



PAPER

Observation of a molecule–metal interface charge transfer related feature by resonant photoelectron spectroscopy

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E-mail: achim.schoell@physik.uni-wuerzburg.de**Keywords:** resonant photoelectron spectroscopy, interface, organic thin films, charge transfer

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**Abstract**

We report the discovery of a charge transfer (CT) related low binding energy feature at a molecule–metal interface by the application of resonant photoelectron spectroscopy (RPES). This interface feature is neither present for molecular bulk samples nor for the clean substrate. A detailed analysis of the spectroscopic signature of the low binding energy feature shows characteristics of electronic interaction not found in other electron spectroscopic techniques. Within a cluster model description this feature is assigned to a particular eigenstate of the photoionized system that is invisible in direct photoelectron spectroscopy but revealed in RPES through a relative resonant enhancement. Interpretations based on considering only the predominant character of the eigenstates explain the low binding energy feature by an occupied lowest unoccupied molecular orbital, which is either realized through CT in the ground or in the intermediate state. This reveals that molecule–metal CT is responsible for this feature. Consequently, our study demonstrates the sensitivity of RPES to electronic interactions and constitutes a new way to investigate CT at molecule–metal interfaces.

1. Introduction

One of the crucial questions for the performance of organic electronics is dynamical charge transfer (CT) across the metal–organic interface. The technique of resonant photoelectron spectroscopy (RPES) is able to investigate this phenomenon 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 CT times has been successfully performed in the fs- and as-regime. Also for large π -conjugated molecules a considerable body of literature with a quantitative analysis of CT times exists [6–10]. 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 RPES data. In order to permit quantitative understanding for these systems first the interaction at the interface and second its consequence for RPES need to be understood in more detail.

In RPES certain signals in the photoelectron spectroscopy (PES) spectrum can get enhanced due to additional autoionization channels which open up in the resonance case. For example the 6 eV satellite in Ni metal [11] was assigned to a two hole final state due to the intensity enhancement and energy dispersion observed while tuning the photon energy ($h\nu$) through a resonance [12, 13]. Furthermore, similar satellites for Cr and Fe metal could only be discovered due to resonant intensity enhancement [14]. In compounds $h\nu$ can be chosen to selectively excite one of its constituents resonantly in order to enhance signals of this particular species [15–17]. Moreover the surface sensitivity of RPES allows to apply the concept of selective resonant enhancement to quasi two-dimensional systems like surface alloys [18]. 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) [12–14, 19]. 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 ($E_B = h\nu - E_K$) [20–22]. 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 with the same E_K of the emitted electron interfere [23, 24] and cannot be distinguished, but above the resonance the 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 often be separated for simple systems [2]. For an adsorbate at a surface the latter can be caused by CT across the adsorbate substrate interface after excitation 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 RPES data a quantitative value for the CT time can be determined [3, 4].

In this work we apply RPES to a model system of a large π -conjugated molecule adsorbed on a metal surface, namely coronene adsorbed on Ag(111). First we present the observation of a low E_B feature in a PES map recorded in the energetic region of the largest resonant enhancement of the highest occupied molecular orbital (HOMO). This low E_B feature is found to originate from the interface and its spectroscopic signature shows characteristics of strongly coupled molecule–metal interfaces. Hence RPES 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 low E_B feature within a cluster model that treats the molecule–metal interface as a system of localized molecular states coupled to the metal substrate. The cluster model has been applied particularly to transition metal oxides, where the correlated localized 3d states are hybridized with the states of the surrounding ligands. In the present case we transfer this concept to the localized, possibly correlated states² of a π -conjugated molecule, which are interacting through hybridization with a bath of conduction electrons, which are considered as (discrete) metal states. In this model the low E_B feature is identified as a resonantly enhanced satellite of the HOMO signal which explains why this feature cannot be detected in direct PES. The thereby employed eigenstates, both the ground and the photoemission final state, are quantum mechanical superpositions of two basis states of which one takes CT between molecule and metal into account. Based on simplifications of the cluster model alternative explanations are discussed. Considering only the main character of the final state assigned to the low E_B feature suggests resonantly enhanced PES from the lowest unoccupied molecular orbital (LUMO) as the mechanism responsible for this feature. Consequently, CT in the ground state is concluded from this interpretation. Reducing the ground state to its predominant character, on the other hand, leads to the conclusion that dynamical CT in the intermediate state needs to be involved in the generation of the low E_B feature. Hence independent of the interpretation the low E_B feature is related to CT between molecule and metal.

