Observation of a molecule-metal interface charge transfer state by resonant photoelectron spectroscopy

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We report the discovery of a novel charge transfer (CT) state at a molecule-metal interface by the application of resonant photoelectron spectroscopy (ResPES). This interface feature is neither present for molecular bulk samples nor for the clean substrate. Within a simplified two-step model this signal is assigned to a particular final state that is invisible in direct photoelectron spectroscopy but in ResPES revealed through relative resonant enhancement. A detailed analysis of the spectroscopic signature of the CT state shows characteristics of electronic interaction not found in other electron spectroscopic techniques. Our study demonstrates the sensitivity of ResPES to such interactions and constitutes a new way to investigate CT at molecule-metal interfaces.

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One of the crucial questions for the performance of organic electronics is the charge transfer across the metal-organic interface. The technique of resonant photoelectron spectroscopy (ResPES) is able to investigate this issue within the core hole clock technique [1]. For small adsorbates like noble gases [2], sulphur atoms [3, 4] and small molecules [5] a quantitative extraction of charge transfer times has been successfully performed in the fs-as-regime. Also for large \( \pi \)-conjugated molecules a rather large body of literature with a quantitative analysis of charge transfer times exist [6–9]. However, the complicated electronic structure of these molecules and possible strong interactions with the substrate pose a tremendous challenge to the quantitative extraction of intensities from the ResPES data. Hence the published charge transfer times of similar systems differ substantially and the significance of many studies remains questionable. In order to permit quantitative investigations for these systems first the interaction at the interface and second its consequence for ResPES need to be understood in more detail.

In ResPES certain signals in the PES spectrum can get enhanced due to additional autoionization (AI) channels which open up in the resonance case. For example the 6 eV satellite in Ni metal [10] was assigned to a two hole final state due to the intensity enhancement and energy dispersion observed while tuning the photon energy (\( h\nu \)) over a resonance [11, 12]. Furthermore similar satellites for Cr and Fe metal could only be discovered due to resonant intensity enhancement [13]. In compounds \( h\nu \) can be chosen to selectively excite in a resonance belonging to one of its constituents in order to enhance signals of this particular species [14–16]. Moreover the surface sensitivity of ResPES allows to apply the concept of selective resonant enhancement to quasi two dimensional systems like surface alloys [17]. However, which signal belonging to the selected species gets enhanced is a matter of localization of the resonantly excited electron. For the excitation into a delocalized d-band of a metal for example it is the incoherent Auger process that mainly gains in intensity and the enhanced signal disperses with a constant kinetic energy \( (E_K) \) [11, 13, 15]. Exciting resonantly into a localized f-orbital on the other hand leads to a coherent and energy conserving process in which the enhanced signal stays at constant binding energy \( (E_B = h\nu - E_K) \) [15, 21]. If a case of intermediate localization is realized both, the coherent and the incoherent signal will be visible. Directly on resonance the continuous PES channel and the discrete Auger channel interfere [22, 23] and cannot be distinguished but above the resonance the constant \( E_K \) dispersion of the Auger signal makes this signal move away from the coherent signal at constant \( E_B \). Consequently the coherent and the incoherent part can be separated for simple model systems [2]. For an adsorbate at a surface the latter can be interpreted as a charge transfer (CT) across the adsorbate substrate interface which in principle allows a determination of the CT time with the core hole clock technique [1]. So if the intensities of the signals corresponding to both channels can be extracted from the ResPES spectrum in a significant way a quantitative value of the CT time can be determined [3, 4].

In this work we apply ResPES to a model system of a large \( \pi \)-conjugated molecule adsorbed on a metal surface, namely a sub-monolayer (SubML) of Coronene adsorbed on Ag(111). First we present the observation of a CT state in a PES map recorded in the energetic region of the largest resonant enhancement of the highest occupied molecular orbital (HOMO). The CT state is found to originate from the metal-organic interface and the spectroscopic signature of this feature shows characteristics of strongly coupled molecule-metal interfaces. Hence ResPES reveals an electronic interaction between Coronene and Ag(111), a system that shows no evidence
for strong coupling in other electron spectroscopic techniques. We then explain the appearance of the CT feature within a simplified two-step model that includes molecule-metal CT. Finally the absence of the CT state in direct PES is explained by relative resonant enhancement of this state with respect to the HOMO.

