Bulk electronic structure of K₃C₆₀ as revealed by soft x-rays

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We present C $1s$ x-ray absorption, x-ray emission, and resonant inelastic x-ray scattering (RIXS) spectra of single-phase crystalline K₃C₆₀. The comparison to valence-band photoelectron spectra from the same sample facilitates identification of the contribution from surface and bulk electronic states in the latter. Bulk-sensitive techniques show that the valence bands of K₃C₆₀ and pure C₆₀ are characterized by spectral features of similar width, in agreement with the predictions of band-structure calculations. Symmetry selectivity in the RIXS process allows us to assign peaks in the C $1s$ absorption spectrum, demonstrating a close correspondence with pure C₆₀ also in the conduction band. The symmetry selectivity is as pronounced in K₃C₆₀ as in pure C₆₀, indicating that the local C₆₀ symmetry is not appreciably affected by the K doping, either in the ground state or intermediate state, on the time scale of 6 fs.

PACS number(s): 78.40.Ri, 73.20.At, 78.70.En, 79.60.−i

I. INTRODUCTION

The fulleride salts of composition A_3C_{60} (where A is an alkali metal) as well as other fullerides have attracted wide interest due to their transport properties, not least because they represent a class of high-temperature superconductors.[1] In a one-electron picture with rigid band filling, the A_xC_{60} compounds should be metallic for $0 < x < 6$, which corresponds to partial filling of the threefold degenerate t_{1u} lowest unoccupied molecular orbital (LUMO) of C₆₀. However, of the observed stable phases with partial filling ($x = 1$, 2, 3, and 4), only a few stoichiometries show metallic properties. In particular, metallic A_3C_{60} has been investigated with the first sample K₃C₆₀ as the primary testing ground.[1]

Band-structure calculations[2] of K₃C₆₀ predict the energy bands to be narrow, similar to bulk (undoped) crystalline C₆₀. However, numerous photoemission spectroscopy (PES) data show broad structures for the K₃C₆₀ stoichiometry.[3–13] A number of theoretical studies have been carried out in order to elucidate the role of effects such as electron-electron correlation or electron-phonon coupling and the Jahn-Teller effect[1,14,15] on the electronic structure.

The most recent work concludes that both of these effects have to be included to describe the K₃C₆₀ electronic structure.[16–18] Notably, transport-related and optical measurements have supplied the necessary parameters for these studies, whereas PES has remained an enigma to the field. PES is normally a natural choice to probe the electronic structure. The earliest PES studies, however, suffered from uncertainties in sample stoichiometry and the presence of multiple phases. Samples were typically produced by evaporating potassium on a film of C₆₀, attempting to enhance the uniformity of intercalation by heating the sample.[3,19] The development of a reliable sample preparation method[20] has led to a convergence of the experimental PES results.[8,10–12] The interpretations of the spectra, however, diverge. Since

the probing depth of PES is limited to the first few molecular layers of the sample,[13,19,21] the important question of whether the bulk and surface have identical stoichiometry and electronic structure has been strongly debated.

We have previously presented a different set of PES measurements which are consistently explained by a model of the surface layer as a correlated two-dimensional insulator and the bulk as metallic, resolving many contradictory claims in the literature and offering an explanation of why transport measurements obtained a higher density of states at E_F, for example.[12,13] There have been no comparable measurements that are truly bulk sensitive to test the hypothesis of a surface effect. A similar issue has emerged in the interpretation of the x-ray absorption spectroscopy (XAS) data, which was attributed to a bulklike surface layer with contributions from symmetry-split core levels.[9]

The techniques of soft x-ray emission spectroscopy (XES), which measures the same final states as PES, and resonant inelastic x-ray scattering (RIXS), which can be used to monitor electronic symmetry, offer the means to accomplish truly bulk-sensitive measurements; their typical probing depth is several thousand angstroms, enabling one to address the issues above from a new perspective. Here we present XES and RIXS spectra of K₃C₆₀ in the vicinity of the C K edge. We find that the spectral features are almost as narrow as in the spectra of pure C₆₀, in agreement with band-structure calculations of bulk K₃C₆₀ and our recent analysis of PES data.[12,13] We also use the symmetry information in RIXS (Ref. 22) to assign the peaks in the XAS spectrum, and we find that the orbital symmetries are virtually uninfluenced by K intercalation, so that the spectrum for the compound has a direct correspondence to that of solid C₆₀. The fact that the excitation energy dependence of RIXS is similarly pronounced in both C₆₀ and K₃C₆₀ indicates that the local symmetry is preserved to a similar extent for the RIXS process of K₃C₆₀ as for solid C₆₀. Overall, the data are consistent with a largely molecular description of K₃C₆₀.