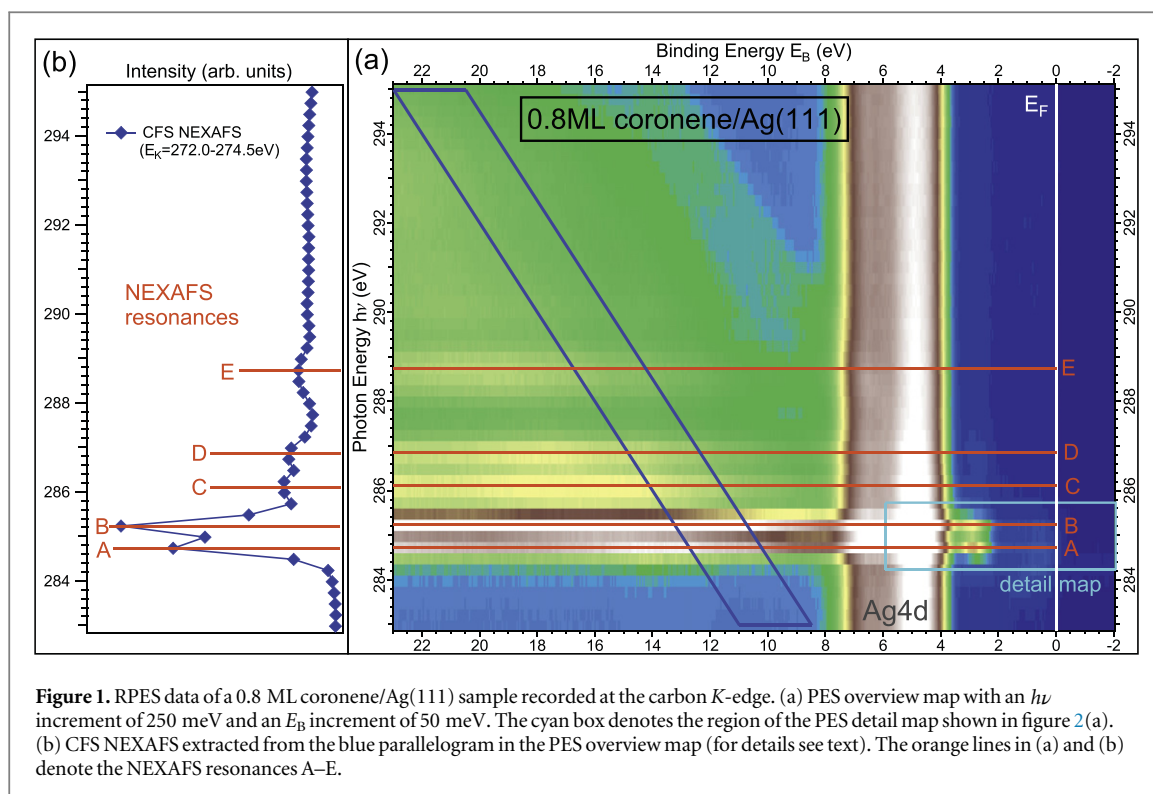
2. Experimental

Measurements were performed at BESSY II at the undulator beamline UE52-PGM ($E/\Delta E > 14\,000$ at $h\nu = 400$ eV, with $c_{ff} = 10$ and 20 μm exit slit [27]) in a UHV chamber with a pressure below 5×10^{-10} mbar. All PES maps were recorded with p-polarized light and 70° angle of incidence with respect to the surface normal, a beamline exit slit of 40 μm , and a c_{ff} value of 10 . This results in a $\Delta h\nu$ better than 40 meV at $h\nu = 290$ eV. Photoelectron intensities were detected with a Scienta R4000 electron analyzer with $\Delta E = 75$ meV for the PES detail map (figure 2(a)). $h\nu$ was calibrated with the Fermi energy (E_F) resulting in an accuracy better than 50 meV (for E_B and $h\nu$). PES intensities were normalized with the ring current and the beamline flux curve which was recorded separately by measuring the clean surface [28]. For the PES detail map (figure 2(a)) the 2nd order C1s signal was subtracted with a reference spectrum of the same sample previous to the normalization with the beamline flux curve. The Ag(111) substrate was cleaned by several sputter and annealing cycles and its cleanliness was confirmed by PES. Coronene molecules were purified by sublimation and evaporated from a Knudsen cell at a pressure below 10^{-8} mbar and at room temperature. Film thickness was determined by core-level intensities of the adsorbate and the substrate, using the effective electron attenuation lengths given in [29].

3. Results and discussion

Figure 1(a) shows a PES overview map at the carbon K -edge of a 0.8 monolayer (ML) coronene/Ag(111) sample. The most prominent signals are the Ag4d bands situated at $E_B = 4 - 8$ eV. Below the onset of the first absorption peak of coronene at approximately 284 eV these are the only significant contribution to the spectra. At larger $h\nu$ (but still below the direct photoionization into vacuum) the situation changes dramatically and signals originating from coronene get strongly enhanced. Integrating over a constant E_K from 272.0 to 274.5 eV (denoted by the blue parallelogram in figure 1(a)) results in the spectrum displayed in figure 1(b). This 1D

² An upper value for the Coulomb energy between two electrons in the same valence state of about 2 eV can be derived from several experiments on similar systems, see for example [25, 26].

