Interface originated modification of electron-vibration coupling in resonant photoelectron spectroscopy

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We present a comprehensive study of the photon energy (hν) dependent line-shape evolution of molecular orbital signals of large π-conjugated molecules by resonant photoelectron spectroscopy (RPES). A comparison to RPES data of small molecules suggests that the excitation into different vibrational levels on the intermediate state potential energy surface of the electronic excitation is responsible for the observed effect. In this simplified picture of electron-vibration coupling the character of the potential energy surfaces involved in the RPES process determines the line-shape of the molecular orbital signal for a particular hν. We use the sensitivity of this effect to probe the influence of different interfaces on the electron-vibration coupling in the investigated systems. The magnitude of the variation in line-shape throughout the particular hν region allows to reveal significant differences within the physisorptive regime.

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I. INTRODUCTION

A generally interesting aspect in the description of quantum mechanical systems is the coupling of different excitations to one another. A prominent example is electron-vibration coupling i.e. the excitation of vibrations accompanied to electronic excitations. Within the Born-Oppenheimer approximation and by the Franck-Condon principle a fairly simple and intuitive picture of electron-vibration coupling in photoelectron spectroscopy (PES) and near edge X-ray absorption fine structure (NEXAFS) spectroscopy is achieved. This allows to obtain information about electron-vibration coupling by analyzing the line-shape of PES spectra of large π-conjugated molecules and thereby extracting a crucial parameter for charge transfer in application relevant systems. With a line-shape analysis of NEXAFS spectra of such molecules parameters of the core excited potential energy surface can be obtained. In special cases an electron-vibration coupling investigation of NEXAFS line-shapes can even serve as a probe for electronic coupling of molecules. Due to the surface sensitivity of PES and partial electron yield NEXAFS these techniques are well suited to study thin films and interfaces. Furthermore NEXAFS excitations at different elements or different chemical species of the same element can provide site specific information for homo-molecular systems. For hetero-molecular systems the excitation can be chosen to obtain molecular specific information.

Resonant PES (RPES) allows to take the investigation of electron-vibration coupling to a next level. RPES experiments on small molecules (CO, N₂, O₂) in the gas phase in comparison to calculations for example reveal that lifetime vibrational interference or detuning can significantly alter the line-shape of molecular orbital derived signals which is determined by the electron-vibration coupling. Using state of the art experimental equipment in combination with theoretical analysis even imaging of theionic molecular potentials and mapping of vibrational wave functions is feasible for a simple molecule as N₂.

A comparable RPES investigation of the intensively studied large π-conjugated molecules leads to a dramatic increase of complexity. Many close lying electronic excitations in the NEXAFS spectrum and the possibility of multiple vibronic modes coupling to each of them and to each other poses a tremendous challenge for an investigation of electron-vibration coupling. However, the application of this powerful technique to such complicated systems does not only raise the level of complexity but in fact allows to obtain additional information with respect to PES or NEXAFS alone, while simultaneously retaining the advantages of both. A selective excitation into highly excited vibrational levels νᵢ in the intermediate state leads to a line-shape of the RPES signal from molecular orbitals which is very sensitive to the character of the involved potential energy surfaces V (ground state V₉, intermediate state Vᵢ and the final state Vᵣ). Thus in principle RPES is able to investigate electron-vibration coupling in the final as well as in the core excited intermediate state if the line-shape of a proper signal can be analyzed in sufficient detail.

In this work we want to push the investigation of electron-vibration coupling in large π-conjugated molecules forward by performing a large comprehensive study on the hν dependent evolution of the line-shape of molecular orbital signals in RPES. This previously observed effect is first discussed for the signal originating from the highest occupied molecular orbital (HOMO) of a copper-phthalocyanine (CuPc) multilayer and then related to RPES investigations of small molecules. This comparison is used to develop a simplified picture in which the character of the involved potential energy surfaces are the only necessary parameters to
consistently discuss the observed line-shape evolutions. Both the discontinuous line-shape evolution of coronene and the continuous line-shape evolution of CuPc and tincathaicyamine (SnPc) in the energy region of interest are related to examples of small molecules. The parallel but NEXAFS resonance specific behavior of the signals from the three frontier molecular orbitals of coronene constitutes an additional successful consistency check of the applied picture. Moreover the sensitivity of the technique is revealed by a comparison of CuPc and SnPc multilayer films and then used to probe the influence of different interfaces. It is found that the adsorption on Au(111) influences the line-shape evolution of the HOMO signal of CuPc and SnPc differently in contrast to the similar modification observed at a hetero-organic interface. In the former case less relative intensity in high final state vibrational levels with respect to the multilayer is observed for CuPc on Au(111) while SnPc exhibits no significant alteration. In the later case both systems show an interface induced enhancement of relative intensity distribution into higher $\nu_f$. Finally we present a resonance specific interface modification of the $\nu$ dependent line-shape evolution by the adsorption of coronene on Ag(111). All observed changes can be consistently discussed on the basis of an influence on the character of the potential energy surfaces involved in the RPES process.