II. EXPERIMENT

The experiments were carried out at the surface branch of beamline I511 at MAX-lab, Lund.[23] The beamline provides linearly polarized light from an undulator source, monochromatized using a Zeiss SX700 plane grating monochromator (Au coated, line density of 1221 lines/mm). The RIXS spectra were recorded using the grazing incidence grating spectrometer with a 1200 lines/mm spherical grating and a 10 μm entrance slit. With these parameters, the resolution of the spectrometer was 0.15 eV. The resolution of the monochromator was set to 0.1 eV. XAS spectra were acquired using a high pass yield detector, set to accept C 1s Auger electrons. The recorded electron yield was normalized to the incoming photon flux using a clean gold mesh placed after the optical elements. The energy resolution in the XAS spectra was better than 20 meV. The base pressure was 2×10^{-10} mbar.

Single-crystal K_3C_{60} was obtained by sublimation of alternating C_{60} and potassium layers onto a clean Cu(111) surface. In every cycle, the stoichiometry was always kept below $x=3$ as checked by PES. The deposition rate was calibrated via the time to obtain a monolayer prior to sample preparation. After ten deposition cycles, a sample approximately 300 Å thick was obtained. Excess C_{60} was then sublimed under controlled temperature conditions similar to the *vacuum distillation* approach.[20] The PES data of the K_3C_{60} sample[12,13] were in good agreement with those of earlier reports.[9–11] A (1×1) (111) surface pattern was confirmed by low-energy electron diffraction, consistent with previous work.[10]

III. RESULTS AND DISCUSSION

A. C 1s excitations

The electronic transitions studied in the present work are illustrated in Fig. 1. The occupied valence levels are represented by the highest occupied molecular orbital (HOMO) and the level below (HOMO-1), and the unoccupied valence levels by the LUMO. XES and RIXS are illustrated in a two-step picture, which often is applicable to XES, but ignores the coherent effects often important in RIXS.[24] In core level and valence level PES, electrons are ejected and the molecule is left in an ionized state. The first step for both techniques consists of the absorption of a photon. The intermediate state in XES resembles a core hole PES final state, whereas in RIXS, the system can be said to have a core exciton. The excited intermediate state decays with the emission of an x-ray photon. The final state in XES is identical to the final state in valence PES, whereas that in RIXS is a valence exciton.

To better understand the RIXS technique, we want to consider the excitation step in more detail. The C 1s XAS spectra of pristine C_{60} and K_3C_{60} are shown Fig. 2. For now, it is useful to note that the energies chosen as excitation steps for RIXS in Fig. 3 are indicated with arrows and labeled by capital and small letters for C_{60} and K_3C_{60}, respectively. Recall that the spectrum of solid C_{60} is quite similar to that of molecular C_{60}, with an intensity distribution related to the
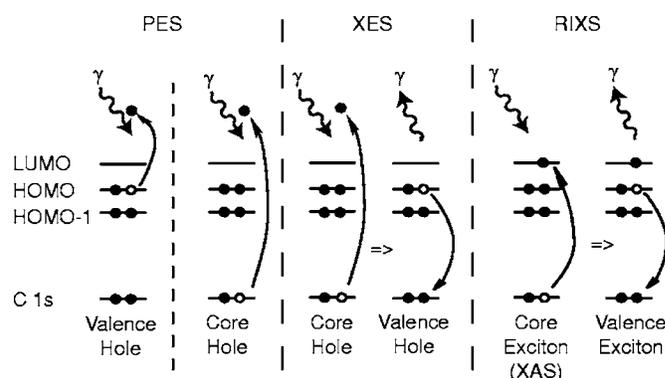
FIG. 1. A schematic of the techniques employed. In each case, the final state of the indicated process is shown, along with the associated excitation and/or deexcitation transitions and associated particles (photon and/or electron) for both photon-in–photon-out techniques. Core-level and valence-level PES provide a starting point, creating hole states. For XES, core photoionization first creates the same state as in PES as shown, followed by a transfer of the hole to the valence states and simultaneous emission of a photon that is detected, which in a single-particle picture creates the same final state as valence PES. In RIXS, which is analogous to XES, the intermediate state corresponds to an XAS excitation, which then decays similarly to XES, but with an extra electron in the initially unoccupied valence levels. RIXS leaves the molecule in a valence-excited state, which leads to different emitted photon energies than in XES, as discussed in detail in the text. The two steps are usually measurably coherent in RIXS, which further differentiates it from XES, as discussed in the text.

