Probing the energy levels in hole-doped molecular semiconductors†

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Understanding the nature of polarons – the fundamental charge carriers in molecular semiconductors – is indispensable for rational material design that targets superior (opto-) electronic device functionality. The traditionally conceived picture of the corresponding energy levels involves singly occupied molecular states within the energy gap of the semiconductor. Here, by employing a combined theoretical and multi-technique experimental approach, we show that this picture needs to be revised. Upon introducing an excess electron or hole into the material, the respective frontier molecular level is split by strong on-site Coulomb repulsion into an upper unoccupied and a lower occupied sub-level, only one of which is located within the semiconductor gap. By including also inter-site Coulomb interaction between molecular ions and circumjacent neutral molecules, we provide a complete picture for the electronic structure of molecular semiconductors in the presence of excess charges. With this understanding, a critical re-examination of previous results is called for, and future investigations of the properties and dynamics of polarons in weakly interacting molecular systems are put on sound footing.

Molecular semiconductors are progressively employed in electronic and optoelectronic devices because of the wide tunability of their optical gap, e.g., in organic light-emitting diodes (OLEDs), their high light absorption cross section, e.g., in organic photovoltaic cells (OPVCs), and also their potential for low-cost large-area processability from solution, e.g., by printing. At the same time, however, the performance of such devices often suffers from the relatively low charge carrier mobility in molecular semiconductors compared to their inorganic counterparts. To address this critical issue, it is of paramount importance to understand in detail the nature of charge carriers (excess electrons and holes) in these materials, where strong coupling of both electrons and holes to (inter- and intra-) molecular vibrations leads to polaron formation.

For a positively charged molecule, that is, for a cation, in a matrix of neutral molecules, Fig. 1(a) shows the relevant single-particle energy levels and their occupation according to the commonly accepted and widely used picture.3,5,7–14 Removing an electron from the highest occupied molecular orbital (HOMO) level of a neutral molecule leads to its geometrical relaxation and a concomitant shift by the reorganization energy \( \lambda \) of the now singly occupied state into the energy gap of the semiconductor.2 Concomitantly with this change of energy levels also the optical transitions of cations change with respect to neutral molecules (usually sub-gap absorption), which, however, are not discussed here.

Based on this picture, it is widely anticipated7,10,11 that (i) the doubly occupied states should be experimentally accessible...
by ultraviolet photoelectron spectroscopy (UPS), (ii) the empty states by inverse photoelectron spectroscopy (IPES) and (iii) the singly occupied state by means of both UPS and IPES; these expectations for the density of states (DOS) in the molecular solid are illustrated in the right panel of Fig. 1(a) (adapted from ref. 7). Despite best efforts by means of UPS,9,15 however, clear spectral evidence for the relaxed cation’s HOMO level within the gap is still missing.

Here, we seek to provide such evidence and realize that it is challenging even to generate the species of interest, i.e., molecular cations in a matrix of neutral but otherwise identical molecules: when generated by p-doping, the singly occupied state of the cation can hardly be distinguished from the filled lowest unoccupied molecular orbital (LUMO) level of the dopant9 and, moreover, strong electronic coupling between molecular HOMO and dopant LUMO cannot generally be excluded,16,17 which might significantly distort the DOS in the relevant energy range. Likewise, electronic coupling to atomically clean metal surfaces is known to not yield integer-charged molecules but to result in pronounced mixing of metal and molecular states instead.18,19

This hybridization with the metal, however, can be inhibited by inserting an insulator between metal and molecules, reminiscent of the situation in a p-type organic field-effect transistor (OFET) under applied (negative) gate voltage.20 Simplifying this approach, cations can be generated by employing a metal-supported, ultra-thin dielectric with a work function (WF) higher than the ionization energy (IE) of subsequently deposited molecules as depicted in Fig. 1(b) and (c). Thereby, the Fermi-level (EF) of the underlying metal is moved into the occupied DOS of the molecules, causing electron transfer from the molecules across the insulator into the metal to establish electronic equilibrium.

In the present study, this was realized with a 1.2 nm thin MoO3 layer (WF = 6.8 eV) supported by an atomically clean Au(111) single-crystal surface. To facilitate the detection of the potentially low cation concentrations, we employed C60 (IE = 6.4 eV) as hole accumulation layer due to its high orbital degeneracy (HOMO:5, LUMO:3); the full heterostructure is sketched in Fig. 1(d) (see also Methods section).