II. EXPERIMENTAL

RPES measurements were performed at BESSY II at the undulator beamline UE52-PGM ($E/\Delta E > 14000$ at 400 eV photon energy, with $\text{cfc}=10$ and $20\, \mu \text{m}$ exit slit) in a UHV chamber with a pressure below $5 \cdot 10^{-10}$ mbar. All PES maps were recorded with p-polarized light in $70^\circ$ angle of incidence with respect to the surface normal, a beamline slit of 40 $\mu$ m and a cff value of 10. This results in an $\nu$ resolution better than $40\, \text{meV}$ at $290\, \text{eV}$. Photoelectron intensities were measured with a Scienta R4000 electron analyzer which was operated in transmission mode with an entrance slit of 300 $\mu$ m. For the PES overview maps (see Fig. 1(a) and 2(a)) a pass energy of 100 eV and for the PES detail maps (see Fig. 1(c), Fig. 2(c) and all 1D energy distribution curve (EDC) waterfall plots) a pass energy of 50 eV was used resulting in an energy resolution of $\Delta E = 150 \, \text{meV}$ for the former and $\Delta E = 75 \, \text{meV}$ for the latter. $\nu$ was calibrated with the Fermi edge ($E_F$) after the measurement of a PES map and the binding energy ($E_B = h\nu - E_K$) and $h\nu$ of the EDCs were shifted rigidly by the obtained offset. The resulting accuracy of both energy scales is better than $\Delta h\nu = \Delta E_B = 50 \, \text{meV}$.

III. RESULTS AND DISCUSSION

In order to identify proper molecular orbital signals for a $h\nu$ dependent line-shape investigation our first step is to record a PES overview map (see Fig. 1(a) and Fig. 2(a)) with the $E_B$ ranging from approximately $-2 \, \text{eV}$ to $23 \, \text{eV}$ and $h\nu$ including the intense $\pi$-resonances. In the resulting PES overview map we are then able to select the area in which the PES detail map (see Fig. 1(c) and Fig. 2(c)) is recorded in a subsequent measurement with smaller increments (see figure captions) for both $h\nu$ and $E_B$. While the $h\nu$ dependent $E_B$ dispersion is more obvious in the 2D PES detail map, a line-shape evolution can be observed better in a waterfall plot of 1D EDCs, especially when signals vary strongly in intensity. Thus for the general discussion of the $h\nu$ dependent line-shape evolution (Fig. 1 and Fig. 2) we present the detail RPES data in both ways and restrict the data presentation to EDC waterfall plots for the following comparison of different systems (Fig. 3 - Fig. 6).