empty density of states, but strongly modified by core hole effects.[25–27] The absorption spectrum of K_3C_{60} shows similar resonances that are, however, somewhat broader than the corresponding excitation in C_{60}, and the absorption edge is slightly shifted to lower energies. It is generally accepted that the reduced intensity in the LUMO-derived resonance of K_3C_{60} is approximately proportional to the number of states
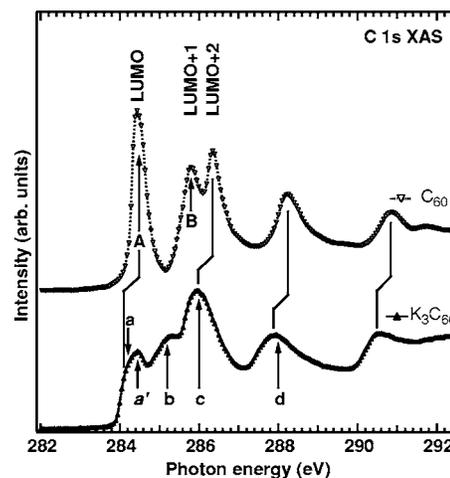
FIG. 2. C 1s XAS of C_{60} and K_3C_{60} measured via Auger electron yield, with the first three resonances of solid C_{60} labeled according to the unoccupied molecular orbitals from which they are derived. The arrows indicate the excitation energies for the spectra in Fig. 3.
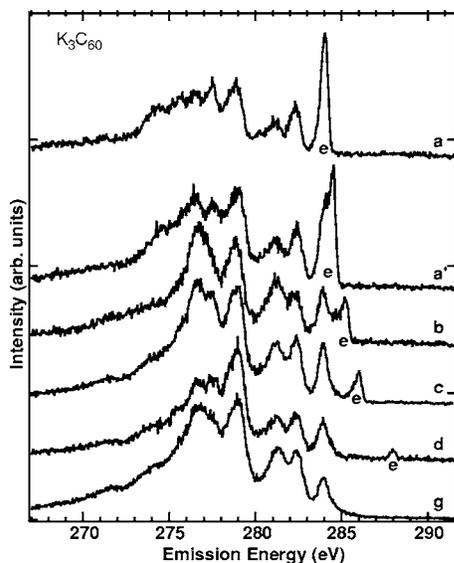
FIG. 3. Photon-in–photon-out spectra for K$_3$C$_{60}$ recorded at the indicated excitations of Fig. 2 (RIXS) and at 306 eV (*g*), which are taken to correspond to off-resonant excitation, i.e., XES. Peak *e* in the spectra is due to elastic (Rayleigh) scattering at the excitation energy.

filled in the ground state.[3,28] This tendency was, however, implicitly challenged recently,[11] and the resolution of these conflicting views is taken up in Sec. III C.

B. Occupied states

The photon-in–photon-out spectra obtained for K$_3$C$_{60}$ are shown in Fig. 3. The spectra show certain similarities at all excitation energies, such as the HOMO-derived peak between 282 and 283 eV, and several other peaks at lower emission energies which can be associated with molecular orbitals of the free molecule. A detailed discussion of such peak assignments was previously given for solid and/or molecular C$_{60}$.[22] For K$_3$C$_{60}$, a different feature is the half-filled LUMO-derived band, apparent at an emission energy of about 284 eV. This band is overlaid by a strong elastic peak as the excitation energy decreases to the lowest values considered here, just above 284 eV. Before considering the general variations as a function of excitation energy, we want to compare the XES and RIXS spectra to PES spectra of the same samples.

