Surface Hubbard *U* of alkali fullerides

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Abstract. We report a combined photoemission spectroscopy (PES) and inverse photoemission spectroscopy (IPES) study of distilled, phase pure films of C_{60} and the monomeric fullerides Cs_6C_{60}, Cs_4C_{60} and *fcc* RbC_{60}. The separation between the highest energy PES and lowest energy IPES features, which is a measure of the barrier to hopping, is 1.45 eV in Cs_4C_{60} and 0.7 eV in RbC_{60} . This difference is large enough to explain, in a correlated electron picture, differences in electronic mobility between the two stoichoimetries. From the PES-IPES energy separation, the value of the Hubbard *U* is estimated to be 1.5 eV in closed-shell C_{60} and Cs_6C_{60}, while in Cs_4C_{60} and RbC_{60} such value is reduced to ~1 eV and 0.7 eV, respectively. This trend can be only partially understood taking into account the different molecular polarizability and crystal structure of the various stoichiometries. The relatively low values found for open-shell compounds indicate that the bulk Hubbard *U* is smaller in open-shell fullerides than usually believed, which might help explain superconductivity and the observation of spin-singlets in odd stoichiometry fullerides.

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1. Introduction

Organic molecular solids constitute a special class of strongly correlated systems in which electron correlation effects are deeply intertwined with molecular features such as intramolecular electron-phonon coupling and polarization screening [1]. Thanks to their rich variety and diversity of electrical behaviours, C_{60}-based solids have become a standard playground to study metallicity and interactions in molecular systems [2]. Charge transfer compounds of C_{60} with alkali atoms, known as alkali fullerides, have features that resemble those of inorganic correlated systems with orbital degeneracy [3,4]. Extensive characterization in the past two decades has shown that alkali fullerides display a high degree of electron localization on individual molecules [5] and strong electron-electron interactions [6,7], and that they lie close to a metal-to-insulator transition [8,9] in which the coupling of valence electrons to intramolecular Jahn-Teller-active modes plays a crucial role [10].

In the usual description of correlated systems, the parameter which determines the insulating or metallic nature of the ground state [11,12] is the ratio between the so-called Hubbard U, defined as the energy needed to transfer an electron from a site with n electrons to a distant equivalent site (*i.e.*, $U = E_{n+1} + E_{n-1} - 2E_n$, where E_ν is the energy of a site with occupancy ν), and the uncorrelated bandwidth W, which is related to the overlap between the molecular orbitals. In the case of fullerides the parameter U is a measure of the intramolecular electron repulsion, and the critical ratio $(U/W)_c$ at which the metal-to-insulator transition takes place depends on the effective degeneracy of the LUMO-derived level [13-15] (three-fold degenerate in the isolated molecule), which can be easily lifted [16] by crystal field splitting or by a dynamic or cooperative Jahn-Teller (JT) effect.

The phase diagram of alkali fullerides A_xC_{60} (where A is an alkali element and x an integer between 1 and 6) can be qualitatively understood in terms of the interplay between these local interactions. The JT interaction is stronger than the on-ball exchange coupling [9,17], leading to low-spin ground states and to the stabilization of even-charge anionic states [18,19]. In compounds of even stoichiometry (x=2,4) charge fluctuations are hindered both by correlation and JT effects [20-22], resulting in insulating and diamagnetic ground states [23-25], while in odd stoichiometries of cubic symmetry metallic behaviour and even phonon-mediated superconductivity (for $x = 3$) are observed [26-28]. In the latter systems a symmetry reduction involving the lifting of the LUMO degeneracy or a lattice expansion lead to an insulating state [8,9,29].

Despite the qualitative success of this description, a full quantitative understanding of metallic behaviour in fullerides is still lacking. While on one side theoretical calculations indicate that odd-stoichiometry compounds should be almost on the insulating side of the correlated metal-to-insulator transition [14,15], the same authors point out that Coulomb interactions must be effectively screened to allow for superconductivity in these salts, as retardation effects are ineffective [30]. The magnitude of the electron-electron interactions and their role for fulleride superconductivity remain highly controversial [10,31-34].

The highly symmetric structure of the C_{60} molecule allows measuring the barrier to hopping (or chemical potential gap) and the on-site Coulomb repulsion in fullerides independently by combinations of electron spectroscopies [6,7,35-37]. The on-ball repulsion was determined experimentally for the isolated C_{60} molecule and for solid C_{60} [38], and it was shown that the value in the solid phase can be derived from the Coulomb repulsion between two electrons on the isolated C_{60} molecule by reducing it by the polarization screening contribution from nearest-neighbour molecules [39,40]. Instead, experiments have not yet been entirely conclusive on the value of U in C_{60} compounds, especially for metallic and superconducting phases [35], and in most discussions the value found in pristine fullerite is used also for alkali fullerides.

However, a recent experimental study on ultra-thin films has shown that the actual value of the Hubbard U is a function of the stoichiometry of the compound, besides being dependent on film thickness [41]. The stoichiometry-dependence is not surprising, as the molecular polarizability varies according to the charge state of the C_{60} anion [40] and the crystal structure and hence the coordination are different depending on the compound, and also because screening may be enhanced in open-shell fullerene compounds by multiplet effects and, in metallic and superconducting phases, by itinerant-carrier-like screening [41]. These possibilities have indeed been taken into consideration in some theoretical work [30,40,42,43], but only very recently explored in experiments.

We present here a photoemission and inverse photoemission study on ordered thin films of C_{60}, RbC_{60}, Cs_4C_{60} and Cs_6C_{60}, from which experimental values for the hopping barrier (ΔE) are obtained that are relevant for the surface of these fullerides. The hopping barrier ΔE is lower by 0.7eV in RbC_{60} with respect to Cs_4C_{60}, a difference which rationalizes their distinct conduction properties. From the value of ΔE the magnitude of the Hubbard U in fullerides can be determined using known values for the gap and the JT pairing energy. We find that the value of U in Cs_6C_{60} is similar to that found in pristine C_{60} (1.5 eV), while it is significantly reduced in A_4C_{60}, and AC_{60} compounds, in agreement with earlier experimental results on K_3C_{60} [35]. The reduction of U in open-shell compounds can be only partially accounted for taking into account the enhanced polarization screening in these open-shell fullerides.

