Impact of interface-state formation on the charge-carrier dynamics at organic-metal interfaces

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Abstract

We study the role of electronic interface states on the electron transfer dynamics between layers of the organic semiconductor 3,4,9,10-perylene-tetracarboxylic acid dianhydride (PTCDA) and the (111) and (100) surfaces of silver. For this purpose, we investigate the change of the decay dynamics of the first \( n=1 \) image-potential state on these surfaces upon adsorption of an ordered monolayer of PTCDA by means of time-resolved two-photon photoemission (2PPE). We find that the already short lifetime of the \( n=1 \)-state on Ag(111) is only slightly further reduced by PTCDA adsorption, whereas a much stronger reduction by a factor of three is observed for adsorption on Ag(100) resulting in similar lifetimes for both orientations. We show by model calculations on the basis of an analytical one-dimensional pseudo-potential that the enhanced decay for PTCDA/Ag(100) can be attributed to the opening of an additional channel for electron-electron scattering by the formation of an interface state which is derived from the Shockley-type surface resonance of Ag(100).

1. Introduction

The microscopic understanding and control of the charge transfer between the molecular orbitals of organic molecules and the delocalized electron system of a metal is not only one of the most challenging problems in interface science but also of great interest for the development of organic semiconductor devices [1–3]. At organic-metal interfaces, electronic states that are located between the Fermi level of the metal and the first unoccupied molecular orbital (LUMO) of the organic semiconductor are expected to mediate the transfer of charge carriers (cf figure 1(a)) [4–7]. Such states will not only lead to an enhanced quenching of excitons near the interface as in traditional semiconductors. Due to the large overlap of their wave functions with both, delocalized metal states on one side and molecular orbitals on the other side, the presence of such interface states should also lead to an enhanced electron injection from the metal into unoccupied electronic states of the organic semiconductor and thus to an improved electrical contact across the interface.

Here, we study a model system for an electrical contact at a metal-organic interface and use image-potential states as a simple and well-defined probe to investigate the role of interface states for the electron transfer through an organic layer into the metal. Image potential states already proved to be an ideal probe for the electron transfer dynamics at surfaces and through thin dielectric layers, by theory and by experiment, in particular, by time-resolved two-photon photoemission (2PPE) studies [8, 9]. Compared to the complex molecular orbitals of typical organic semiconductors, image-potential states constitute a much simpler class of unoccupied electronic states. In most cases they exhibit a high degree of translational symmetry parallel to the metal surface even in the presence of overlayers [10]. This allows for a realistic theoretical treatment of the many body interactions in their decay even within an one-dimensional (1D) description [8]. Although the interface states of metal/organic systems are laterally stronger corrugated and have a hybrid organic/metal character [11], it has been shown that a rather accurate calculation of their energy and wave function is possible for many systems within a similar description based on an analytic...
Figure 1. (a) Scheme of the level alignment of the interface state (IS) and the molecular orbitals of the organic layer as well as possible electron and hole transfer processes. The energetic positions of these electronic states are indicated with horizontal bars. Bulk states of the metal substrate are indicated in dark (light) gray. (b) Probability densities of the interface state and the \((n = 1)\) image-potential state in direction perpendicular to the interface together with the optical excitation and photoemission scheme for 2PPE of the image-potential state. The position of the first organic layer is marked by the dashed vertical line.

effective 1D model potential \([12]\). This includes ordered thin films of the molecular organic semiconductor 3,4,9,10-perylene-tetracarboxylic acid dianhydride (PTCDA) grown on Ag(111) and Ag(100) surfaces. These structures are two of the most well defined and already well characterized model systems for metal-organic interfaces \([2, 13–21]\). It has been shown at first for PTCDA/Ag(111) that in such systems an interface-specific electronic state (IS) emerges, in close analogy to the Shockley states of clean metal surfaces, by the symmetry break at the interface \([6, 22, 23]\). Meanwhile, similar interface states have been identified at a variety of other organic/metal interfaces \([7, 11, 24–31]\). This includes PTCDA/Ag(100) where the IS is formed from the broad unoccupied surface resonance (SR) of Ag(100) \([32]\).