Figure 4 provides such a comparison for C$_{60}$ and K$_3$C$_{60}$. To plot the data on a common energy scale, we must first consider the energetics of the different processes in a common framework. For the sake of simplicity, we focus on the analysis of the HOMO and start with solid C$_{60}$. As discussed elsewhere[29,30] in some detail, the energetics for PES are relatively straightforward: (1) The core hole energy is given by the C $1s$ ionization potential (IP) of 289.6 eV.[29] (2) The HOMO hole energy is given by the HOMO IP of 6.9 eV.[29] (3) This yields an XES energy for the HOMO of (1)−(2) =282.7 eV, since the XES energy is to first order merely the difference between these states, in excellent agreement with our measurements. The energetics for RIXS are obtained by
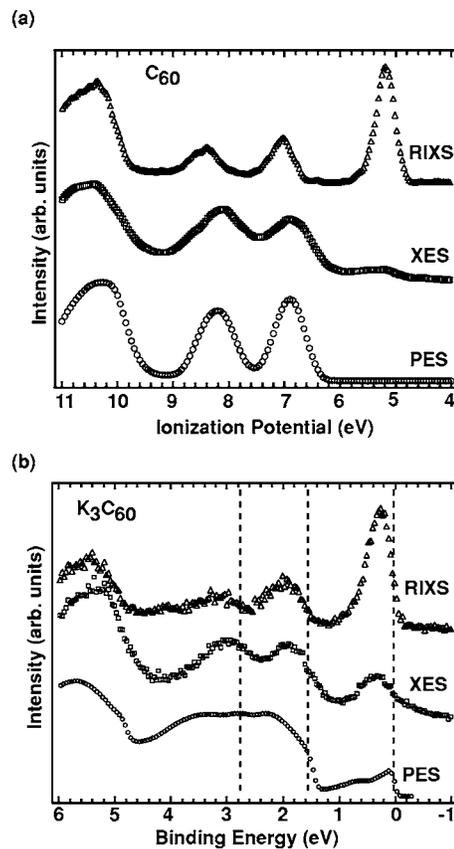
FIG. 4. Valence band PES, XES, and RIXS data of the indicated samples, measured with the excitation energies 110 eV (PES), 306 eV (XES), and as indicated by arrows *a* and *A* in Fig. 2 for RIXS. The positions of bulk contributions to the PES spectrum in (b) are marked by dashed lines.

a similar series of considerations: (4) The C $1s$→LUMO resonance has an energy of just under 284.5 eV.[25] (5) The HOMO→LUMO exciton can be considered to have an ionization potential of 4.8 eV.[30] (6) Thus the HOMO→LUMO transition itself has, for the present purposes, an energy given by (2)−(5)=2.1 eV. (7) This places the HOMO-derived final state in RIXS at (4)−(6)=282.4 eV, i.e., the RIXS data for this transition should lie about 0.3 eV lower in photon energy than the same feature in XES, which is consistent with the experimental results (present work and Ref. 22).

For K$_3$C$_{60}$ a similar analysis proceeds as follows: (1) Because ionization potentials have not been measured for K$_3$C$_{60}$, we take E_F as the reference level, for which the C $1s$ binding energy is[11,13] 285.0 eV. (2) The HOMO binding energy is[11,13] 2.3 eV. (3) This yields an XES energy for the HOMO of (1)−(2)=282.7 eV, the same value as for solid C$_{60}$, which is several tenths of an eV higher than the value seen, e.g., for transition "g" in Fig. 3. (4) The C $1s$→LUMO resonance has an energy of approximately 284.3 eV, as seen in Fig. 2. (5) The separation of the HOMO from the unoccupied LUMO is equal to its binding energy in the present case, giving 2.3 eV. (6) This places the HOMO-derived final state in RIXS at (4)−(5)=282.1 eV, which is too low compared to the experimental result of 0.2−0.3 eV.

These simple calculations, which ignore screening effects in the intermediate state, Jahn-Teller contributions, and general vibrational broadening, give nevertheless a semiquantitative description of the energetics, suggesting that such effects are limited to a scale of several tenths of an eV. These considerations, furthermore, show that placing the XES and RIXS spectra on the PES binding energy scale is not possible on the basis of energetics for K_3C_{60}, as it clearly is for pure C_{60}.