2. Experimental details

Ultraviolet photoemission spectroscopy (PES) and inverse photoemission spectroscopy (IPES) measurements were carried out on well-ordered phase pure C_{60}, Cs_xC_{60} (x = 0, 4, 6) and RbC_{60} films grown on metallic single crystal substrates. The IPES measurements were performed at the ISM IPES Trieste laboratory [44]. Experimental details are given elsewhere [45]. All IPES spectra are normalized at each point to the incident electron beam current.

C_{60} films were grown by vacuum deposition. The RbC_{60} films were obtained by the standard vacuum distillation procedure of Poirier *et al*. [46]. The PES data on *fcc* RbC_{60} were collected [47] at 525K with a photon energy of 129 eV in the ultra high vacuum experimental chamber of the SuperESCA beamline [48] at the Elettra synchrotron radiation facility. The photon energy calibration was obtained by comparing first- and second-order photoemission signal from suitable core levels. The IPES spectrum of the same phase was measured at 470 K since this compound polymerizes at room temperature [47].

The Cs-doped films were prepared on a Au (110) substrate by modifications of the vacuum distillation procedure. The PES and IPES measurements on Cs_xC_{60} were carried out at room temperature on films prepared under the same conditions and thoroughly characterized by Auger electron spectroscopy and low energy electron diffraction (LEED) to ensure that the desired phases were obtained. The PES measurements on the Cs-doped films were carried out with a standard He discharge lamp, using the He I resonance (21.2 eV). The energy resolution, as measured on the Fermi edge of the clean substrate, was 0.15 eV for PES and 0.45 eV for IPES. The energy scale for both PES and IPES spectra was referenced to the vacuum level.

3. Results

Figure 1(a) shows a schematics of PES and IPES processes occurring at the surface of a C_{60} compound (large circles indicate the surface C_{60} monomers, for clarity dopant ions are omitted and only the surface and first subsurface C_{60} layers are shown). In both processes the probed film is initially in the ground state. In valence band PES a photon is absorbed by a molecular ion with *n* valence electrons and a photoelectron is emitted, leaving behind a molecule with *n–1* valence electrons (indicated as a positive charge in the figure). In the IPES process, an electron is captured by a molecule thereby resulting in an *n+1* state (a negative local excess charge).

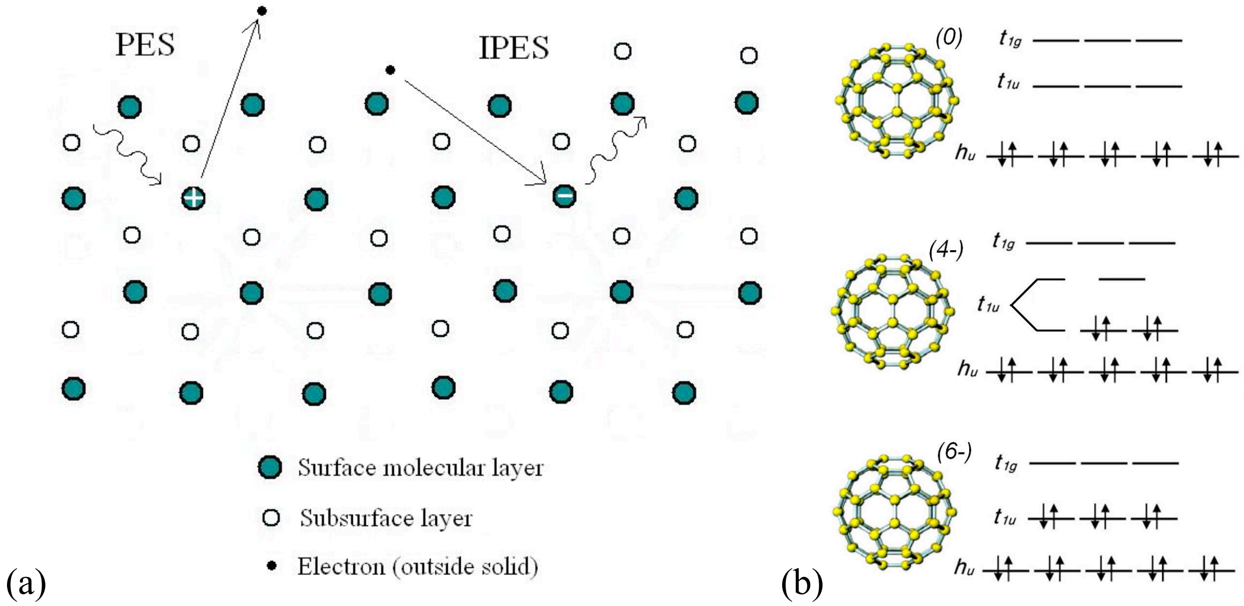

Figure 1. (a) Schematic top view of the surface of a fulleride (for simplicity taken to have a hexagonal structure), showing the comparison between the PES and IPES processes. (b) Energy level diagram for the isolated C_{60}, $C_{60}^{(4-)}$ and $C_{60}^{(6-)}$ monomers. In the $C_{60}^{(4-)}$ anion the gap derives from the (dynamic) Jahn-Teller splitting of the t_{1u} (LUMO) states. The three molecular gaps give rise to the semiconducting bandgap of condensed-phase C_{60}, Cs_4C_{60} and Cs_6C_{60}. No gap is present in the $C_{60}^{(1-)}$ anion nor in RbC_{60} (the same is true for A_3C_{60} compounds).

When both processes are considered together, the net final state is equivalent to that produced when a valence electron is transferred from a molecule in the ground state to a (distant) equivalent molecule. Since the minimum energy required for such electron transfer is precisely the hopping barrier (ΔE), the energy separation (taken centroid to centroid) between the features closest to the Fermi level in the PES and IPES spectra is a direct measure of ΔE.