Measurements were performed at BESSY II at the undulator beamline UE52-PGM ($E/\Delta E > 14000$ at $400 \text{ eV}$ photon energy, with $\text{ccf}=10$ and $20 \mu\text{m}$ exit slit [24]) in a UHV chamber with a pressure below $5 \times 10^{-10} \text{ mbar}$. All PES maps were recorded with p-polarized light and $70^\circ$ angle of incidence with respect to the surface normal, a beamline exit slit of $40 \mu\text{m}$ and a cff value of 10. Photoelectron intensities were detected with a Scienta R4000 electron analyzer with an energy resolution better than $\Delta E = 35 \text{ meV}$ for the PES detail map (Fig. 2(a)). $h\nu$ was calibrated with the Fermi edge ($E_F$) resulting in an accuracy better than $50 \text{ meV}$ (for $E_B$ and $h\nu$). PES intensities were normalized to the ring current and the beamline flux curve which was recorded separately by measuring the clean surface [24]. For the PES detail map (Fig. 2(a)) the 2nd order C1s signal was subtracted with a reference spectrum of the same sample previous to the normalization procedure. The Ag(111) substrate was cleaned by several sputter and annealing cycles and its cleanness was confirmed by PES. Coronene molecules were purified by sublimation and evaporated from a Knudsen cell at a pressure below $10^{-8} \text{ mbar}$ and at room temperature (RT). Film thickness was determined by core level intensities of the adsorbate and the substrate, using the effective electron attenuation lengths given in Ref. [25].

Fig. 1(a) shows a PES overview map at the carbon K-edge of a SubML Coronene/Ag(111). The most prominent signals are the Ag4d bands in between a $E_B$ of $4 \text{ eV}$ and $8 \text{ eV}$. Below the onset of the first absorption peak of Coronene at approximately $284 \text{ eV}$ these are the only significant contribution to the spectra. At higher $h\nu$ (but still below the direct photoionization into vacuum) the situation changes dramatically and signals originating from the Coronene get massively enhanced. At higher $E_B$ than the Ag4d bands both, low lying molecular orbitals (MO) [27] and KVV Auger peaks, are situated. The former can be seen as enhanced PES signals due to AI after photon absorption while the latter are a consequence of core hole decays. Integrating over a constant $E_K$ from 272.0 eV to 274.5 eV denoted by the blue box in Fig. 1(a) results in the spectrum displayed in Fig. 1(b). This spectrum is equal (within the chosen $h\nu$ increment) to the partial electron yield near edge X-ray absorption fine structure spectroscopy (PEY NEXAFS) spectrum but only consists of a certain $E_K$ window instead of all emitted electrons above a retarding voltage as for the PEY NEXAFS. Since its signal mainly originates from several KVV Auger decays we call it KVV NEXAFS (for further details see Ref. [28]). In the $h\nu$ region of two most intense NEXAFS resonances A and B we further observe a substantial intensity enhancement of the HOMO which is located at slightly lower $E_B$ than the rising edge of
the Ag4d bands. For closer inspection of these signals the area within the cyan box in Fig. 1(a) is recorded in a subsequent measurement with lower energy increments and higher resolution.

Fig. 2(a) displays this PES detail map. Here not only the intensity enhancement of the HOMO but also its line shape variation as a function of $h\nu$ becomes obvious. This effect is due to a difference in the vibrational progression of the HOMO which is a consequence of the particular vibronic excitations within the photon absorption (29) and hence a function of $h\nu$ (for a detailed discussion see Ref. 28). The focus of this work lies on the additional feature centered at approximately 0.5 eV $E_B$ below $E_F$ which becomes clearly visible after the intensity of the PES detail map is multiplied by a factor of 10 within the thick black lines. Integrating over the constant $E_B$ windows marked by the hatched areas in Fig. 2(a) results in the filled symbols displayed in Fig. 2(b). Here it is revealed that the HOMO and the low $E_B$ feature exhibit a very similar intensity variation as a function of $h\nu$ and that the relative intensity of the low $E_B$ feature with respect to the HOMO intensity is found to be approximately 5%. An integration over the same $E_B$ region of a corresponding PES detail map of the clean Ag(111) (red) results in the open symbols displayed in Fig. 2(b). Here it is revealed that the feature originates from the metal-organic interface since neither the clean Ag(111) nor the pure Coronene film (without interface contribution) exhibits such a signal. Hence an interaction of the Ag(111) substrate with the Coronene adsorbate film must be present.