Thus the comparison in Fig. 4(b) is based on positioning the LUMO-derived part of the XES and RIXS spectra near zero binding energy as carefully as possible. What is obvious for both samples is that the peaks derived from the frontier valence bands can be clearly identified. For K_3C_{60}, most of these features are preserved in the XES and RIXS spectra, whereas in PES, they are greatly broadened and cannot be easily distinguished.

The spectral features of the two samples have similar shapes and widths in RIXS and XES. In contrast, the PES data of K_3C_{60} show structures which are substantially broader. Both techniques differ significantly in their probing depth. The present observations suggest that PES of K_3C_{60} displays contributions not limited to the bulk electronic structure, i.e., that the surface electronic structure has to be different and make a strong contribution to the PES data. The observations noted above do not allow us to be conclusive on this point, because satellites appearing due to K doping may appear with different intensities in PES and RIXS spectra. However, the present observations of simpler XES and RIXS spectra, more in line with the theoretical expectations of narrow bands, support our analysis elsewhere[12,13] that the surface electronic structure is different. To summarize, we find here that the valence bands of bulk C_{60} and K_3C_{60} are similar, in agreement with band-structure calculations.

Another difference between the two compounds in the photon-based spectroscopies is an intensity enhancement of the LUMO-derived band. Starting with pure C_{60}, in the simplest picture the XES spectra reflect the occupied states, and hence we do not expect any LUMO intensity. The observed LUMO intensity can be explained by the fact that the emission does not exclusively come from pure core hole states, but also from multiply excited states populated via shake-up processes as also observed in Auger.[31–33] We therefore assume that recombination of an electron which has been shaken up to the LUMO in the excitation process gives rise to the observed "LUMO intensity" in the XES spectrum of C_{60}. This implies that the electron in the LUMO is localized at the core hole site during the core hole lifetime, consistent with work aimed directly at this question.[34–36] This is in sharp contrast to the LUMO+1 state which, in spite of a shake-up probability comparable to that of the LUMO,[37] does not give rise to any measurable recombination intensity in the XES spectrum. While we cannot explain this, we suggest that there are at least two factors to be considered in explaining this observation: (1) Using XAS as a guide, the LUMO-derived state has a cross section which is higher by approximately at least a factor of 2, and likely much higher, given the effects of vibronic broadening and the predicted electronic cross sections[25]; (2) the proclivity of electrons excited to the LUMO+1 to hop to a nearest-neighbor molecule before the core transition[34,36] could be important in this respect.

The K_3C_{60} features are significantly broader than in C_{60}, both in the XES and RIXS spectra. In XES, the broadening is largely due to a superposition of emission from inequivalent states due to shakeup and different spin configurations[38] populated in the excitation process. Note, however, that the width of the LUMO peak in K_3C_{60} is less than 1 eV. The simplest interpretation is that this represents the upper limit to the energy separation of all initial states contributing to the XES spectrum, and hence, indicates that the binding energies of the C 1s levels corresponding to nonequivalent carbon atoms differ by less than 1 eV. One could speculate that different core levels, as proposed by Goldoni *et al.*,[9] lead to excitation to LUMO levels which are qualitatively different, e.g., differently hybridized with neighbor molecular levels; this more complicated scenario is, however, not supported by the angle independence of the XAS (Ref. 11) and RIXS results presented here. Thus, we suggest that the narrow XES LUMO peak is inconsistent with the interpretation of level splitting[9,11] in bulk K_3C_{60}, implicitly supporting an alternative interpretation.[12,13]

On the other hand, the broadening of the XES spectrum is sufficiently large to smear out any obvious Fermi cutoff, which is clearly visible in PES. In analogy to the broadening of the LUMO-derived peak in pure C_{60}, the broadening of the LUMO-derived peak in K_3C_{60} can be attributed to emission from a continuum of intermediate core-excited states populated in shake-up processes during the excitation. This implies that the screening of the core hole is incomplete during the lifetime[39] of the intermediate states, although the system is metallic. This behavior is in contrast to what is observed for simple metals, where the screening is fast and the Fermi cutoff is readily observable in XES.[40,41]