A. The photoelectron spectroscopy map

In the here presented study RPES is always performed at the carbon K-edge and the Cls electrons are excited into delocalized molecular orbitals with mainly $\pi$-character. On resonance PES signals stemming from the adsorbed organic molecules are massively enhanced with respect to the substrate PES signals. The states produced in the RPES process are one-hole final states along with additional two-hole final states which can further be divided into those with an additional electron in an excited state and those without. Above ionization threshold this electron cannot be present since it has been excited into vacuum. In the PES overview map (Fig. 1(a) and Fig. 2(a)) the features at high $E_B$ ($8-23 \, \text{eV}$) consist of both two-hole final states and one-hole final states from lower lying molecular orbitals. These are located at the same $E_B$ as in an off-resonant (or direct) PES measurement. Integrating a constant $E_K$ window (black
Figure 1. (color online). Full RPES data set of a multilayer CuPc/Ag(111) sample recorded at the carbon K-edge. The PES maps are normalized according to the procedure given in the text. (a) PES overview map with $h\nu$ increment of 250 meV and $E_B$ increment of 50 meV. (b) CFS NEXAFS extracted from the black box in the PES overview map (for details see text). The cyan lines denote the region probed by the PES detail map. (c) PES detail map with $h\nu$ increment of 100 meV and $E_B$ increment of 15 meV. The feature around 0 eV $E_B$ at the bottom of the PES map that disperses to lower $E_B$ with increasing $h\nu$ is the the 2nd order C1s signal. (d) EDCs from the PES detail map (black) presented in a waterfall plot in comparison to corresponding EDCs from a PES detail map of a multilayer CuPc/Ag(111) sample prepared and measured at $T = 100$ K (red). The EDCs of equivalent $h\nu$ positions within resonance B (resonance maximum denoted by the larger $h\nu$) are compared to each other (for details see text). The black axes ($E_B$ and intensity) correspond to the black EDCs and the red axes to the red EDCs. The red $E_B$ axis is shifted by -70 meV with respect to the black one. The intensities of the $T = 300$ K EDCs are unchanged while for each of the $T = 100$ K EDCs an offset was added for a matching pre-peak plateau (differently damped substrate signal) and a scaling factor for best comparability of the line-shape of the HOMO signal is applied.
Figure 2. (color online). Full carbon K-edge RPES data set of a multilayer coronene/Ag(111) sample prepared and measured at $T = 100$ K. The PES maps are normalized according to the procedure given in the text. (a) PES overview map with $h\nu$ increment of 250 meV and $E_B$ increment of 50 meV. (b) CFS NEXAFS extracted from the black box in the PES overview map (for details see text). The cyan lines denote the region of the PES detail map. (c) PES detail map with $h\nu$ increment of 100 meV and $E_B$ increment of 15 meV. The dotted vertical lines are a guide to the eye and represent the roughly parallel evolution of the MO peak maxima. The feature around 1 eV $E_B$ at the bottom of the PES map that disperses to lower $E_B$ with increasing $h\nu$ is the the 2nd order C1s signal. (d) EDCs from the PES detail map presented in a waterfall plot.

B. Photon energy dependent line-shape evolution of molecular orbitals

In Fig. 1 the complete RPES data set of a multilayer CuPc/Ag(111) is presented. Fig. 1(a) shows the PES overview map from which the CFS NEXAFS was extracted (integration of black box in Fig. 1(a) leads to the spectrum in Fig. 1(b)) and used for the identification of the NEXAFS resonances A-D. A pronounced increase in intensity of the HOMO signal is observed in resonance B so this part of the PES overview map (cyan box) is selected for closer inspection by a PES detail map (Fig. 1(c)). Here the resonance maximum (dashed red line) is defined to be the EDC with the largest intensity at the $E_B$ position of the HOMO signal in direct PES. Starting closely before the resonance maximum the maximum of the HOMO signal continuously disperses to higher $E_B$ with increasing $h\nu$. The EDC waterfall plot (Fig. 1(d)) allows to identify this effect as a grad-
ual redistribution of intensity towards higher $E_B$ within the HOMO signal. This results in a line-shape evolution from symmetric to more and more asymmetric and finally to two separated peaks. The black EDCs which originate from the PES detail map in Fig. 1(c) hereby evolve parallel to the red EDCs which stem from a corresponding PES detail map of a multilayer CuPc prepared and measured at $T = 100$ K. The EDCs are aligned at the same position within resonance B, i.e. both EDCs of the resonance maximum are compared to each other and so on. Interestingly the EDCs of the 300 K sample, which grows in a Stranski-Krastanow mode, have to be shifted in $h \nu$ and $E_B$ for comparison to the 100 K sample exhibiting layer-by-layer type growth. However, both samples show an identical line-shape evolution. An imprecise energy calibration can be excluded as a reason for the energy mismatch since the HOMO $E_B$ positions exhibit the same shift in the corresponding off-resonant ($h \nu = 120$ eV) PES data. Apparently the difference in growth mode influences the peak positions in (R)PES and NEXAFS spectroscopy but not the origin of the $h \nu$ dependent line-shape evolution. This is further confirmed by a comparison to the EDCs of a multilayer CuPc/Au(111) which exhibit the same line-shape evolution as the two systems displayed in Fig. 1(d).