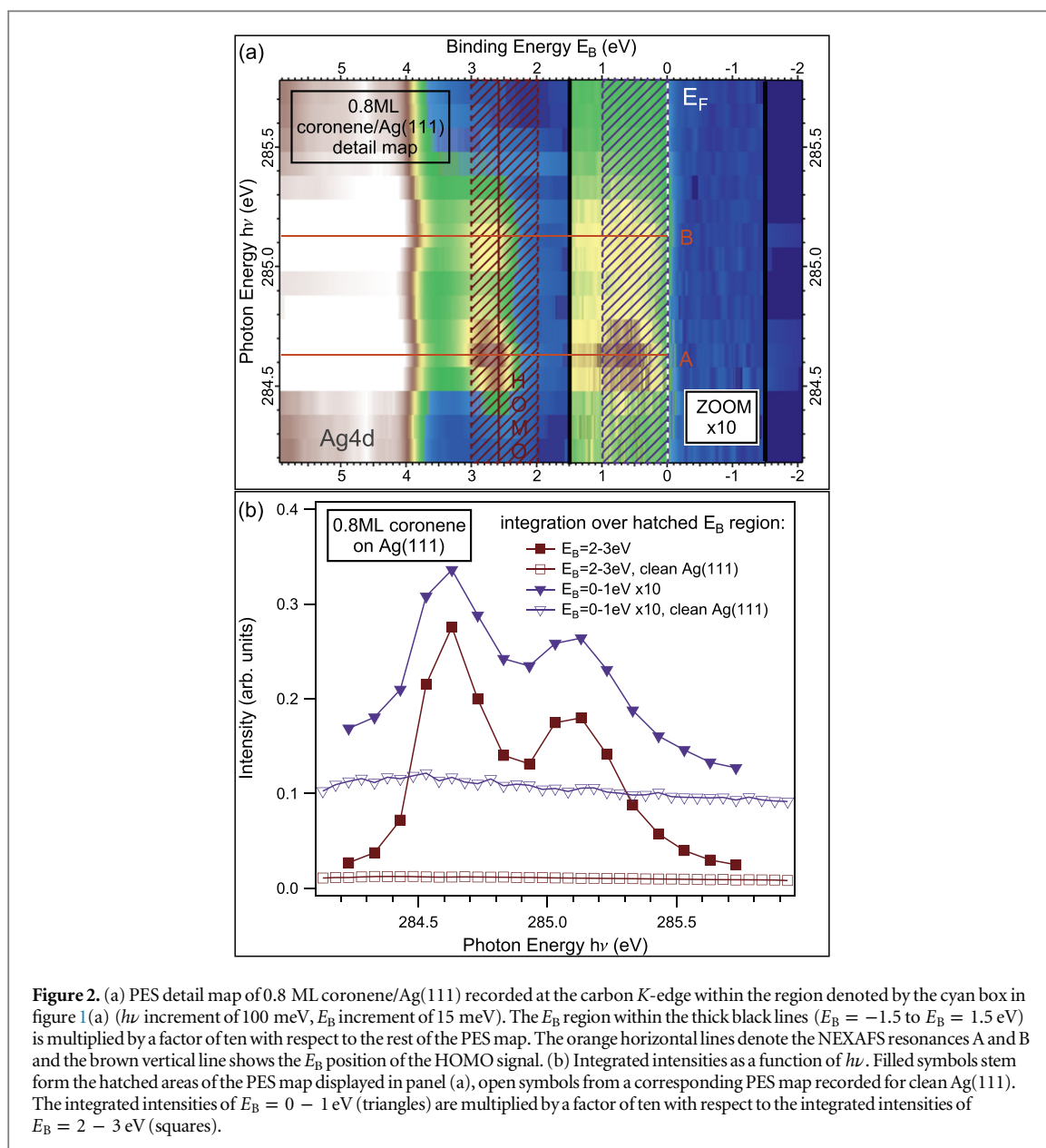


spectrum is equal (within the chosen $h\nu$ increment) to the partial electron yield near edge x-ray absorption fine structure spectroscopy (NEXAFS) spectrum and can be used for the identification of the NEXAFS resonances. Since the measurement of a constant E_K window is referred to as constant final state (CFS) spectroscopy we call the obtained 1D spectrum CFS NEXAFS in the following (for further details see [30]). In the $h\nu$ region of the two most intense NEXAFS resonances A and B we further observe a substantial intensity enhancement of the HOMO signal which is located at slightly lower E_B than the rising edge of the Ag4d bands. These NEXAFS resonances A and B can be assigned to an excitation into the LUMO [31]. Resonances C–E, which are not in the focus of the following analysis, are due to transitions into higher unoccupied orbitals [31]. For closer inspection the area within the cyan box in figure 1(a) is recorded in a subsequent measurement with lower energy increments and higher resolution.

Figure 2(a) displays this PES detail map. Here not only the intensity enhancement of the HOMO signal but also its line-shape variation as a function of $h\nu$ becomes obvious. This effect is due to a difference in the vibronic progression of the HOMO signal which is a consequence of the particular vibronic excitations within the photon absorption [32] and hence a function of $h\nu$ (for a detailed discussion see [30]). Here we focus on the additional feature centered at $E_B \approx 