In RIXS the spectral features are substantially narrower than in XES. The energy selectivity of the excitation reduces the distribution of the intermediate states,[36] and we see that the RIXS spectrum of C_{60} is in almost perfect agreement with the PES results. This is in spite of the fact that the RIXS final states have an additional electron in the LUMO orbital. The close correspondence indicates that this electron does not significantly influence the valence electron system, as previously discussed for resonant Auger.[36] An important point for RIXS and XES is that the molecular charge state does not change in the emission step, further minimizing the effects of an additional electron on the emitting molecule with respect to electron spectra.

The K_3C_{60} RIXS spectra show an excess broadening as compared to those of C_{60}. Since the LUMO-derived orbital in K_3C_{60} has an occupancy of 3, there is an unpaired electron in the ground state. At resonant excitation, the spin of the excited electron may be parallel or antiparallel to this electron. Therefore, two exchange-split states for each final state configuration are expected to be populated. The exchange splitting for LUMO excitation is estimated to be 0.3 eV,[17] which cannot be resolved, but which would account for the observed additional broadening.

C. Unoccupied bulk electronic states

The XAS of K_3C_{60} is typically measured using electron yield, which implicitly involves bulk and surface contribu-

tions. The surface contribution will be reflected in the ratio of surface to bulk intensity. For a significantly shifted surface signal, the weight of different parts of each peak in the spectrum will be modified. This issue should be considered when trying to understand why Goldoni *et al.*[11] observed only small variations in the XAS spectrum as a function of electron detection energy, i.e., of the relevant mean free path, showing that the surface and bulk contributions do not differ enough to have a strong impact on the spectrum.

A general shift of the K$_3$C$_{60}$ spectrum to higher energy by approximately 0.35 eV would make most of the spectral features coincide with those of the C$_{60}$ spectrum. The largest differences between the two compounds are found close to the edge, in the region of the LUMO and LUMO+1 resonances. The relative depletion of the LUMO intensity is easily understood by considering that the LUMO is half-filled in the ground state of K$_3$C$_{60}$. The region just above the LUMO(-derived) absorption is also strongly modified. These modifications have provoked a proposal that the peak between the C$_{60}$ LUMO and LUMO+1 absorption energies is not a LUMO+1-derived level, as commonly assumed, but of different origin. For instance, split states, which are discussed as the reason for the broad photoemission lineshape of the LUMO-derived band,[9] would be expected to appear as additional peaks in the XAS. As shown in Fig. 2, the LUMO-derived resonance shifts more strongly than the other peaks, which indeed raises important questions about the changes in the spectrum upon K intercalation.

We show here that this issue can be settled by studying how the RIXS spectra change as the excitation energy is varied across the different absorption resonances. Figure 5 shows that changing the excitation energy from the LUMO to the second absorption resonance has a large impact on the RIXS spectrum. For pure C$_{60}$, this variation has been analyzed in detail elsewhere.[22] In the dipole approximation, the RIXS process is governed by the selection rules for second-order optical processes. For systems with inversion symmetry, parity must be conserved; i.e., if a gerade (ungerade) orbital is excited in the absorption step, only radiative decay from gerade (ungerade) orbitals is allowed. In systems with large vibronic coupling (like C$_{60}$), and systems where the symmetry is slightly disturbed (like K$_3$C$_{60}$), the selection rules are relaxed to *propensity rules*, which nevertheless determine important characteristics of the excitation energy dependence of the RIXS spectra.[22]

From this discussion and previous work, it can be understood that scattering at the *ungerade* LUMO-derived (t_{1u}) intermediate state in C$_{60}$ emphasizes the E_1 and E_5 features of the emission band, exclusively, corresponding to *ungerade* valence orbitals. Consequently, these features are attenuated when the excitation energy is tuned to the *gerade* LUMO+1 resonance. Raising the excitation energy from the LUMO-derived band in K$_3$C$_{60}$ to the absorption structure "b" produces changes in the emission band, which in great detail correspond to the changes in the C$_{60}$ emission when the energy is raised from the LUMO to the LUMO+1 resonance. Hence, it is straightforward to assign *gerade* parity to the "b" resonance, and we conclude that the state labeled as "b" in the XAS is indeed LUMO+1 derived.