The definition of ΔE includes all energy terms which are relevant for the charge transfer process, such as the relaxation energy at both sites, possible Jahn-Teller (JT) terms, and most importantly the energy gap E_g which separates the highest occupied and lowest unoccupied state, if present. In gapped correlated systems such as even-stoichiometry fullerides (see Fig. 1(b)), the total barrier to hopping ΔE is the sum of the Hubbard U plus the energy gap E_g, which for a molecular insulator includes the effect of relaxation and JT coupling on the molecular orbitals. No gap is present instead in odd-stoichiometry fullerides, where the hoping barrier is fundamentally a measure of U (see also below).

The discussion in terms of occupancy of individual sites and of a molecular U is justified by the fact that valence electrons in fullerides are strongly localized on single molecules (also in the more conductive RbC60 compound [5]). We point out that other authors (see *e.g.* Refs. [49] and [50]) use a different decomposition of the hopping barrier ΔE in terms of the ionization potential and electron affinity of the isolated molecules, while we prefer here to relate ΔE to physical quantities proper of the condensed phase such as the gap in the solid and the Hubbard U. Estimates for the gap can be obtained theoretically with the GW approximation [51] to the density functional scheme, which has been shown to give quite accurate results for the band gap of inorganic semiconductors, and experimentally from the on-set of direct (non-excitonic) transitions in high resolution electron-energy loss spectroscopy (HREELS).

Figure 2 shows the PES and IPES spectra of C_{60} and Cs_6C_{60}, normalized so that the area under the leading peaks is roughly proportional to the occupation of the corresponding energy bands. The energy and shape of the features in the spectra of pristine C_{60} are in agreement with published work, testifying the good alignment of the Fermi level in our spectra and that our film is thick enough so that screening from the metallic substrate [41] is negligible. The experimental HOMO-LUMO energy separation is 3.6eV as previously observed [36,52,53].

Both C_{60} and Cs_6C_{60} are insulators. As pointed out above, in these closed-shell systems the smallest PES-IPES energy separation is $\Delta E = U + E_g$, where E_g is the energy gap [54] between the highest occupied band and the lowest empty band. The value of E_g in solid C_{60} calculated with the GW method is 2.15 eV [55], which coincides with the energy of the first direct inter-band (non-excitonic) transition observed with HREELS [56]. This gives $U \approx 1.5$ eV, in agreement with previous estimates [35-37,57].

In Cs_6C_{60} the three-fold degenerate LUMO-derived band is filled completely by the six electrons per molecule provided by the Cs counter-ions. The LUMO-derived feature in the PES spectrum is centred 7.1 eV below the vacuum energy, while the LUMO+1-derived feature in IPES appears 4.4 eV below the vacuum level. To more accurately determine the energy of the latter feature, we have performed a fit of the lower energy part of the IPES spectrum using two Gaussians (not shown). The smallest energy separation between PES and IPES found with this procedure is 2.7 eV.

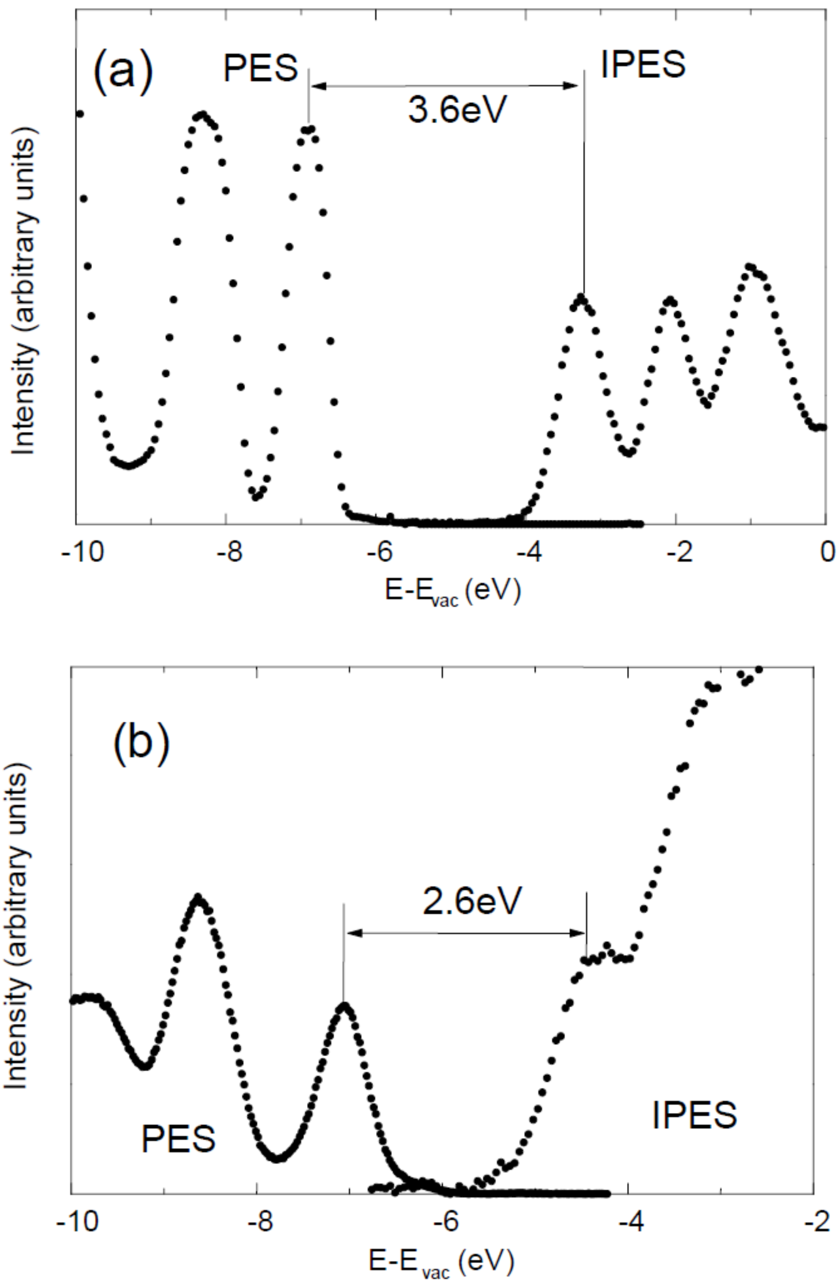

Figure 2: (a) Vacuum level referenced PES and IPES from a thin C_{60} film. (b) PES and IPES spectra of a distilled Cs_6C_{60} sample.