To confirm the presence of C60 cations, X-ray photoelectron spectroscopy (XPS) was first used to probe the C1s core-levels, which are known to be at different binding energy for the molecule in its neutral and cationic state.21 Fig. 2(a) shows the C1s spectra for increasing C60 coverage, together with the results of the applied fitting procedure. The bottom curve in the figure shows that no carbon is adsorbed on the pristine MoO3. Upon C60 deposition, two distinct C1s peaks emerge, which are split by ~0.7 eV and evidence the coexistence of cationic (high binding energy − red) and neutral (low binding energy − green) molecules at the interface. This literature-based assignment21 is also fully in line with the expectation of a decreasing fraction of charged

Fig. 1 Traditional view of the molecular single-particle energy levels and how they can be created and measured: (a) single-particle energy levels for neutral molecules (green) surrounding a cation (red) with respect to a common vacuum level \( \phi_{\text{vac}} \); their experimental accessibility to (inverse) photoelectron spectroscopy depending on their occupancy and the resulting density of states (DOS) on a logarithmic scale, \( \ln(\text{DOS}) \), as proposed according to common assumptions in ref. 7. (b) Single-particle energy level diagrams for a neutral molecule on an intermediate and (c) a high work-function substrate causing electron transfer that results in cations.2,3,7–10 The latter is realized here with the Au/MoO3/C60-heterostructure (d).
molecules with increasing coverage in the monolayer regime,\textsuperscript{22,23} as the cation component becomes weaker compared to the neutral one with increasing coverage. Notably, the fraction of C\textsubscript{60} cations is in the range of 40% below 1 Å nominal coverage (for other thicknesses see ESI†). From 1 Å nominal coverage onwards, a third C1s peak (blue) is required to maintain the quality of the fit. We attribute this additional component to neutral C\textsubscript{60} molecules in a second layer, as illustrated in the inset of Fig. 2(c). While its presence is of no further consequence for the discussion below, it supports the notion of hole accumulation within the first layer, as it is energetically aligned according to the electrostatics of energy level bending (see ESI†).\textsuperscript{24–26}

Regarding the electrostatics within the hole-accumulating (sub)monolayer itself, it is important to note that, here, the neutral molecules observed in XPS reside within the Coulomb potential well created by nearby cations, as schematically sketched at the bottom of Fig. 2(a). Thereby, all energy levels of these neutral C\textsubscript{60} molecules are shifted rigidly to higher binding energy (by an amount \(V\)). This ensures that their (fully occupied) HOMO levels now come to lie entirely below \(E_F\), thus preventing them from undergoing electron transfer to the underlying metal and, consequently, from becoming cations themselves. This process enables the coexistence of neutral and cationic molecules in the monolayer.\textsuperscript{23} The magnitude of \(V\) can be estimated by comparing the experimentally obtained core-level shift to that calculated by density functional theory (DFT) for a single C\textsubscript{60} molecule in both its neutral and its charged state (see Methods section). Because calculations performed on single molecules cannot account for the mutual Coulomb interaction present in experiment, comparing the theoretically and experimentally obtained C1s binding energy differences of \(\sim 1.2\) eV and \(\sim 0.7\) eV, respectively, suggest \(V \approx 0.5\) eV.
Having confirmed the presence of C\textsubscript{60} cations in the (sub-)monolayer, we now turn to UPS to study its valence electronic structure, as shown in Fig. 2(b). With increasing coverage, molecular spectral features arise until, at about 30 Å (see ESI†), the typical thick-film spectrum of neutral C\textsubscript{60} is obtained.\textsuperscript{27,28} For < 1 Å coverage, however, subtraction of such a spectrum and the substrate contribution (each suitably scaled) inevitably yields a residual that resembles another C\textsubscript{60} thick-film spectrum over a wide binding energy range (see ESI†). This implies the presence of a second, chemically intact, but energy-shifted C\textsubscript{60} species as, in fact, expected from XPS. Indeed, the superposition of suitably scaled contributions from the substrate and two energetically shifted C\textsubscript{60} spectra, one accounting for the neutral molecules and one for the cations, perfectly reconstructs the measured thin-film data, as depicted in Fig. 2(b). This spectral deconvolution is further justified by our DFT results, which confirm that the shape of the DOS is almost identical for neutral and cationic C\textsubscript{60}, as shown in the bottom of Fig. 2(b) and (c).

Because, as in XPS, the high binding energy spectral contribution decreases with increasing submonolayer coverage, the assignment of these two C\textsubscript{60} species – also fully supported by DFT – has to be: the low binding energy component corresponds to neutral molecules (green) and the component at 0.8 eV higher binding energy corresponds to molecular cations (red). This is in clear contrast to the expectations outlined for UPS in Fig. 1(a) and (c).

To assess the validity of these expectations also for the unoccupied states, we applied the complementary spectroscopic technique IPES. The spectral intensity associated with C\textsubscript{60} was retrieved by subtracting a suitably scaled substrate contribution from the raw data (see ESI†). Fig. 2(c) shows the obtained difference-spectra for increasing nominal film thickness, starting with a C\textsubscript{60} coverage of 1 Å; for lower coverages the IPES intensity is insufficient due to the inherently low photon yield of the method. A superposition of three C\textsubscript{60} contributions (one each for cations in the monolayer, neutral molecules in the monolayer, and neutral molecules in the second layer) with relative weights and energy offsets in accordance with both XPS and UPS satisfactorily reproduces the obtained IPES spectra.