0.5$ eV which becomes clearly visible after the intensity of the PES detail map is multiplied by a factor of 10. Integrating over the constant E_B windows marked by the hatched areas in figure 2(a) results in the filled symbols displayed in figure 2(b). Figure 2(b) reveals that the intensity of the low E_B feature amounts to about 5% of the intensity of the HOMO signal. Moreover, the low E_B feature and the HOMO signal obviously exhibit a very similar intensity variation as a function of $h\nu$. Interestingly, a comparison to the corresponding data of the clean Ag(111) substrate (open symbols in figure 2(b)) demonstrates the absence of the low E_B feature for the bare Ag(111) surface. Such a feature is furthermore not observed in the corresponding PES data of a coronene multilayer film [30]³. This leads to the conclusion that the low E_B feature in figure 2(a) originates from the metal–organic interface and hence a particular 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 figure 3. Here energy distribution curves (EDC) from the PES detail map (figure 2(a)) are compared to corresponding EDC from clean Ag(111). The broad and smeared out resonantly enhanced intensity of the 0.8 ML coronene/Ag(111) film is similar to the signals observed for strongly coupled molecule–metal interfaces [33], which are characterized by an occupied LUMO [34]. Interestingly, in direct PES (with $h\nu = 40.8$ eV) a possible LUMO signal is found to be below the detection limit of approximately 1% with respect to the intensity of the HOMO