No GW calculation of the band gap is available for A_6C_{60}. HREEL spectra of A_6C_{60}, both in reflection [58,59] and transmission mode [60,61], display the lowest most intense energy peak at 1.2-1.3eV, which we take to be a measure of the bandgap in this material. A comparison between HREELS data on C_{60} and A_6C_{60} [61,62] indeed shows that the energy of the first intense (non-excitonic) transition is reduced by roughly 1 eV in A_6C_{60} with respect to pristine C_{60}, confirming our estimate for E_g in Cs_6C_{60}. With this value we get $U_C(Cs_6C_{60})$ = 1.4 - 1.5 eV, in perfect agreement with the value reported for K_6C_{60} (1.5 eV [35]).

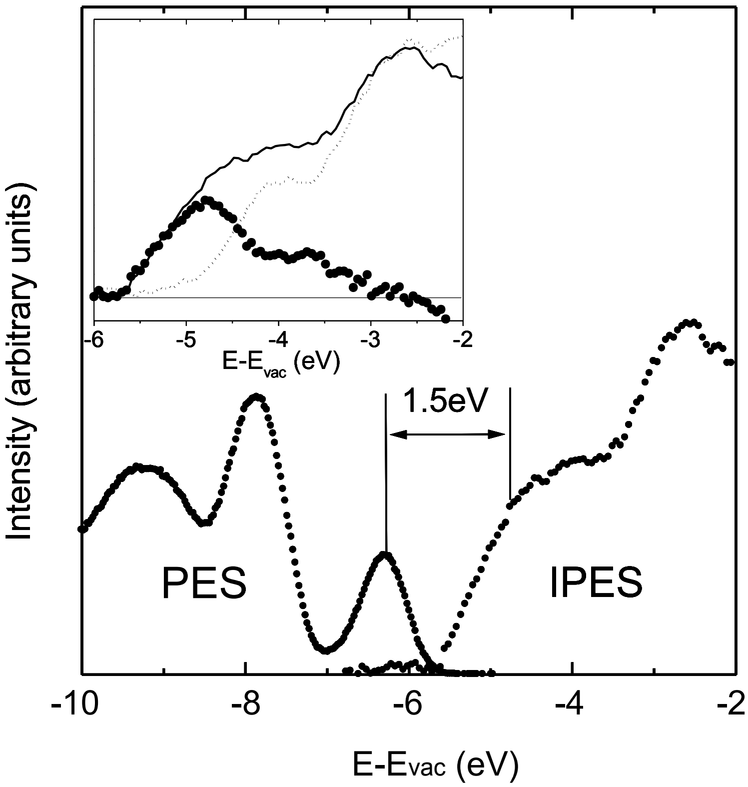

Figure 3: Vacuum referenced PES and IPES spectra of a phase pure Cs_4C_{60} thin film. The inset shows the method by which the centroid of the LUMO derived states was obtained: the dotted line is the IPES spectrum of Cs_6C_{60}, whose LUMO+2 feature has been aligned with and normalised to that of Cs_4C_{60}. The larger dots represent the difference between the Cs_4C_{60} spectrum and the shifted Cs_6C_{60} spectrum, which provides an estimate of the unoccupied portion of the LUMO for the former.

The PES and IPES spectra of Cs_4C_{60} are shown in figure 3. The width of the first IPES structure is anomalously large compared with that of the C_{60} and Cs_6C_{60} features. Such feature results from the superposition between the empty LUMO-derived states and the LUMO+1 band, which shifts non-rigidly with increasing doping [63]. A similar overlap is observed in the IPES spectrum of Rb_4C_{60} [64]. To separate the two contributions, we have subtracted the IPES spectrum of Cs_6C_{60} from that of Cs_4C_{60}. The Cs_6C_{60} lineshape was appropriately normalized and shifted so that the feature derived from the LUMO+2 orbital appeared at the same energy and had the same intensity as that of the Cs_4C_{60} spectrum, as shown in the inset of figure 3.

Because of the non-rigid shift of the electronic states upon filling, such procedure is not fully justified; however, it is less arbitrary than a fit of the IPES spectrum with three Gaussians, and it has the advantage of incorporating (even if perhaps overestimating) the effects of electronic relaxation due to the filling of the

LUMO orbital on the spectral position of the higher-lying molecular orbitals. This procedure allows us to locate the peak corresponding to the unoccupied portion of the LUMO at 4.8 ± 0.1 eV below the vacuum level (energy position of the intensity maximum in the difference spectrum). A small uncertainty exists in the position and shape of the LUMO-derived peak as obtained by the subtraction procedure due to differing backgrounds in the IPES spectra of the two phases. The energy separation between the filled and unfilled portions of the LUMO-derived band, marked by vertical lines in figure 3, is $\Delta E = 1.5 \pm 0.1$ eV. The value of E_g for A_4C_{60} (including JT effects) was calculated by Chibotaru and coworkers [65] with the GW method, and found to be 0.5 eV. A very similar value in the range 0.5 - 0.6 eV was reported in HREELS measurements [66]. The gap in A_4C_{60} arises from the Jahn-Teller splitting of the t_{1u} states, and indeed the JT pairing energy for the isolated $(C_{60})^{4-}$ anion is estimated to be 0.2 - 0.4 eV [18,19,67], a good fraction of the bandgap. With the values for ΔE and E_g given above we find $U_C = 1 \pm 0.1$ eV in Cs_4C_{60}. This indicates that the bare U_C is better screened in A_4C_{60} than in the closed-shell systems, which cannot be due to a higher coordination number as the number of first neighbours is lower in the body centred tetragonal (*bct*) structure of Cs_4C_{60} than in the *fcc* structure of pristine C_{60}. The origin of the screening enhancement is discussed in Section 4.