More importantly, however, both experiment and theory reveal the presence of an unoccupied HOMO-derived state of the cation, attributed to one out of ten electrons missing in the fivefold degenerate HOMO of neutral C\textsubscript{60} (see ESI† for a discussion of the reliability of this assertion and experimental details). This spectral feature is located close to and above \( E_F \) (in IPES: \(-0.25 \pm 0.25 \) eV binding energy) as deduced from the magnified comparison of calculated DOS and experimental spectrum in Fig. 2(c).

So, disconcertingly, the IPES results fulfil the expectations outlined in Fig. 1(a) and (c) while the UPS results are in strong contrast. To elucidate this striking discrepancy, we start out the discussion with Fig. 3(a): the energy required to remove an electron from a neutral molecule in the solid (IE\textsuperscript{0}) via UPS...
implies that literature-based expectations on their spectral version of which is provided in the rightmost panel of Fig. 3(b), which we suggest should replace the hitherto followed charge carriers in weakly interacting molecular systems, in particular, those induced by the electrical doping of molecular semiconductors through admixing strong electron donors or acceptors.

**Methods**

All samples were fabricated under ultra-high-vacuum conditions on an atomically clean Au(111) single crystal (MaTeK, repeated Ar⁺-ion-sputtering and annealing cycles up to 550 °C). MoO₃ (density = 4.7 g cm⁻³) and C₆₀ (density = 1.65 g cm⁻³) were purchased from Sigma Aldrich, purified via re-sublimation prior to use, and deposited from resistively heated crucibles. The evaporation rates (0.5–2 Å min⁻¹) and the nominal film thicknesses were monitored using a quartz-crystal microbalance. The pressure during the evaporation did not exceed 5 × 10⁻⁸ mbar (preparation chamber) and samples were transferred to the interconnected analysis chamber (base pressure 3 × 10⁻¹⁰ mbar) without breaking the vacuum.

To assess the electronic structure across the Au/MoO₃/C₆₀ heterostructures, in situ X-ray photoelectron spectroscopy (XPS: photon energy hν = 610 eV) and UPS (hν = 21 eV) spectra were collected at the end station SurICat (beamline PM4) of the synchrotron light source BESSY II (Berlin, Germany) using a hemispherical electron-energy analyser Scienta SES 100. IPES was performed in-house at HU-Berlin (incident electron energy range: 5–15 eV, NaCl-coated photocathode, SrF₂ window).

Density-functional theory (DFT) calculations on isolated C₆₀ molecules were performed with a hybrid exchange-correlation functional, mixing the generalized-gradient approximation developed by Perdew, Burke and Ernzerhof with a fraction z of Hartree–Fock (HF) exchange. In the spirit of ref. 38–40, z was determined by imposing Janak’s theorem, that is, by requiring that the total-energy difference between neutral and positively charged molecule (at the neutral-molecule equilibrium structure) equals the eigenvalue of the highest occupied molecular orbital
of neutral C$_{60}$. To capture the screening of the excess hole on the fullerene by the environment (MoO$_3$ and surrounding molecules), a polarizable continuum model$^{42}$ with 3.5 as relative dielectric constant was employed. After repeatedly cycling through the determination of $x$ and the geometry relaxation of the neutral molecule, an optimal value of $x = 0.3147$ finally emerged. The so-obtained hybrid-functional was then employed to relax the fullerene also to its (symmetry-broken) cation equilibrium geometry. The so-obtained hybrid-functional was then employed to relax the fullerene also to its (symmetry-broken) cation equilibrium geometry.

The core-level density of states (DOS) was obtained by broadening the entire manifold of C1s-related eigenvalues with area-normalized Gaussians of full-width at half-maximum (FWHM) of 0.7 eV. The valence DOS was produced by first broadening each valence-orbital eigenvalue with an area normalized Gaussian of standard deviation $\sigma = 0.22$ eV to emulate disorder, by subsequent multiplication with a room-temperature Fermi function (UPS) or one minus a Fermi function (IPES), and by finally convoluting the result with an area-normalized Gaussian of $\sigma = 0.14$ eV (UPS) or $\sigma = 0.34$ eV (IPES) to account for detector broadening. For the spin-polarized cations, possessing one more spin-up than spin-down electrons, two possible spin-multiplicities (singlet and triplet) in the final state of the UPS/IPES experiment were taken into account: removing a further spin-down electron from the cation by UPS (or adding another spin-up electron in IPES) results in one of three possible triplet states, while removing a spin-up electron by UPS (or adding a spin-down electron in IPES) results in a singlet final state. Therefore, the spin-down DOS for UPS (and the spin-up DOS in IPES) has been multiplied by a factor three before adding the spin-up DOS for UPS (and the spin-down DOS for IPES) to yield the final result displayed in Fig. 2 of the main text.

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