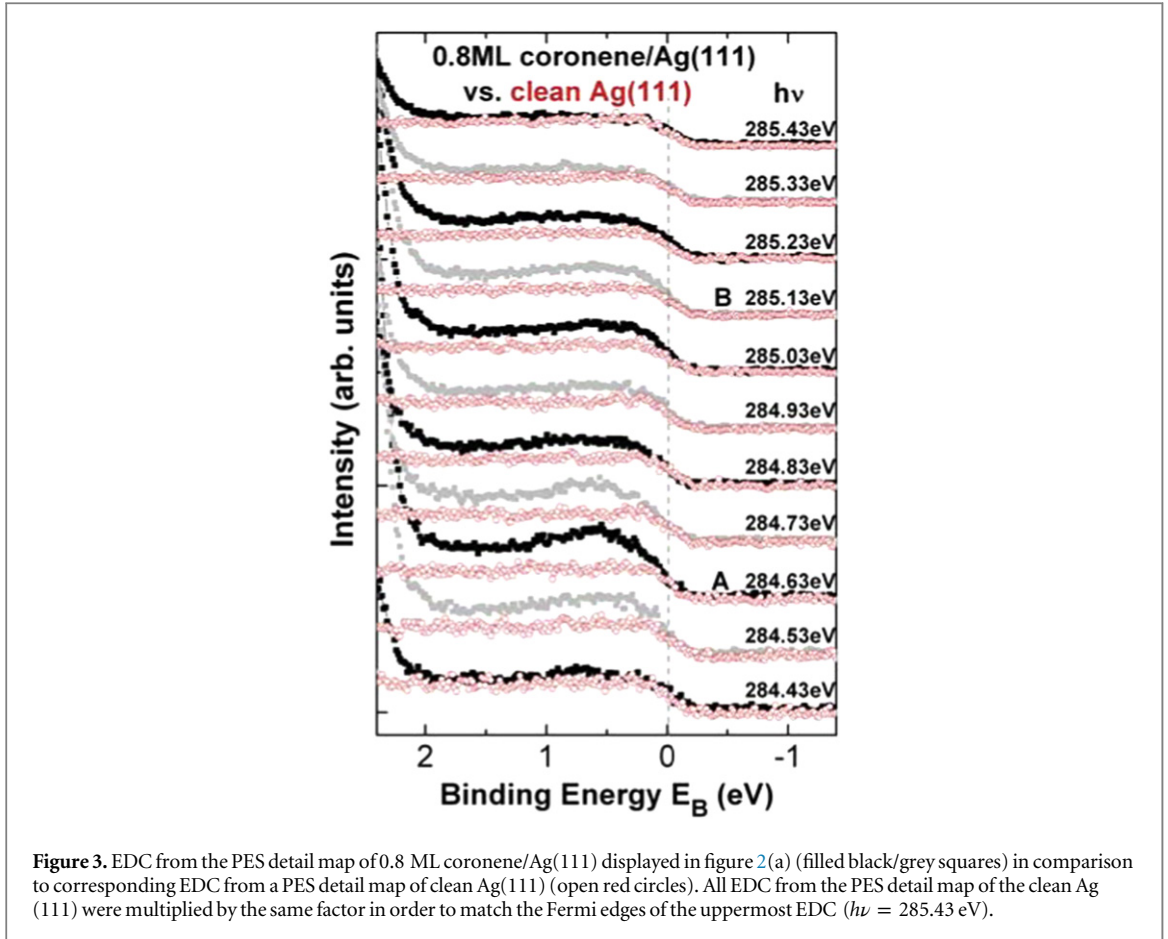
³ Note that in contrast to figure 2(c) in [30] the 2nd order C1s signal has been subtracted from the 0.8 ML data so a contribution by this signal can be excluded.