Figure 4 shows the PES and IPES spectra acquired on the high-temperature *fcc* phase of RbC_{60}. The energy separations between the LUMO and LUMO+1 and the LUMO+1 and LUMO+2 features in the IPES spectrum are similar to those observed in C_{60}, but the width of the spectral features is much larger than in C_{60} and Cs_6C_{60}, and the first peak at 7.5 eV below the vacuum level appears to be structured, with a shoulder at lower energy. The PES valence band features are also anomalously broad, suggesting the contribution of more than one component to the spectral lineshape. We have recently shown [47,68] that two different C_{60} valence states, namely neutral ($C_{60}^{(0)}$) and charged ($C_{60}^{(1-)}$) are present at the surface of vacuum-distilled RbC_{60} thin films. The same charge states should be visible in the IPES spectrum, and in the inset of figure 4 we present a model of the IPES spectrum of RbC_{60} as the sum of two C_{60} IPES lineshapes (the same spectrum displayed in figure 2). The components are separated by 0.4 eV, an energy similar to the binding energy difference found between the two components in the valence band PES spectrum (0.5 eV [47]). We point out that the component arising from the charged monomers could in principle be broader or more structured than the neutral one, as there are different possible final states in this case (corresponding to the different total-spin configurations of the two LUMO electrons). Our model provides nevertheless a reasonable fit of the IPES spectrum of *fcc* RbC_{60}.

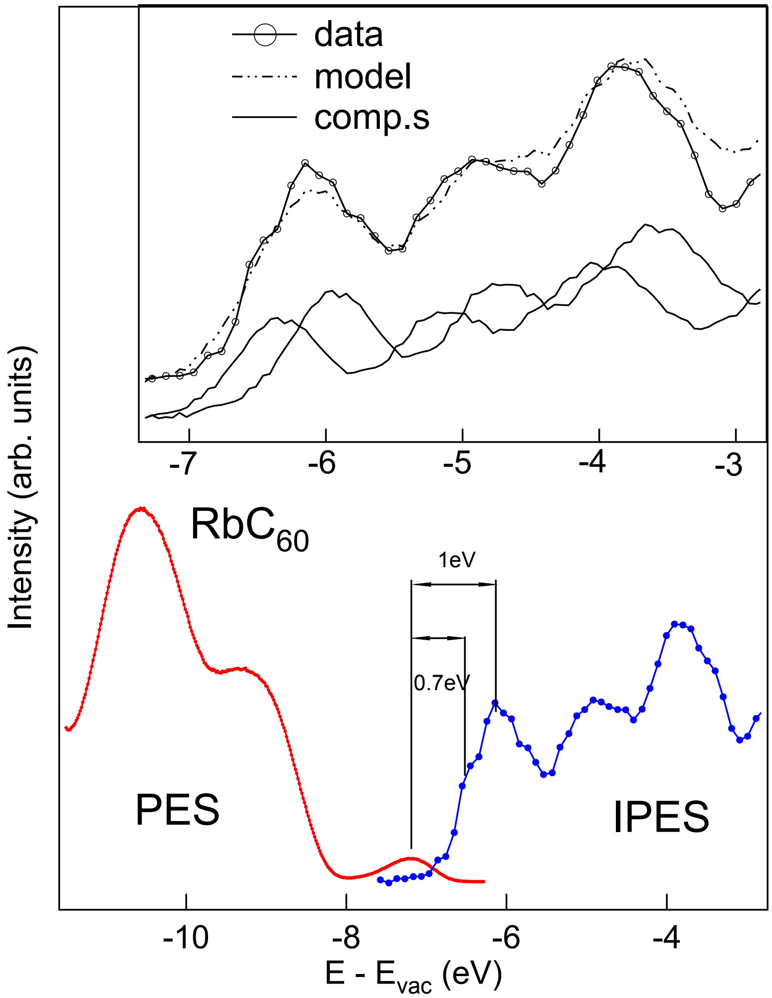

Figure 4: Vacuum referenced PES and IPES spectra of a phase pure RbC_{60} thin film in the *fcc* phase. The inset shows a model of the IPES spectrum as the sum of two components (two IPES spectra of pristine C_{60}) corresponding to the two different molecular charge states present at the film surface (see text for details).

The smallest LUMO-LUMO separation in the RbC_{60} spectra is 0.7 eV. Since $E_g=0$ in this system, this value is fundamentally a measure of U, though a small contribution might also come from the Jahn-Teller pairing energy for the $(C_{60})^{1-}$ anion, which is of the order of 0.1 - 0.2 eV [18,19,67]. Since photoemission processes occur on very short timescales (< 1fsec), it is unclear which Jahn-Teller relaxation processes contribute to our experimental measure of the hopping barrier. Even assuming a full contribution, the purely Coulombic Hubbard Uwould then be at most $U = 0.8 - 0.9$ eV. This quantity is 50% larger than the PES binding energy difference between the two charge components, which is consistent with the relationship between these two quantities established in our previous study of *fcc* RbC_{60} [47].

The value of U in RbC_{60} is much smaller than that found in C_{60} and Cs_6C_{60}, while it is closer to that found for Cs_4C_{60}, and it also matches the energy separation observed between the Auger fine structure and the self-convoluted valence band PES spectrum in K_3C_{60} [35]. Since the effect of correlation can be expected to be similar in the two odd stoichiometries (both of which are metallic), this indicates that the energy separation found in Ref. [35] can be taken as a valid estimate for the Hubbard U in K_3C_{60}, contrary to the conclusions put forth by these authors. In *fcc* RbC_{60} (and also in K_3C_{60}) the coordination number is the same as in C_{60}, hence we must look for alternative explanations for the more efficient screening of U in these compounds.