We employ time-resolved 2PPE to observe how adsorption of a PTCDA adlayer enhances the decay of the initially unoccupied first \((n = 1)\) image-potential state on the Ag(111) and Ag(100) surfaces. 2PPE is the most powerful technique for investigating unoccupied states and charge carrier dynamics at surfaces and interfaces \([8, 33–41]\) and was essential to reveal the role of the Shockley state in the formation of the interface state for the PTCDA/Ag systems \([6, 7, 28, 32]\). We compare the observed change of the \(n = 1\) lifetime upon PTCDA adsorption with model calculations of the corresponding change of the \(n = 1\) wave-function and its overlap with the IS wave function for both surfaces. We will show that the formation of the IS from the SR for PTCDA/Ag(100) opens an additional decay channel for the image-potential states which leads to a much stronger reduction of the \(n = 1\) lifetime as compared to PTCDA/Ag(111) where the occupied Shockley state already represents an important decay channel on the bare Ag(111) surface.

2. Experiment

The time-resolved 2PPE experiments were conducted with an experimental setup described earlier \([40]\). The excitation and detection scheme is sketched in figure 1(b). Ultraviolet (UV) laser pulses with photon energy of \(h\omega_a = 4.68\) eV and a repetition rate of 80 MHz excite the first \((n = 1)\) image-potential state. Its transient population is subsequently probed by time-delayed photoemission using near infrared (NIR) pulses of photon energy \(h\omega_b = 1.56\) eV. The emitted photoelectrons are detected in normal emission by a hemispherical electron analyzer. The population dynamics of the \(n = 1\) state is acquired by measuring the number of detected photoelectrons (2PPE signal) as a function of time delay between the two laser pulses. The Ag(111) and Ag(100) substrates were prepared in an ultrahigh vacuum (UHV) chamber with a base pressure of \(4 \times 10^{-11}\) mbar by standard sputter and annealing cycles. Characterization was done by low-energy electron diffraction (LEED), x-ray photoemission spectroscopy (XPS), and by examining 2PPE spectra of the \(n = 1\) state \([32, 40]\). PTCDA monolayer films were evaporated onto the substrate at low evaporation rates of 0.2–0.4 ML min\(^{-1}\) which ensures a high degree of crystallinity \([6, 28, 32]\). The structure of the ordered films was checked using LEED \([14, 17, 18, 42, 43]\). All experiments were carried out at room temperature.

Figure 2(a) shows the transient 2PPE signal of the \(n = 1\) image-potential state in normal emission for the clean Ag(100) and Ag(111) surfaces as well as for a monolayer coverage of PTCDA. Positive time delays correspond to the UV pulses arriving on the sample first. Obviously, the decay on the clean Ag(111) surface is much faster as compared to Ag(100). PTCDA adsorption accelerates the decay and results in comparable dynamics on both surfaces. All four transients can be well described by a rate-equation model that takes
Figure 2. (a) 2PPE signal of the image-potential states of Ag(100) (top) and Ag(111) (bottom) for the bare substrates (open symbols) and for a coverage of one monolayer of PTCDA (filled symbols) in normal emission as function of time delay. The solid lines show fits of the data using a rate equation model that includes the cross correlation of the laser pulses (dashed line) and an exponential population decay. (b) and (c) Surface bandstructure of Ag(100) and Ag(111), respectively. The parabolic curves depict the $n = 1$ image-potential state, the surface resonance (SR) and the Shockley surface state (SS) of the bare surfaces as well as the interface states (IS) which emerges upon adsorption of PTCDA. Occupied (unoccupied) projected bulk bands are indicated by dark (light) gray shaded areas according to data shown in Ref. [49].

