface, where the amount of charge transferred to the fullerene molecules has been estimated from photoemission to be $1.6e$.⁶

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- ¹L. Sánchez, R. Otero, J. María Gallego, R. Miranda, and N. Martín, *Chem. Rev. (Washington, D.C.)* **109**, 2081 (2009).
- ²R. C. Haddon, A. F. Hebard, M. J. Rosseinsky, D. W. Murphy, S. J. Duclos, K. B. Lyons, B. Miller, J. M. Rosamilia, R. M. Fleming, A. R. Kortan, S. H. Glarum, A. V. Makhija, A. J. Muller, R. H. Eick, S. M. Zahurak, R. Tycko, G. Dabbagh, and F. A. Thiel, *Nature (London)* **350**, 320 (1991).
- ³A. F. Hebard, M. J. Rosseinsky, R. C. Haddon, D. W. Murphy, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez, and A. R. Kortan, *Nature (London)* **350**, 600 (1991).
- ⁴H. Imahori, Y. Kashiwagib, T. Hasobe, M. Kimurab, T. Hanadac, Y. Nishimurad, I. Yamazakid, Y. Arakie, O. Itoe, and S. Fukuzumib, *Thin Solid Films* **451–452**, 580 (2004).
- ⁵E. I. Altman and R. J. Colton, *Surf. Sci.* **295**, 13 (1993).
- ⁶C.-T. Tzeng, W.-S. Lo, J.-Y. Yuh, R.-Y. Chu, and K.-D. Tsuei, *Phys. Rev. B* **61**, 2263 (2000).
- ⁷A. J. Maxwell, P. A. Brühwiler, A. Nilsson, N. Mårtensson, and P. Rudolf, *Phys. Rev. B* **49**, 10717 (1994).
- ⁸P. A. Brühwiler, O. Karis, and N. Mårtensson, *Rev. Mod. Phys.* **74**, 703 (2002).
- ⁹J. Schnadt, P. A. Brühwiler, L. Patthey, J. N. O'Shea, S. Södergren, M. Odellius, R. Ahuja, O. Karis, M. Bässler, P. Persson, H. Siegbahn, S. Lunell, and N. Mårtensson, *Nature (London)* **418**, 620 (2002).
- ¹⁰L. C. Mayor, J. B. Taylor, G. Magnano, A. Rienzo, C. J. Satterley, J. N. O'Shea, and J. Schnadt, *J. Chem. Phys.* **129**, 114701 (2008).
- ¹¹J. B. Taylor, L. C. Mayor, J. C. Swarbrick, and J. N. O'Shea, *J. Chem. Phys.* **127**, 134707 (2007).
- ¹²J. B. Taylor, L. C. Mayor, J. C. Swarbrick, J. N. O'Shea, and J. Schnadt, *J. Phys. Chem.* **111**, 16646 (2007).
- ¹³R. Nyholm, J. N. Andersen, U. Johansson, B. N. Jensen, and I. Lindau, *Nucl. Instrum. Methods Phys. Res. B* **467–468**, 520 (2001).
- ¹⁴J. V. Barth, H. Brune, G. Ertl, and R. J. Behm, *Phys. Rev. B* **42**, 9307 (1990).
- ¹⁵C. J. Satterley, L. M. A. Perdigão, A. Saywell, G. Magnano, A. Rienzo, L. C. Mayor, V. R. Dhanak, P. H. Beton, and J. N. O'Shea, *Nanotechnology* **18**, 455304 (2007).
- ¹⁶X.-X. Wang, Y.-B. Xu, H.-N. Li, W.-H. Zhang, and F.-Q. Xu, *J. Electron Spectrosc. Relat. Phenom.* **165**, 20 (2008).
- ¹⁷J. Schnadt, J. Schiessling, and P. A. Brühwiler, *Chem. Phys.* **312**, 39 (2005).
- ¹⁸J. Schnadt, J. N. O'Shea, L. Patthey, J. Krempasky, N. Mårtensson, and P. A. Brühwiler, *Phys. Rev. B* **67**, 235420 (2003).
- ¹⁹J. M. Lanzafame, R. J. D. Miller, A. A. Muentner, and B. A. Parkinson, *J. Phys. Chem.* **96**, 2820 (1992).
- ²⁰J. M. Lanzafame, S. Palese, D. Wang, R. J. D. Miller, and A. A. Muentner, *J. Phys. Chem.* **98**, 11020 (1994).
- ²¹L. Kjeldgaard, T. Käåmbre, J. Schiessling, I. Marenne, J. N. O'Shea, J. Schnadt, C. J. Glover, M. Nagasono, D. Nordlund, M. G. Garnier, L. Qian, J.-E. Rubensson, P. Rudolf, N. Mårtensson, J. Nordgren, and P. A.

Brühwiler, *Phys. Rev. B* **72**, 205414 (2005).

²²K. J. Franke, G. Schulze, N. Henningsen, I. Fernandez-Torrente, J. I. Pascual, S. Zarwell, K. Rueck-Braun, M. Cobian, and N. Lorente, *Phys. Rev. Lett.* **100**, 036807 (2008).

²³S. J. Chase, W. S. Bacsa, M. G. Mitch, L. J. Piloni, and J. S. Lannin, *Phys. Rev. B* **46**, 7873 (1992).

²⁴S. Veenstra, A. Heeres, G. Hadziioannou, G. Sawatzky, and H. Jonkman, *Appl. Phys. A: Mater. Sci. Process.* **75**, 661 (2002).