signal at any point in the probed k -space [35]. Moreover, the strong changes of the interfacial PES core level⁴ and NEXAFS spectra with respect to the multilayer spectra, which are generally observed for strongly coupled molecule-metal systems, cannot be found for coronene. From these experiments one would conclude that electronic interaction in the present system is weaker compared to the cases discussed in [33, 34]. Thus the finding of signatures of electronic interaction at the here investigated molecule-metal interface demonstrates the sensitivity of RPES to such interactions. We would like to note that any metallic interface states cannot explain this observation of an additional signal at the coronene/Ag(111) interface since it does not appear in direct PES [36, 37] thus demanding for an alternative explanation.

The similar $h\nu$ dependent intensity variation of the low E_B feature and the HOMO signal suggests that the former feature is a satellite excitation of the latter. The fact that the low E_B feature originates from the metal-organic interface further requires an involvement of a metal state in the responsible excitation process. An established theoretical description which is capable of treating such excitations in a simplified way is the cluster model [38–41]. In order to apply this theory to the coronene/Ag(111) interface the coronene molecule has to be seen as an impurity with localized states (molecular orbitals) coupled to metallic states (Ag(111) s - p bands) similar to the single impurity Anderson model [42]. The cluster model emerges from the Gunnarsson-Schönhammer theory [43, 44] by setting the bandwidth of the metallic band to zero. Consequently, the molecule-metal interface is treated as a ‘cluster’ of a molecule coupled to several metal ligand atoms with

⁴For completeness, the C1s peak maximum is at 285.02 eV for 0.8 monolayers of coronene/Ag(111).



energetically discrete metallic ligand states M . The coupling of the molecular states H (HOMO) and L (LUMO) to the metal states M is incorporated in the cluster model Hamiltonian by the consideration of hopping matrix elements $V_{L,M}$ and $V_{H,M}$ [38–40, 42–44]. The simplest cluster model description of the system coronene/Ag(111) requires a two state orthonormal basis with which the eigenstates of the Hamiltonian are constructed. Diagonalization of this Hamiltonian results in eigenstates $|\Phi_g\rangle$ of the initial state of the form

$$|\Phi_g\rangle = \alpha_g |C^2H^2L^0M^n\rangle + \beta_g |C^2H^2L^1M^{n-1}\rangle. \quad (1)$$

Hereby C stands for the C1s core level of one chemical species. All states except the single particle states C , H , L , and M of the system are omitted. The superscript denotes the occupation of the particular level ($n \in \mathbb{N}$) i.e., $|C^2H^2L^0M^n\rangle$ denotes a basis state with two electrons each in C1s and HOMO, zero in LUMO, and n in the metal states, while in case of $|C^2H^2L^1M^{n-1}\rangle$ an additional electron is found in the LUMO and one is missing in the metal. The latter basis state thus is the CT state. Hence the eigenstate described in equation (1) is a hybrid state of two basis states, with and without CT. The corresponding PES final state consists of eigenstates $|\Phi_f\rangle$ of the photoionized system of the form

$$|\Phi_f\rangle = \alpha_f |C^2H^1L^0M^n\rangle + \beta_f |C^2H^2L^0M^{n-1}\rangle \quad (2)$$