Table 1. Experimental and theoretical values for the binding energy of the SS/SR/IS with respect to the Fermi level $E_F$, inelastic lifetime $\tau_{n=1}$ of the $n = 1$ state determined by the 2PPE, calculated bulk penetration ($p$), and the calculated integrated overlap ($o$) of its wave function with the SS (bare Ag(111)), the SR wave packet (bare Ag(100)) and the IS for a coverage (cov.) of one ML PTCDA on Ag(111) and Ag(100).

| Substrate | Cov. (ML) | $E_{SS/SR/IS} - E_F$ (eV) | $\tau_{n=1}$ (fs) | $p$ (%) | $o$ (%) |
|-----------|----------|---------------------------|-------------------|--------|--------|
| Ag(111)   | 0        | -0.064$^a$ -0.059         | 25(2)             | 34.86  | 46.9   |
|           | 1        | 0.60(1)$^b$ 0.40          | 18(4)             | 43.28  | 42.3   |
| Ag(100)   | 0        | 1.3$^c$ 1.25              | 59(2)             | 5.30   | 34.3   |
|           | 1        | 2.25(3)$^d$ 2.25          | 20(3)             | 5.94   | 45.7   |

$^a$Reference [54] for $T = 300$ K.
$^b$References [6, 45].
$^c$Reference [50].
$^d$Reference [32].
band gap, represents an important additional decay channel due to the large overlap of their wave functions. In the case of Cu(111), it contributes with 40% to the $n = 1$ decay rate [47, 48]. This decay channel is strongly suppressed on the (100) noble metal surfaces where the symmetry break at the surface results instead in a broad surface resonance located within the projected bulk bands above the Fermi level [50]. On Ag, the decay of image-potential states can be further accompanied by excitation of surface plasmons which are strongly affected by $d$-electron screening. Because of the different impact of the screening on the local and nonlocal contributions, this decay channel counterintuitively results in a net reduction of the $n = 1$ decay and is, together with a reduced phase space for the decay, jointly responsible for the rather long lifetime on Ag(100) [46].

PTCDA adsorption has two main effects on the decay of the $n = 1$ image potential state: (i) it modifies its wavefunction and therewith its bulk penetration. (ii) The interaction of the PTCDA molecules with the metal surface shifts the SS/SR up in energy and transform it into the IS. This changes its wavefunction overlap with the $n = 1$ state and the phase space for decay of the $n = 1$ into the IS.