Up to now a proper treatment of electronic interference effects in the RPES process or lifetime vibrational interference is not feasible due to the complexity of the electronic and vibrational structure of the investigated large $\pi$-conjugated molecules. Not even the assignment of electronic transitions that contribute to the NEXAFS resonance B of CuPc is unambiguously determined in literature. Hence we cannot draw any conclusion from theoretical calculations performed on the here investigated system. Instead we compare the RPES data of CuPc to studies of smaller molecules for which RPES calculations are feasible. In several studies of small molecules (CO, N$_2$, O$_2$ and OCS) a quite similar $h \nu$ dependent line-shape evolution of the molecular orbital signals (usually denoted as participator decays in these publications) is observed. The case of CO constitutes the simplest scenario of one electronic transition in the NEXAFS spectrum and one vibration coupling to it. Therefore the different vibronic peaks contributing to the molecular orbital signals can be resolved and a selective excitation into one particular vibrational level ($\nu_i = 0, 1, 2$) of the intermediate state potential energy surface ($V_\nu$) in RPES is possible. In CO it is found that the higher the $\nu_i$ of the excitation into the $V_\nu$ the more relative intensity is distributed into higher vibrational final state levels $\nu_f$ of the molecular orbital signals. In a Franck-Condon picture this means that the character of the potential energy surfaces govern the relative intensities of the different $\nu_f$ contributions to the molecular orbital signal for a particular $h \nu$. Relative intensity changes between the $\nu_f$ peaks for EDCs recorded with different $h \nu$ are thus the reason for the line-shape evolution. If the different $\nu_f$ peaks cannot be resolved this electron-vibration coupling originated effect leads to successively growing relative intensity in the high $E_B$ part of the molecular orbital peak with increasing $h \nu$. This is exactly the observation seen for the CuPc HOMO signal in Fig. 1(d). So we conclude that this $h \nu$ dependent line-shape evolution can be discussed analogously to CO. Hence the excitation into different $\nu_i$ and the consequential characteristic distribution of relative intensity (Franck-Condon factors) of the $\nu_f$ is the basis for the following discussion. Consequently the character of the potential energy surface in the ground state ($V_\nu$), in the intermediate state ($V_f$) and in the final state ($V_f$) are the parameters which determine the line-shape evolution in the picture we use to discuss the large $\pi$-conjugated molecules in this work. Furthermore the observation of a continuous line-shape evolution...
evolution in Fig. 1(d) points towards one dominating electronic contribution to the RPES in $h\nu$ direction so that despite its complicated electronic structure CuPc can be compared to CO. Multiple electronic transitions with a small difference in $h\nu$ would also result in a continuous line-shape evolution and cannot be excluded. In this case we would have to speak of one effective electronic transition that is responsible for the observed HOMO signal in RPES in Fig. 1(d). However, the comparability to CO is reasonable in both cases.

We would like to note that in a previous discussion of the RPES data of SnPc the line-shape evolution of molecular orbital signals was explained by $h\nu$ detuning from the contributing electronic transition in the NEXAFS spectrum. Based on the present large data set we consider the above described excitation into different $\nu_i$ the dominating effect for the observed line-shape changes within the investigated $h\nu$ regime.

For a multilayer coronene/Ag(111) a complete RPES data set is presented in Fig. 2 analogous to CuPc in Fig. 1. The PES detail map (Fig. 2(c)) and the EDC waterfall plot (Fig. 2(d)) of this system do not show the same overall continuous line-shape evolution as for CuPc. In coronene the HOMO peak maximum first disperses to higher $E_B$ with increasing $h\nu$ starting at the maximum of resonance A. Then, between the resonances A and B, it moves back to its original $E_B$ position and remains almost unchanged with further increasing $h\nu$. This non-continuous evolution scenario is quite similar to H$_2$CC(91) and NO(11). In the former multiple simultaneously exited vibronic modes contribute to the NEXAFS spectrum with one electronic transition. In the latter multiple electronic transitions are present in the NEXAFS spectrum with the single vibrational mode of NO coupling to them. Both scenarios are generally possible for the $h\nu$ region from 284.4 eV to 285.6 eV in the RPES data of coronene. NEXAFS calculations suggest that there is one electronic transition in resonance A and another two in resonance $f$ and the line-shape of the high resolution partial electron yield NEXAFS spectrum (not shown) corroborates this scenario of multiple electronic transitions. A significant contribution to the RPES from the single transition in resonance A is clearly observed. Hence for the $h\nu$ region around resonance A ($h\nu = 284.55$ eV–284.95 eV) the HOMO signal line-shape evolution of coronene can be explained in the same way as for CuPc described above. Further data on a sample of a multilayer coronene/Ag(111) prepared and measured at 300 K and recorded with a 50 meV $h\nu$ increment (not shown) confirms the continuous evolution observed for the HOMO signal around resonance A. Whether there is a contribution to the RPES from none, one or two electronic transitions in NEXAFS resonance B cannot be concluded from the data. However in any of these cases the intensity and line-shape evolution can be discussed analogously since for a second electronic transition as well as a higher excited vibrational series of the first electronic transition higher $\nu_i$ are excited by higher $h\nu$.