4. Discussion

As mentioned in the introduction, the values of U found in our study are appropriate for the surface, rather than the bulk, of each compound, and bulk values are expected to be lower than those discussed so far, as screening efficiency is enhanced due to the higher coordination number [39]. The relatively low values of U found in open-shell compounds (RbC_{60}, Cs_4C_{60}, K_3C_{60}) thus entail even smaller correlation energies in the bulk of these systems. Motivated by these findings and by a recent study of potassium fulleride thin films [41], we have investigated to what extent molecular polarization screening can account for our observations. We assume the contribution of molecular polarization screening only, as the atomic polarizability of the alkali counter-ions is negligible in comparison to that of C_{60} species. Taking into account local field effects [69], the reduction of U due to molecular polarizability can be estimated as [70]:

$$\text{Eq. (1)} \quad \delta U = \frac{14.4L(0)}{4\pi \cdot d}\left(1-\frac{1}{\varepsilon}\right)eV\,,$$

where ε is the relative dielectric constant of the medium, d the distance in Å between nearest neighbour molecules, and $L(0)$ is the appropriate lattice sum for the corresponding crystal structure, equal to 25.34 for *fcc* C_{60}, RbC_{60} and K_3C_{60}, and to 22.64 for *bcc* Cs_6C_{60}. For *bct* Cs_4C_{60}, the lattice sum was taken to be equal to that of the *fcc* structures and an “effective” d was calculated as the cube root of the molecular volume. We estimate that the error associated with this procedure is less than 10% (*i.e.*, the percent difference between the lattice sums for two cubic structures). As for the relative dielectric constant ε, the value available in the literature was used for the C_{60} case, namely 4.4 [71], while for the other fullerides it was calculated from the Clausius-Mossotti relation using the theoretical molecular polarizability of the $(C_{60})^{n-}$ anion [42].

The theoretical values of the screened bulk U_C obtained by such method are reported in Table I for the compounds studied here and for K_3C_{60}. We assume that the Coulomb repulsion for the isolated molecule is the same for all charge states, namely U^{mol} = 3eV, which is the accepted value for neutral C_{60} as derived from both theory and experiment [38,40,72]. This assumption is supported by theoretical calculations which indicate that the energy cost for introducing one electron into the t_{1u} level of the isolated molecule is approximately the same, regardless of the initial reduction state [39]. In Table I also the comparison with the experimental (surface) values is presented.

compound	Structure and *d*, in Å	α (Å^3)	E	bulk δU (th. eV)	bulk U (th., eV)	surface U (exp., eV)
C_{60}	*fcc* (10.02)	89.8	4.4	2.2	0.8	1.5
RbC_{60}	*fcc* (9.95)	163.7	194	2.9	0.1	0.8
K_3C_{60}	*fcc*(10.06)	129.4	10.0	2.6	0.4	0.7
Cs_4C_{60}	*bct* (9.4)	138.6	7.93	2.4	0.6	1
Cs_6C_{60}	*bcc* (10.21)	150.9	11.05	2.3	0.7	1.4-1.5

Table I. Comparison between the experimental value of the surface U and the theoretical bulk estimates, for a number of fulleride compounds. The bulk U is calculated as $U = U^{mol} - \delta U$, where U^{mol}=3eV and δU is determined from Eq. (1). The relative dielectric constant ε of the bulk fullerides was calculated using the Clausius-Mossotti relation from the theoretical polarizability α of the corresponding anion, available from Ref. [42].

In all cases the estimated bulk value is lower than the experimental surface one, as expected due to the reduction in polarization screening brought about by the lower coordination at the surface [39]. In the RbC_{60} case the predicted bulk value is extremely low; in this case, however, the calculation gives an unrealistic value of almost 200 for the relative dielectric constant. In closed-shell C_{60} and Cs_6C_{60}, the difference between the experimental surface value and the theoretical bulk U is also rather large. These results indicate that our simple model probably leads to an overestimate of the screening. Some interesting conclusions can however be reached from this comparison.

The fact that the value of U in Cs_6C_{60} is the same as for pristine C_{60} can be rationalized as the enhanced anionic polarizability in the former compound [42] balances the effect of the reduced coordination and the larger intermolecular separation. The calculation predicts a relatively large difference in U between these two close-shell compounds and the gapless compounds K_3C_{60} and RbC_{60}, and only a minor difference with the other open-shell compound Cs_4C_{60}. The theoretical differences are however not as marked as the experimental ones.

The pronounced reduction of U in open-shell compounds cannot be fully justified on the grounds of molecular polarization screening alone, which suggests that another source of screening might be present in the latter case. It is interesting to note that a recent tunnelling spectroscopy study has found evidence for enhanced screening in potassium fulleride thin films at low temperature, presumably due to itinerant charge carriers [41]. The occurrence of superconductivity in A_3C_{60} [26,27] and of long-lived spin-singlets in AC_{60} [73,74]

similarly suggests that an efficient screening of the Hubbard *U* is available in the bulk at low temperatures [30,43]. Although the precise nature of such carrier-related screening is not known (a free-electron-metal type of screening can in fact be ruled out in fullerides [35,47]), its existence only in open-shell compounds is in line with the difference in electric behaviour of open- and closed-shell fullerides: the resistivity of K_4C_{60} at 475 K is the same as that of KC_{60} and only about an order of magnitude higher than that of K_3C_{60}, while K_6C_{60} and pristine C_{60} have a resistivity which is at least two orders of magnitude higher than KC_{60} and K_4C_{60} [75].

Whether or not it can be justified on the basis of polarization screening alone, the observation of a surface Hubbard *U* of the order of 0.7 - 0.8 eV in metallic fullerides is quite remarkable. Indeed, it entails that the bulk *U* is much smaller than usually believed in these systems. Taking the bulk to surface difference to be of the order of 0.3 - 0.4 eV as estimated for the C_{60} case [39], the bulk *U* in metallic fullerides turns out to be comparable to the Jahn-Teller pairing energy, and of the same magnitude or smaller than the full uncorrelated bandwidth. With this set of parameters the occurrence of metallicity and superconductivity in fullerides is not as puzzling as has been hitherto believed, and may be envisioned to stem from the balance between electron-electron and electron-phonon interactions of equal strength. Our results show that a full understanding of transport in fullerides cannot be obtained by considering only the interplay of electron correlation and Jahn-Teller distortions, but that also a more thorough understanding of electronic screening is necessary.

5. Summary

In conclusion, we have presented a combined PES and IPES study on vacuum distilled, phase pure films of C_{60}, Cs_6C_{60}, Cs_4C_{60} and *fcc* RbC_{60}. The lowest PES-IPES energy separation amounts to 0.7eV in RbC_{60} and 1.45eV in Cs_4C_{60}, respectively. This difference is large enough to determine, in a correlated picture, the different metallic behaviour of these compounds. The value of the screened Hubbard *U* was estimated for all compounds and found to vary significantly with the stoichiometry. While *U* is similar in the close-shell systems C_{60} and Cs_6C_{60}, it is strongly reduced in Cs_4C_{60} and RbC_{60}. This can only partially be ascribed to the enhanced molecular polarizability of the fullerene anions, suggesting that a more efficient source of screening, possibly related to the presence of itinerant charge carriers, is at work in open-shell fullerides.