plus a photoelectron. In order to describe a valence PES experiment these eigenstates are sufficient while for a treatment of RPES the introduction of intermediate states $|\Phi_i\rangle$ (similar to [40, 41]) of the form

$$|\Phi_i\rangle = \alpha_i |C^1H^2L^1M^n\rangle + \beta_i |C^1H^2L^2M^{n-1}\rangle \quad (3)$$

is necessary. The prefactors α and β of these eigenstates are functions of the cluster model parameters. This parameter set consists of the single particle energies of all considered states (ϵ_M for the state M etc.), the hopping matrix elements ($V_{L,M}$ and $V_{H,M}$; note that all hopping matrix elements are in the latter evaluation set equal, independent of the core level occupation) and Coulomb interaction parameters that take into account the mutual repulsion of electrons in molecular orbitals and the attraction of electrons in molecular orbitals by a core hole (see [38–40]). Furthermore, the eigenenergies of the given eigenstates are also functions of these cluster model parameters.

The quantities extracted from the valence PES and RPES experiments which can be calculated within the cluster model are the energetic separation and the intensity ratio of the main line and its satellite. In case of PES

intensities can be calculated by the matrix elements of the respective initial and final states and the corresponding perturbation operator. In case of RPES double matrix elements have to be taken into account, which consider RPES as PES through the intermediate states in equation (3). The resonant enhancement of the satellite is incorporated in the theory by a weighting of the autoionization (AI) matrix elements in the following way

$$\begin{aligned} \langle C^2H^2L^0M^{n-1} | \mathcal{H}_{AI} | C^1H^2L^2M^{n-1} \rangle &= \gamma > 1 \\ \langle C^2H^1L^0M^n | \mathcal{H}_{AI} | C^1H^2L^1M^n \rangle &= 1 \end{aligned} \quad (4)$$

with the autoionization operator of the form $\mathcal{H}_{AI} = (\mathbf{c}_{H,\sigma} + \gamma \cdot \mathbf{c}_{L,\sigma'}) \mathbf{c}_{C,\sigma}^\dagger \mathbf{c}_{L,\sigma}$ with \mathbf{c} and \mathbf{c}^\dagger denoting fermionic annihilation and creation operators, respectively. Furthermore, the subscripts C , H , and L stand for the state in which the particular operator annihilates (or creates) an electron with spin σ . Hereby the factor γ is introduced to weight an autoionization matrix element which includes the state L twice with respect to the other one that includes H and L . It is reasonable to assume a larger value for an autoionization matrix element containing the same molecular orbital twice with respect to an autoionization matrix element ($\gamma > 1$ which includes two different molecular orbitals). The energetic separation of the main line and its satellite in PES and RPES is equal and can be calculated by taking the difference of the eigenenergies of the final eigenstates in equation (2).

The measured intensity ratio in PES (where no significant signal can be observed and an upper limit of 1% can thus be estimated) and RPES (approximately 5%) and the energetic separation of the main line and its satellite (approximately 2.1 eV) can be successfully reproduced with a physically reasonable set of parameters. A detailed discussion of the individual choices is quite cumbersome and shall not be given here in detail, because the main physical concept is already described above. An extensive description of the cluster model, the selection of parameters and a discussion of their meaning can be found in [45]. With these parameters an energetic separation of more than 2 eV is obtained for the eigenenergies of the eigenstates $|\Phi_g\rangle$ in the initial state. Since the initial state is in a thermodynamic equilibrium (in contrast to the intermediate and the final state) only the energetically favorable eigenstate has to be considered as the ground state. Hence the two peaks in RPES originate from a transition from one ground state $|\Phi_g\rangle$ to two final eigenstates $|\Phi_{f,1}\rangle$ and $|\Phi_{f,2}\rangle$ (equation (2)), which differ in the prefactors α_f and β_f . Most importantly a weighting factor of only $\gamma = 6$ is sufficient to obtain the found relative resonant enhancement of the low E_B feature with respect to the HOMO signal from PES to RPES. In the cluster model the intensity ratio, or in other words the probability for the production of a satellite, depends on cluster model parameters. Especially the energetic differences of the single particle energies and the Coulomb parameters determine the intensity of the satellite with respect to the main line. So the energetics of a particular system leads to the corresponding intensity of satellite excitations. The difference of the cluster model approach with respect to the discussion of the energetics as in [1] is that in the former a possibility of energetically unfavorable satellite excitations exists. Moreover, the comparison of energies in the core excited intermediate state in [1] is based on a single-particle picture which might not be justified when correlations come into play.