The $E_B$ dispersion of the HOMO peak in between resonance A and B is most probably a consequence of the decreasing intensity at higher $\nu_i$ within NEXAFS resonance A and a simultaneous increase of the intensity at low $\nu_i$ within NEXAFS resonance B. So a peak with more relative intensity at higher $E_B$ gradually transforms into a peak with more relative intensity at lower $E_B$. For the $h\nu$ region around resonance B ($h\nu = 285.15$ eV–285.45 eV) a less pronounced redistribution of relative intensity to higher $E_B$ with increasing $h\nu$ is found. In the Franck-Condon picture discussed above this is a consequence of a difference of the $V_i$. The fact that all three visible molecular orbital signals in Fig. 2(c) evolve in an almost parallel way (see dotted vertical lines which roughly represent the peak maximum) but different in resonances A and B further corroborates this conclusion. The observed resonance specific line-shape evolution requires an explanation with a parameter determined by the excitation such as $V_i$. The parallel evolution then suggests similar $V_f$ for the three molecular orbital signals which is reasonable due to the $\pi$-dominated character of these frontier molecular orbitals.

The comparison of the $h\nu$ dependent line-shape evolution in RPES for CuPc and SnPc multilayers displayed in Fig. 3 serves as another consistency check for the consideration of the character of the potential energy surfaces as the dominant parameters. Both molecules have a very similar overall electronic structure and in particular a basically equal HOMO because there is no contribution by the center metal atom to it. Thus the geometric difference between the two molecules constitutes the most reasonable explanation for the observed difference visible in the HOMO signal line-shape evolution. A difference in electron-vibration coupling in the RPES process is not surprising for the bent SnPc with respect to the flat CuPc. Hence the character of the potential energy surfaces can also explain the origin of the difference between these two systems. The fact that both HOMO signal line-shapes are almost equal at the lowest $h\nu$ in Fig. 3 but then evolve differently throughout the resonance reveals the sensitivity of the technique. Even in a moderate $E_B$ resolution leading to symmetric and similar peaks for both molecules in direct PES a difference in the HOMO signal line-shape evolution is found. In the following section we explore the potential of this line-shape evolution in RPES as a probe for variations in the molecular environment.

C. Modification of the electron-vibration coupling by different interfaces

Comparing the line-shape evolution of a multilayer CuPc/Au(111) with a submonolayer CuPc/Au(111) in Fig. 4 exposes a clear difference between the two systems. As already seen in Fig. 3 an equal line-shape at the lowest $h\nu$ evolves differently at higher $h\nu$. In this example the difference can be characterized as less dis-
Figure 4. (color online). Waterfall plot of EDCs from a multilayer CuPc/Au(111) (red) compared to EDCs from a 0.7 ML CuPc/Au(111) (black). The EDCs of equivalent $h\nu$ positions within the resonance (resonance maximum denoted by the larger $h\nu$) are compared to each other (for details see text). The black axes ($E_B$ and intensity) correspond to the black EDCs and the red axes to the red EDCs. The red $E_B$ axis is shifted by 300 meV with respect to the black one. The PES detail maps from which the EDCs originate are normalized according to the procedure given in the text. For the 0.7 ML CuPc/Au(111) EDCs the scaled Au(111) substrate EDCs at equal $h\nu$ are subtracted and the intensities are unchanged. To each of the multilayer CuPc EDCs an offset is added for a matching pre-peak plateau (clean Au(111) subtracted only for the 0.7 ML CuPc EDCs) and a scaling factor for best comparability of the line-shape of the HOMO signal is applied.