This conclusion is corroborated by the broad line shape of the low $E_B$ feature which is presented in Fig. 3. Here energy distribution curves (EDCs) from the PES detail map of a SubML Coronene/Ag(111) displayed in Fig. 2(a) (black/grey) in comparison to corresponding EDCs from a PES detail map of clean Ag(111) (red). All EDCs from the PES detail map of the clean Ag(111) were multiplied by the same factor in order to match the Fermi edges of the uppermost EDCs ($h\nu = 285.43$ eV).
map (Fig. 2(a)) are compared to EDCs from the corresponding PES detail map of clean Ag(111) in the relevant $E_B$ region. The broad and smeared out resonantly enhanced intensity of the SubML Coronene/Ag(111) film is similar to the signals observed for strongly coupled molecule-metal interfaces [30] which are characterized by an occupied lowest unoccupied molecular orbital (LUMO) [31]. Interestingly, in direct PES (with $h\nu$ below the resonance) a possible LUMO signal is found to be below the detection limit of approximately 1% with respect to the HOMO intensity at any point in the probed $k$-space region [27]. Moreover, the generally observed strong variation of PES core level and NEXAFS spectra of the strongly coupled molecule-metal systems with respect to the multilayer spectra cannot be found for Coronene. The only hint for an electronic interaction is a broadening of the single vibronic components of the HOMO in the high resolution PES spectrum of 1 ML Coronene/Ag(111) with respect to 1 ML Coronene/Au(111) [32]. Thus the finding of electronic interactions at the here investigated molecule-metal interface demonstrates the sensitivity of ResPES to such interactions.

An explanation for the observed low $E_B$ feature can be given on the basis of a simplified two-step picture (step (a) and (b)) including CT from the metal to the molecule. The NEXAFS resonances A and B can be assigned to an excitation into the LUMO [33] thus this constitutes step (a) of the mechanism. Step (b) is the subsequent AI process. The channel leading to the enhanced HOMO signal (denoted as channel (I)) can be written in the following way:

(Ia) \[ |C^2H^2L^0M^n\rangle + h\nu \xrightarrow{\text{NEXAFS}_{\text{no CT}}} |C^1H^2L^1M^n\rangle \]

(Ib) \[ |C^1H^2L^1M^n\rangle \xrightarrow{\text{AI}} |C^2H^1L^0M^n\rangle + e^- \]

Hereby $C$ stands for the Cls core level, $H$ for the HOMO, $L$ for the LUMO, $M$ for the metal and $e^-$ is the emitted electron. All other levels of the system are omitted. The used nomenclature for the wave function of the molecule in contact to a metal is based on the cluster model description of transition metal oxides [34–39]. The superscript denotes the occupation of the particular level. In the same way we can write down the mechanism including CT:

(IIa) \[ |C^2H^2L^0M^n\rangle + h\nu \xrightarrow{\text{NEXAFS}_{\text{CT}}} |C^1H^2L^2M^{n-1}\rangle \]

(IIb1) \[ |C^1H^2L^2M^{n-1}\rangle \xrightarrow{\text{AI}} |C^2H^1L^1M^{n-1}\rangle + e^- \]

(IIb2) \[ |C^1H^2L^2M^{n-1}\rangle \xrightarrow{\text{AI}} |C^2H^2L^0M^{n-1}\rangle + e^- \]

This channel (denoted as channel II) can lead to two different final states ((1) and (2)) through AI which both could lead to the low $E_B$ feature in ResPES. Due to the involvement of interface CT in the mechanism leading to this state we will call it CT state. The fact that this CT state is not observed in direct PES requires a relative enhancement of this state with respect to the HOMO in PES at the K-edge. In other words the probability for the responsible step must be larger than the one for step (Ib). For the steps (IIb1) and (Ib) equal states, namely $C$, $H$ and $L$, are involved in the AI process so a different probability is highly unlikely. In contrast, step (IIb2) involves $C$ and the state $L$ twice. It is reasonable to expect the overlap matrix element of $L$ with itself to be larger than the ones of (Ib) and (IIb1) in which an overlap of $L$ and $H$ is included. Thus we assign the final state \[ |C^2H^2L^0M^{n-1}\rangle \] to the observed CT state in ResPES. In principle this final state could also appear in a direct PES measurement as long as the coupling between the substrate states and the MO is nonvanishing. The probability for this state to be produced is apparently unlikely and hence it can only be detected through the resonant enhancement due to the AI channel in ResPES.

An equivalent and quantitative description of the process responsible for the valence satellite can be conducted on the basis of the Cluster Model along the lines of Ref. [27]. Here the involved states are represented as a quantum mechanical superposition of a state with CT and another one without CT. A consistent description of the SubML Coronene/Ag(111) data with physically reasonable Cluster Model parameters requires a weighting factor of only \( \frac{(\text{IIb2})}{(\text{Ib})} = 6 \) in order to reproduce the observed relative resonant enhancement from PES to ResPES. This ratio of two overlap matrix elements containing different MO seems to be of reasonable magnitude. Details will be given in a future publication.

In conclusion the finding of a CT state in ResPES applied to a molecule-metal interface provides evidence for interfacial CT and electronic interaction not deduced by results from other electron spectroscopic techniques. Through the description of the responsible mechanism within a simple two-step model we were able to assign a particular final state to this CT state. The found process requires the involvement of metal states and CT into the molecule. In addition to manifesting the power of ResPES in revealing electronic interaction at interfaces, our experiments demonstrate a novel route to identify and characterize charge transfer processes at molecule-metal interfaces.

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