To explain the larger shift of the LUMO+1-derived feature, we postulate a hybridization of the K valence orbital
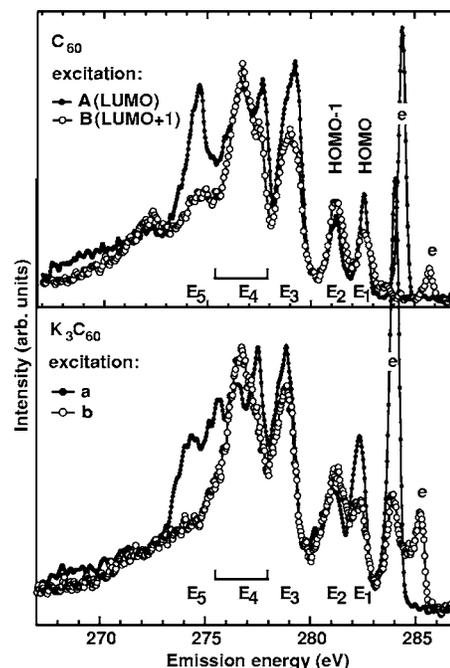
FIG. 5. Resonant inelastic scattering via the two lowest-energy absorption resonances. Excitation energies as marked in Fig. 2 by *a* and *b* (K$_3$C$_{60}$, lower panel), and *A* and *B* (C$_{60}$, upper panel). (The *e* in each spectrum marks the elastic-scattering peak.)

with the LUMO+1, which shows a nonrigid shift in the spectra. This state consistently shows the strongest effects of such interactions compared to the neighboring frontier states.[34,42–45]

The separation of surface and bulk contributions in the electron yield spectrum cannot be solved quantitatively here. The LUMO intensity is, as pointed out above, expected to be about 1/2 that of pure C$_{60}$ for the bulk, but significantly higher for the surface molecules.[12,13] To explain the excess broadening of the spectral features compared to pristine C$_{60}$, we suggest that one should also consider the exchange splitting, expected in the absorption spectrum due to the unpaired electron in the ground state. Important to note, however, is that the energy of the LUMO resonance could be quite similar for each of the three charge states suggested for molecules near the K$_3$C$_{60}$ surface, since the excitation is neutral and local to the probed molecule.

There is still an open question regarding the expected intensity of possible satellites in XES compared to PES for such systems. Since recent work on bulk K$_3$C$_{60}$ (Refs. 12 and 13) suggests that such satellites are weak, as shown directly for surface compounds,[46] employment of Occam's Razor would lead one to reject an important role for satellites in the present data. Nevertheless, calculations of XAS, XES, and RIXS of such materials would be useful to fully explore the implications of the present data. The parity selectivity of RIXS in K$_3$C$_{60}$ is observed even when higher intermediate states are involved, as clearly observable in Fig. 3: the excitation dependence of the relative intensities of the emission spectral peaks closely follows the behavior in pristine C$_{60}$ (see, e.g., Ref. 22), and we can therefore conclude that the local symmetry is well preserved upon the K intercalation at

this composition. This conclusion is valid both regarding static symmetry breaking in the ground state and any additional dynamic symmetry breaking in the RIXS process. Any departure from C_{60} symmetry would readily appear as a relaxation of the parity selection rules associated with the full symmetry.

IV. SUMMARY

In conclusion, XAS, XES, and RIXS consistently show strong analogies between single-phase K_3C_{60} and pristine C_{60}. The lines in the photon spectra are narrower than the corresponding valence-band PES lines from K_3C_{60}. As XES and RIXS are sensitive to the bulk of the material, and PES to the surface layer, this points to differences in the bulk and surface electronic structure of K_3C_{60}. This strongly supports the earlier proposition that the surface layer has a stoichiom-

etry and associated electronic structure which differ from the bulk.[12,13]

Considering the parity selection rules in the RIXS process, we also find that the C_{60} symmetry largely is preserved in K_3C_{60}, both in the ground state and during core excitations. This allows an unambiguous assignment of the absorption peaks to unoccupied energy levels with molecular C_{60} character, contradicting the notion of on-ball chemical shifts.

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