3. Model calculations

In order to investigate the change of the $n = 1$ bulk penetration and its wave function overlap with the IS, we have calculated 1D wave functions of the $n = 1$ and the IS by numerically solving the 1D Schrödinger-equation on the basis of an analytical, parametrized model potential which is depicted for PTCDA/Ag(111) in figure 3(a). The model potential was initially developed for the description of image-potential states in graphene/metal systems [51] but it has been recently shown that it can also be applied for flat lying molecular layers with similar $\pi-\pi$ interaction as in graphene [12]. Compared to an \textit{ab initio} approach, like density functional theory (DFT), this method explicitly takes the long-range image-potential into account. It does not only provide a quantitative correct description of image-potential states but can also well approximate other delocalized surface and interface states on metal surfaces as long as lateral corrugation can be neglected. In brief, the model potential consists of a superposition of a potential for the metal bulk, for the surface and for the graphene-like two-dimensional $\pi$-conjugated carbon plane. The latter describes the elementary properties of the carbon backbone of the organic molecules at the $\Gamma$-point. The parameters of the bulk and surface potentials are determined by the energetic position of the projected $sp$ band gap and the binding energies of the image-potential states of the respective bare Ag surface as described in reference [52]. The organic layer is parametrized by the distance $d_g$ between the topmost metal atom and the center of the carbon backbone of the organic molecules and the change $\Delta \Phi$ of the substrate’s work function $\Phi$ upon adlayer adsorption. The latter accounts for the charge transfer between metal and molecular layer, whereby the energy of the IS most sensitively depends on $d_g$. The functional groups of the organic molecules are not taken into account. Beside their contribution to charge transfer and bonding to the substrate [20], they mediate the lateral interaction between the molecules which results in periodic corrugation of the organic films [21]. Nevertheless, the simple 1D model only slightly underestimates the energy of the IS for a variety of metal-organic systems including PTCDA/Ag(111) [12]. For this system, the calculated energy of the IS already fits within 0.2 eV with the experimental observation if we use the experimentally determined parameters $d_{\text{PTCDA/Ag(111)}} = 2.86 \, \AA$ [15], $\Phi_{\text{Ag(111)}} = 4.56 \, \text{eV}$ [52], and $\Delta \Phi_{\text{PTCDA/Ag(111)}} = +0.13 \, \text{eV}$ [53] (cf table 1). The systematic underestimation of the IS’s energy, however, increases for systems with stronger bonding of the functional groups, such as PTCDA/Ag(100), for which also DFT clearly underestimates the energy of the IS with respect to $E_F$ [32]. One reason might be that the stronger interaction of the anhydride oxygen atoms results in a bending of the PTCDA molecules towards the surface with reduced metal-carbon distance at the edges [20]. This motivates us to compensate the larger deviation for PTCDA/Ag(100) by using a reduced value of $d_{\text{PTCDA/Ag(100)}} = 2.38 \, \AA$ instead of the experimental value of 2.81 Å determined by x-ray standing wave [20] because for the purpose of the present work it is important to well reproduce the wave function of the IS whose bulk penetration and therefore also its overlap with the image-state depends on its energy position with respect to the close-by upper edge of the projected lower $sp$ bulk band of Ag [32]. Together with $\Phi_{\text{Ag(100)}} = 4.43 \, \text{eV}$ [52] and $\Delta \Phi_{\text{PTCDA/Ag(100)}} = +0.22 \, \text{eV}$ (this work) we can well reproduce the experimentally observed energy of the IS with the reduced distance as can be seen in table 1.

4. Results and discussion

For Ag(111), we find solutions at discrete energies within the projected bulk band gap which can be assigned to the $n = 1$ state and the SS of the bare substrate as well as the $n = 1$ state and the IS of the PTCDA covered substrate. The corresponding wavefunctions and the spatial overlap $\Psi_{\text{SS/SR/IS}} \times \Psi_{n=1}$
between the SS/SR/IS and the $n=1$ state are depicted in figure 3(b). The associated binding energies of the SS/IS are listed together with the integrated overlap of the normalized wave functions $a = \int |\Psi_{\text{SS/IS}}|^2 \, dz$ and the bulk penetration $p$ of the $n=1$ state in table 1. The bulk penetration is the fraction of the integrated $n=1$ probability density in the metal bulk assuming that the crystal edge is located at half an interlayer spacing from the last atomic layer $[52]$.

For Ag(100), solutions at discrete energies within the projected bulk band gap are found for the $n=1$ state of the bare substrate as well as for the $n=1$ state and the IS on the PTCDA covered surface. The wavefunction of the SR within the lower project $sp$ bulk band is represented by a wave packet that consists of continuum wave functions $\Psi_z(E)$ for closely adjacent energies within the lower project $sp$ bulk band. In this way, the oscillations of the bulk Bloch continuum wave functions destructively interfere within the bulk and the wave packet can be normalized in space. This makes it possible to calculate the wave function overlap with the $n=1$ state in the same way as for Ag(111). The resulting normalized wave function of the SR, plotted in figure 3(c), has a close resemblance to the wave function of the SS on Ag(111) but has more weight at the surface and decays faster into the bulk. The energy of the SR is determined by the maximum of the probability density $\int_{E>0} |\Psi(z,E)|^2 \, dz$ of the continuum wave function in front of the surface. This value agrees well with the energy of the SR determined by inverse photoemission (cf table 1).