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References

1) E.A. Silinsh, V. Čápek, *Organic Molecular Crystals: interaction, localization and transport phenomena*, AIP Press (American Institute of Physics) 1994
2) R. Macovez and P. Rudolf, *Electronic structure of fullerene based materials*, Encyclopedia of Materials: Science and Technology 2008, pages 1-9. Ed.s: Jürgen Buschow, Merton Flemings, Robert Cahn, Patrick Veyssière, Edward Kramer, Subhash Mahajan. Elsevier Ltd, Amsterdam, The Netherlands. Available online at: www.sciencedirect.com)
3) M. Imada, A. Fujimori, Y. Tokura, Rev. Mod. Phys. 70, 1039 (1998)
4) Y. Tokura, N. Nagaosa, Science 288, 462 (2000)
5) O. Chauvet, G. Oszlányi, L. Forró, P. W. Stephens, M. Tegze, G. Faigel, and A. Jánossy, Phys. Rev. Lett. 72, 2721 (1994)
6) R.W. Lof, M.A. van Veenendaal, B. Koopmans, A. Heessels, H.T. Jonkman, G.A. Sawatzky, Int. J. Mod. Phys. B 6, 3915 (1992)
7) P.A. Brühwiler, A.J. Maxwell, N. Martensson, Int. J. Mod. Phys. B 6, 3923 (1992)
8) P. Durand, G. R. Darling, Y. Dubitsky, A. Zaopo and M. J. Rosseinsky, Nature Materials 2, 605 (2003)
9) Y. Takabayashi, A. Y. Ganin, P. Jeglic, D. Arcon, T. Takano, Y. Iwasa, Y. Ohishi, M. Takata, N. Takeshita, K. Prassides, M. J. Rosseinsky, Science 323, 1585 (2009)
10) O. Gunnarsson, Rev. Mod. Phys. 69, 575 (1997)
11) A. Georges, G. Kotliar, W. Krauth, and M. J. Rozenberg, Rev. Mod. Phys. 68, 13 (1996)
12) This is true also in the extended Hubbard model which explicitly includes the nearest-site Coulomb interaction V, at least for small values of $V < U/2$ (see M.B.J. Meinders, L.H. Tjeng, G.A. Sawatzky, Phys. Rev. Lett. 73, 2937 (1994); J. van den Brink, M.B.J. Meinders, J. Lorenzana, R. Eder, G.A. Sawatzky, Phys. Rev. Lett. 75, 4658 (1995)), since the Hubbard U is by definition a local quantity and does not contain contributions from the inter-site coupling.
13) J.P Lu, Phys. Rev. B 49, 5687 (1994)
14) O. Gunnarsson, E. Koch, R.M. Martin, Phys. Rev. B 54, R11026 (1996)
15) E. Koch, O. Gunnarsson, R.M. Martin, Phys. Rev. B 60, 15714 (1999)
16) N. Manini, G.E. Santoro, A. Dal Corso, E. Tosatti, Phys. Rev. B 66, 115107 (2002)
17) Lüders M., Manini N., Gattari P., Tosatti E., Eur. Phys. J. B 35, 57 (2003)
18) A. Auerbach, N. Manini, E. Tosatti, Phys. Rev. B 49, 12998 (1994)
19) N. Manini, E. Tosatti, A. Auerbach, Phys. Rev. B 49, 13008 (1994)
20) M. Fabrizio, E. Tosatti, Phys. Rev. B 55, 13465 (1997)
21) M. Knupfer, J. Fink, Phys. Rev. Lett. 79, 2714 (1997)
22) L.F. Chibotaru, A. Ceulemans, S.P. Cojocaru, Phys. Rev. B 59, R12728 (1999)
23) R.F. Kiefl, T.L. Duty, J.W. Schneider, A. MacFarlane, K. Chow, J. Elzey, P. Mendels, G.D. Morris, J.H. Brewer, E.J. Ansaldo, C. Niedermayer, D.R. Noakes, C.E. Stronach, B. Hitti, J.E. Fischer, Phys. Rev. Lett. 69, 2005 (1992)
24) M. Kosaka et al., Chem. Phys. Lett. 203, 429 (1993)
25) F. Stepniak, P.J. Benning, D.M. Poirier, J.H. Weaver, Phys. Rev. B 48, 1899 (1993)
26) R.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, F.A. Thiel, Nature 350, 320 (1991)