Figure 5. (color online). Waterfall plot of EDCs from a multilayer CuPc/Ag(111) prepared and measured at $T = 100$ K (black) compared to EDCs from a 0.7 ML CuPc/1 ML PTCDA/Ag(111) (red). The EDCs of equivalent $h\nu$ positions within the resonance (resonance maximum denoted by the larger $h\nu$) are compared to each other (for details see text). The black axes ($E_B$ and intensity) correspond to the black EDCs and the red axes to the red EDCs. The red $E_B$ axis is shifted by -570 meV with respect to the black one. The PES detail maps from which the EDCs originate are normalized according to the procedure given in the text. For the 0.7 ML CuPc/1 ML PTCDA/Ag(111) EDCs scaled 1 ML PTCDA/Ag(111) EDCs at equal $h\nu$ (from Ref. [36]) are subtracted and each EDC is scaled for best comparability of the line-shape of the HOMO signal.

The contribution of relative intensity into the higher $E_B$ part of the HOMO signal for CuPc adsorbed on Au(111). In other words the excitation of higher $\nu_f$ in the RPES process is somewhat prohibited. Such an influence due to the adsorption on a metal surface on the character of the involved potential energy surfaces is reasonable and thus fits into the overall discussion. A comparison of electron-vibration coupling in direct PES of submonolayer or ML samples with respect to multilayer films is usually hindered by broadening due to disorder in the multilayer. In RPES the involvement of an additional $V_i$ and the possibility to excite high $\nu_i$ in this $V_i$ results in changes of the line-shape beyond the broadening due to disorder. So for the here investigated molecules the $h\nu$ dependent line-shape evolution of molecular orbital signals in RPES allows to identify interface originated modifications of electron-vibration coupling. Additionally both systems compared in Fig. 4 are usually characterized as weakly interacting because there is no significant electronic interaction that manifests itself in strongly altered PES spectra of the adsorbed molecule with respect to the multilayer film. The revelation of differences within this so called physisorptive regime further
Figure 6. (color online). Waterfall plot of EDCs from a multilayer coronene/Ag(111) prepared and measured at $T = 100$ K (red) compared to EDCs from a 0.8 ML coronene/Ag(111) (black). The EDCs of equivalent $h\nu$ positions within the resonance (resonance maximum denoted by the capital letters A and B) are compared to each other (for details see text). The black axes ($E_B$ and intensity) correspond to the black EDCs and the red axes to the red EDCs. The red $E_B$ axis is shifted by 130 meV with respect to the black one. The PES detail maps from which the EDCs originate are normalized according to the procedure given in the text. For the 0.8 ML coronene/Ag(111) EDCs scaled Ag(111) substrate EDCs at equal $h\nu$ are subtracted and the intensities are unchanged. Each of the multilayer coronene EDCs is scaled for best comparability of the line-shape of the HOMO signal. (a) $h\nu$ region of NEXAFS resonance A. (b) $h\nu$ region of NEXAFS resonance B.

indicates the sensitivity of the effect. Remarkably the analogous comparison of a submonolayer SnPc/Au(111) with a multilayer SnPc/Au(111) (not shown) exhibits a parallel $h\nu$ dependent line-shape evolution of the SnPc HOMO signal. Hence the potential energy surfaces of SnPc are not significantly altered by the adsorption on Au(111). Consequently the electron-vibration coupling of the bent SnPc molecule not only differs from the one of the flat CuPc but also a difference in the influence of the Au(111) surface on the electron-vibration coupling in both molecules is observed.

By depositing a submonolayer or ML of SnPc/Au(111) or CuPc/Au(111) onto 1 ML PTCDA/Ag(111) a stable and vertically well defined interface can be prepared. The comparison of the $h\nu$ dependent line-shape evolution of the CuPc HOMO signal of this hetero-organic system with a multilayer of CuPc/Ag(111) is displayed in Fig. 5. In contrast to the adsorption on Au(111) the excitation of higher $\nu_f$ in the RPES process is enhanced at this interface with respect to the multilayer film. For the SnPc/1 ML PTCDA/Ag(111) hetero-molecular interface the same variation is found with respect to the SnPc multilayer. The smaller $h\nu$ increment of the here presented data makes a clear identification of a continuous evolution possible and therefore shows that both SnPc and CuPc in the hetero-molecular system can be discussed in the same way as all other systems in this work. The similar change of both molecules in the hetero-molecular system with respect to a multilayer sample becomes particularly interesting considering the fact that the reaction on the adsorption on Au(111) is different. We would like to note that additional RPES data of several systems with strong interfacial bonding and ground state charge transfer into the molecule (1 ML PTCDA/Ag(110), 1 ML 1,4,5,8-naphthalene-tetracarboxylic dihydride/Ag(111) and 1 ML CuPc/Ag(111)) show very strong and characteristic line-shape changes with respect to the corresponding multilayer sample and have to be described within
a different model. Hence in terms of interface modifications of electron-vibration coupling observed in RPES both SnPc and CuPc on PTCD/Ag(111) have to be considered weakly interacting, which is in contrast to another conclusion in literature. A detailed investigation of RPES applied to the strongly interacting systems mentioned above will be given in a future publication.