For both substrates, PTCDA adsorption pushes the maximum of the $n=1$ wave function away from the metal surfaces. Nevertheless, the bulk penetration increases. It is only slightly enhanced for Ag(100) where it is restricted to a surface near region. In the case of Ag(111), the increase of the work function exceeds the increase of the $n=1$ binding energy upon PTCDA adsorption. This shifts the $n=1$ energy closer to the lower edge of the upper projected $sp$ band which significantly increases the penetration of its wave function into the bulk by about 24%. Therefore, the bulk penetration and therewith the local contributions to the decay rate increase two times stronger for Ag(111) as compared to Ag(100).

Compared to the SS on the bare Ag(111) surface, the IS has a smaller penetration into the Ag substrate. Together with the enhancement of the bulk penetration of the $n=1$ state upon PTCDA adsorption, the integrated total wave function overlap between the $n=1$ state and the IS is about 11% smaller as compared to the overlap between the $n=1$ state and the SS on the bare Ag(111) surface. The reduction of the wave function overlap is therefore about half as large as the increase of the $n=1$ bulk penetration. If we transfer the result for Cu(111) that 40% of the total $n=1$ decay rate is given by the decay into the SS $[47, 48]$, the enhancement of the decay due to the enhanced bulk penetration should finally outrun the reduction of the decay into the IS which can explain the observed slight reduction of the $n=1$ lifetime upon PTCDA adsorption on Ag(111). For Ag(100), PTCDA adsorption enhances both, the wave function overlap between the $n=1$ state and the SR/IS by 33% as well as the bulk penetration which is enlarged by 12%. Therefore, the resulting decay rate should be enlarged much stronger as compared to Ag(111). A simple scaling of the decay rate with the bulk penetration and the wave function overlap, however, cannot quantitatively explain the observed reduction of the lifetime by a factor of three and might be too simplified. In particular we might overestimate the decay of the $n=1$ into the SR wavepacket on the clean Ag(100) surface in this way.
because it has been shown that the different lifetimes of the $n = 1$ state on Cu(100) and Cu(111) appear mainly due to the presence of the Shockley state on Cu(111) [48]. Moreover, we have neglected the different change of the phase space for the decay due to the different energies of the IS on both surfaces as well as modifications of the nonlocal contributions. The latter are enhanced in the vicinity of the metal surface [48] where the wave functions change most upon PTCDA adsorption. We have also not considered decay into other unoccupied more localized molecular orbitals of PTCDA which cannot be described by our model. We expect, however, that the interaction between the delocalized image-potential state and localized molecular orbitals is much smaller as compared to its interaction with the delocalized IS. Furthermore, such contribution to the decay should be also similar on both substrates which would not change our conclusions.

5. Summary and conclusions

In summary, we have shown by time-resolved 2PPE experiments that the emergence of the interface state upon PTCDA adsorption on Ag surfaces leads to a three times larger reduction of the lifetime of the first image-potential state on Ag(100) as compared to Ag(111) and therewith results in comparable lifetimes for both crystal orientations. This result for a well-defined model system exemplarily demonstrates that such interface specific electronic states can have a strong impact on the electrical contact at metal-organic interfaces. Our model calculations based on a one-dimensional analytic parametrized potential show that the transformation of the initially occupied Shockley surface state into the unoccupied interface state on Ag(111) only moderately modifies the already strong decay of the image-potential state into this state and that the observed slight further enhancement is mostly governed by the increased penetration of the image-potential state into the metal. For PTCDA/Ag(100), the latter plays a minor role and the strongly enhanced decay on this surface is governed by the transformation of the unoccupied surface resonance of Ag(100) into the interface state which then plays a similar role for the decay as for PTCDA/Ag(111).