27) A.F. Hebard, M.J. Rosseinsky, R.C. Haddon, D.W. Murphy, S.H. Glarum, T.T.M. Palstra, A.P. Ramirez, A.R. Kortan, Nature 350, 600 (1991)
28) K. Holczer, O. Klein, S.-M. Huang, R.B. Kaner, K.-J. Fu, R.L. Whetren, F. Diederich, Science 252, 1154 (1991)
29) K. Prassides, S. Margadonna, D. Arcon, A. Lappas, H. Shimoda, and Y. Iwasa, J. Am. Chem. Soc. 121, 11227-8 (1999)
30) E. Koch, O. Gunnarsson, R.M. Martin, Phys. Rev. Lett. 83, 620 (1999)
31) S. Chakravarty, S.A. Kivelson, Phys. Rev. B 64, 064511 (2001)
32) M. Capone, M. Fabrizio, C. Castellani, E. Tosatti, Science 296, 2364 (2002)
33) J.E. Han, O. Gunnarsson, V.H. Crespi, Phys. Rev. Lett. 90, 167006 (2003)
34) Y. Iwasa, T. Takenobu, J. Phys. Condens. Matter 15, R495 (2003)
35) P.A. Brühwiler, A.J. Maxwell, A. Nilsson, N. Martensson, O. Gunnarsson, Phys. Rev. B 48, 18296 (1993)
36) R.W. Lof, M.A. van Veenendaal, B. Koopmans, H.T. Jonkman, G.A. Sawatzky, Phys. Rev. Lett. 68, 3924 (1992)
37) R. Schwedhelm, L. Kipp, A. Dallmeyer, M. Skibowski, Phys. Rev. B 58, 13176 (1998)
38) P. Rudolf, M.S. Golden, P.A. Brühwiler, J. El. Spec. Rel. Phen. 100, 409 (1999)
39) V.P. Antropov, O. Gunnarsson, O. Jepsen, Phys. Rev. B 46, 13647 (1992)
40) M.R. Pederson, A.A. Quong, Phys. Rev. B 46, 13584 (1992)
41) Y. Wang, R. Yamachika, A. Wachowiak, M Grobis, M. F. Crommie, Nature Materials 7, 194 (2008)
42) F. Guinea, J. Gonzalez, M.A.H. Vozmediano, Phys. Rev. B 50, 5752 (1994)
43) P.E. Lammert, D.S. Rokhsar, S. Chakravarty, S. Kivelson and M. I. Salkola, Phys. Rev. Lett. 74, 996 (1995)
44) M. Pedio, K. Hevesi, N. Zema, M. Capozi, P. Perfetti, R. Gouttebaron, J.J. Pireaux, R. Caudano, P. Rudolf, Surf. Sci. 437, 249 (1999)
45) See http://www.tasc-infm.it/research/ipes/instrume.php
46) D.M. Poirier, D.W. Owens, J.H. Weaver, Phys. Rev. B, 51, 1830 (1995)
47) R. Macovez, P. Rudolf, I. Marenne, L. Kjeldgaard, P.A. Brühwiler, T. Pichler, P. Vilmercati, R. Larciprete, L. Petaccia, G. Bertoni, A. Goldoni, Phys. Rev. B 75, 195424 (2007)
48) A. Abrami et al., Rev. Sci. Instrum**.** 66, 1618 (1995)
49) I. G. Hill, A. Kahn, Z. G. Soos, R. A. Pascal Jr., Chem. Phys. Lett. 327, 181 (2000)
50) Z. G. Soos, E. V. Tsiper, A. Painelli, J. Lumin. 110, 332 (2004)
51) L. Hedin, Phys. Rev. 139, A796 (1965)
52) T. Takahashi, S. Suzuki, T. Morikawa, H. Katayama-Yoshida, S. Hasegawa, H. Inokuchi, K. Seki, K. Kikuchi, S. Suzuki, K. Ikemoto, Y. Achiba, Phys. Rev. Lett. 68, 1232 (1992)
53) J.H. Weaver, P.J. Benning, F. Stepniak, D.M. Poirier, J. Phys. Chem. Solids 53, 1707 (1992)
54) The HOMO-LUMO gap in C_{60} cannot be inferred from the PES spectrum of Cs_6C_{60} because of the non-rigid band filling upon alkali intercalation (relaxation effects). The HOMO-LUMO separation in Cs_6C_{60} (1.6 eV) is indeed smaller than the GW band-gap in pristine C_{60}.
55) E.L. Shirley, S.G. Louie, Phys. Rev. Lett. 71, 133 (1993)
56) A. Lucas, G. Gensterblum, J.J. Pireaux, P.A. Thiry, R. Caudano, J.P. Vigneron, Ph. Lambin, W. Krätschmer, Phys. Rev. B 45, 13694 (1992)
57) A.J. Maxwell, P.A. Brühwiler, D. Arvanitis, J. Hasselström, N. Mårtensson, Chem. Phys. Lett. 260, 71 (1996)
58) M.R.C. Hunt, P. Rudolf, S. Modesti, Phys. Rev. B 55 (1997) 7889
59) K. Ueno, Y. Uchino, K. Iizumi, K. Saiki, A. Koma, Appl. Surf. Sci. 169-170, 184 (2001)
60) E. Sohmen, J. Fink, W. Krätschmer, Europhys. Lett. 17, 51 (1992)
61) E. Sohmen, J. Fink, Phys. Rev. B 47, 14532 (1993)

62) T. Pichler, M. Matus, J. Kürti, H. Kuzmany, Solid State Commun. 81, 859 (1992)
63) M.S. Golden, M. Knupfer, J. Fink, J.F. Armbruster, T.R. Cummins, H.A. Romberg, M. Roth, M. Sing, M. Schmidt, E. Sohmen, J. Phys.: Condens. Matter 7, 8219 (1995)
64) A. Brambilla, L. Giovanelli, P. Vilmercati, A. Cattoni, P. Biagioni, A. Goldoni, M. Finazzi, L. Duò, J. El. Spectr. Rel. Phenom. 144-147, 803 (2005)
65) L.F. Chibotaru, A. Ceulemans, S.P. Cojocaru, Phys. Rev. B 59, R12728 (1999)
66) M. Knupfer, J. Fink, Phys. Rev. Lett. 79, 2714
67) O. Gunnarsson, Phys. Rev. B 51, 3493 (1995)
68) R. Macovez, J. Schiessling, C. Castellarin-Cudia, P. Vilmercati, L. Petaccia, G. Bertoni, A. Goldoni, P. Rudolf, New J. Phys. 11, 023035 (2009)
69) J.C. Wang, Phys. Rev. B 22, 2725 (1980)
70) J. van den Brink, PhD thesis, University of Groningen (1997), available on-line at http://dissertations.ub.rug.nl/faculties/science/1997/j.v.d.brink/
71) A. F. Hebard, R. C. Haddon, R. M. Fleming, A. R. Kortan, Appl. Phys. Lett., 59 (1991) 2109
72) V. de Coulon, J.L. Martins, F. Reuse, Phys. Rev. B 45, 13671 (1992)
73) V. Brouet, H. Alloul, F. Quéré, G. Baumgartner and L. Forró, Phys. Rev. Lett. 82, 2131 (1999); V. Brouet, H. Alloul and L. Forró, Phys. Rev. B 66, 155123 (2002)
74) R. Macovez, A. Goldoni, L. Petaccia, P.A. Brühwiler, P. Rudolf, Phys. Rev. Lett. 101, 236403 (2008)
75) R. Hesper, L. H. Tjeng, A. Heeres, and G. A. Sawatzky, Phys. Rev. B 62, 16046 (2000)