The cluster model explains in the present case the experimental findings with the assignment of $|\Phi_{f,1}\rangle$ to the HOMO signal and $|\Phi_{f,2}\rangle$ to the low E_B feature. It is the successful reproduction of the measured quantities within this model which shows that the low E_B feature in the RPES data can indeed be explained as a resonantly enhanced HOMO signal satellite. With the chosen parameter set it follows that $\alpha_{f,1} \gg \beta_{f,1}$ and $\alpha_{f,2} \ll \beta_{f,2}$.

Hence the final state $|\Phi_{f,2}\rangle$ has almost entirely the character of the basis state $|C^2H^2L^0M^{n-1}\rangle$. This allows another interpretation of the low E_B feature. Considering that in a PES experiment this basis state can only be produced by the creation of a hole in the state L of the basis state $|C^2H^2L^1M^{n-1}\rangle$ identifies the transition leading to the basis state $|C^2H^2L^0M^{n-1}\rangle$ as PES from the LUMO. Consequently, the emergence of the low E_B feature in the RPES data can be interpreted as resonantly enhanced PES from the LUMO. Hence CT in the ground state is included in the mechanism that leads to the low E_B feature in this interpretation. However, if the admixture of the basis state $|C^2H^2L^1M^{n-1}\rangle$ was significant in the ground state $|\Phi_g\rangle$ a LUMO signal should also be visible in direct valence PES. In agreement with this finding the cluster model calculations obtain $\alpha_{g,1} \gg \beta_{g,1}$. Hence it is also reasonable to consider a ground state with pure character of the basis state $|C^2H^2L^0M^n\rangle$. In this case the emergence of a photoionized final state with the main character of the basis state $|C^2H^2L^0M^{n-1}\rangle$ requires the production of an intermediate state with an admixture of the basis state $|C^1H^2L^2M^{n-1}\rangle$ in a different way. This can be achieved by CT from M to L during the time scale of the core hole life time. In this interpretation the low E_B feature is a signature of dynamical interface CT. Consequently, the interpretation of the low E_B feature depends on the initial choice of the picture in which the process that leads to this feature is described. In the cluster model explanation CT is included in one of the basis states with which the eigenstates are constructed as a quantum mechanical superposition. In the simplified picture of states with one predominant basis state, CT is either considered in the ground state or in the intermediate state. Thus independent of the applied picture the low E_B feature is an indicator for a significant CT between molecule and metal.

4. Conclusion

In conclusion we find an interface induced low binding energy (E_B) feature in the RPES data of the molecule–metal interface system coronene/Ag(111) which is absent in the direct PES spectra. A detailed analysis of the line-shape of this feature provides evidence for electronic interaction not observed by other electron spectroscopic techniques. Its emergence is explained within a cluster model which identifies this feature as a resonantly enhanced satellite of the HOMO. Interpretations of this feature are based on considering only the predominant character of the employed eigenstates. In the cluster model these eigenstates are quantum mechanical superpositions of the chosen basis states of which one includes transfer of an electron between molecule and metal. Reducing the final eigenstate assigned to the low E_B feature to its main character identifies resonantly enhanced PES from the LUMO as the responsible mechanism. On the other hand the assumption of a pure initial state without CT requires the involvement of dynamical CT in the process which generates the low E_B feature. Hence our finding and interpretation of the low E_B feature constitutes a new way to investigate CT at molecule–metal interfaces.

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