For a multilayer of coronene a different line-shape evolution in RPES is found for the NEXAFS resonances A and B (see Fig. 6). This discussed difference in the character of the particular $V_i$ also manifests itself in the reaction on the adsorption on a Ag(111) surface. A comparison of the submonolayer film on Ag(111) to the multilayer sample is displayed in Fig. 6. The $h\nu$ region around resonance A (Fig. 6(a)) shows a parallel line-shape evolution starting with the resonance maximum while for the EDCs at the lowest $h\nu$ a broader HOMO signal is observed for the multilayer. This difference can be explained by increased inhomogeneity in the multilayer film. However, this effect becomes negligible as soon as the electron-vibration coupling originated line-shape evolution alters the HOMO signal to a much larger extend. In the vibration coupling originated line-shape evolution this becomes negligible as soon as the electron-vibration coupling originated line-shape evolution alters the HOMO signal to a much larger extend. In the vibration coupling originated line-shape evolution this becomes negligible as soon as the electron-vibration coupling originated line-shape evolution alters the HOMO signal to a much larger extend.

**IV. SUMMARY AND CONCLUSION**

In summary we present a comprehensive RPES study of several large $\pi$-conjugated molecules in multilayer films and at different interfaces. By the comparison to RPES investigations of small molecules we are able to discuss the observed $h\nu$ dependent line-shape evolution of molecular orbital signals within a picture based on electron-vibration coupling. The relative intensity distribution among excitations of vibrations in the final state for a particular $h\nu$ is suggested as the origin for the observed line-shape evolution. Within this simplified picture all systems and the differences in between them are consistently discussed by the character of the potential energy surfaces involved in the RPES process. Consequently the influence of the particular interface on the mechanism of the excitation of these vibrations is given as the origin for changes with respect to the multilayer sample. We show that depending on the specific interface the relative intensity distributed into high vibrational levels in the final state can remain unchanged, can be partially quenched or enhanced. On Au(111) the excitation of high vibrational levels is partially quenched for CuPc while no influence is found for SnPc. Opposite to that, an enhancement of the high vibrational levels occurs at the hetero-organic interface of SnPc and CuPc on top of 1ML PTCD/Ag(111). With the adsorption of coronene on Ag(111) we present an example for a resonance specific modification of electron-vibration coupling. In comparison to the multilayer film an enhancement of the contribution of high vibrations to the HOMO signal is demonstrated only in one of the two NEXAFS resonances.

This work illustrates the potential of line-shape investigations of molecular orbital signals in RPES as a sensitive probe for electron-vibration coupling in large $\pi$-conjugated molecules. By the presented magnitude of the $h\nu$ dependent variation inhomogeneous broadening and moderate energy resolution can be overcome which allows to reveal effects that are not visible in direct PES and NEXAFS spectroscopy alone. Therefore a smaller influence of an interface on electron-vibration coupling can be investigated by RPES with an equally high surface sensitivity. The fact that all the interface originated modifications found constitute differences within the physisorptive regime further demonstrates the sensitivity of the applied technique.

A detailed investigation of the specific character of the potential energy surfaces involved in RPES, like the role of coupling in between multiple vibronic modes and lifetime vibrational interference can only be studied by direct comparison of our data with calculations. These are to our best knowledge not feasible for the investigated systems at this point. The same applies for electronic interference effects or a possible insufficiency of the Born-Oppenheimer approximation. We would like to stress that the importance of these effects cannot be excluded on the basis of this experimental work. However, the given discussion based on the comparison to small molecules draws a consistent picture for a large data set using the character of the potential energy surfaces as the only required parameters. With this work we hope to stimulate a significant advance in the theoretical treatment of RPES applied to the here presented systems which is necessary to elevate the understanding of this technique to the next level.
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