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References

[1] Nitzan A and Ratner M A 2003 Science 300 1384
[2] Tautz F S 2007 Prog. Surf. Sci. 82 479
[3] Koch N, Ueno N and Wee A (ed) 2013 The Molecule-Metal Interface (Weinheim: Wiley)
[4] Temirov R, Soubatch S, Luican A and Tautz F S 2006 Nature 444 350
[5] Zhu X Y 2004 Surf. Sci. Rep. 56 1
[6] Schwab C H, Sachs S, Marks M, Schöll A, Reinert F, Umbach E and Höfer U 2008 Phys. Rev. Lett. 101 146801
[7] Marks M, Schöll A and Höfer U 2014 J. Electron Spectrosc. Relat. Phenom. 195 263
[8] Echenique P M, Berndt R, Chulkov E V, Fauster T, Goldmann A and Höfer U 2004 Surf. Sci. Rep. 52 219
[9] Güdde J, Berthold W and Höfer U 2006 Chem. Rev. 106 4261
[10] Rohleder M, Duncker K, Berthold W, Güdde J and Höfer U 2005 New J. Phys. 7 103
[11] Zaitsev N L, Nechaev I A, Echenique P M and Chulkov E V 2012 Phys. Rev. B 85 115301
[12] Armbrust N, Schiller F, Güdde J and Höfer U 2017 Sci. Rep. 7 46561
[13] Jung M, Baston U, Schnitzler G, Kaiser M, Papst J, Porwol T, Freund H J and Umbach E 1993 J. Mol. Struct. 293 239
[14] Glocker K, Seidel C, Soukoup A, Sokolowski M, Umbach E, Böhringer M, Berndt R and Schneider W-D 1998 Surf. Sci. 405 1
[15] Hauschildt A, Karl K, Cowie B C C, Rohlfing M, Tautz F S and Sokolowski M 2005 Phys. Rev. Lett. 94 036106
[16] Rohlfing M, Temirov R and Tautz F S 2007 Phys. Rev. B 76 115421
[17] Ikonomov J, Bauer O and Sokolowski M 2008 Surf. Sci. 602 2061
[18] Zou Y, Kilian L, Schöll A, Schmidt T, Fink R and Umbach E 2006 Surf. Sci. 600 1240
[19] Kilian L et al 2008 Phys. Rev. Lett. 100 136103
[20] Bauer O et al 2012 Phys. Rev. B 86 235431
[21] Sabitova A, Temirov R and Tautz F S 2018 Phys. Rev. B 98 205429
[22] Dyer M S and Persson M 2010 New J. Phys. 12 063014
[23] Zaitsev N L, Nechaev I A and Chulkov E V 2010 J. Exp. Theor. Phys. 110 114
[24] Heinrich B W, Limot L, Rastie M V, Iacovita C, Bucher J P, Djimbi D M, Massobrio C and Boero M 2011 Phys. Rev. Lett. 107 216801
[25] Andrews K M and Pearl T P 2010 J. Chem. Phys. 132 214701
[26] Scheybal A, Müller K, Bertschinger R, Wahl M, Bendsouan A, Aebi P and Jung T A 2009 Phys. Rev. B 79 115406
[27] Yamane H, Kanai K, Ouchi Y, Ueno N and Seki K 2009 J. Electron Spectrosc. Relat. Phenom. 174 28
[28] Marks M, Zaitsev N L, Schmidt B, Schwab C H, Schöll A, Nechaev I A, Echenique P M, Chulkov E V and Höfer U 2011 Phys. Rev. B 84 081301
[29] Caplins B W, Suich D E, Shearer A J and Harris C B 2014 J. Phys. Chem. Lett. 5 1679
[30] Jakob P, Zaitsev N L, Namgalis A, Tonner R, Nechaev I A, Tautz F S, Höfer U and Sanchez-Portal D 2016 Phys. Rev. B 94 125436
[31] Lerch A et al 2017 J. Phys. Chem. C 121 25353
[32] Galbraith M C E, Marks M, Tonner R and Höfer U 2014 J. Phys. Chem. Lett. 5 50
[33] Szymanski P, Garrett-Roe S and Harris C B 2003 Prog. Surf. Sci. 78 1
[34] Stähler J, Gahl C, Bovensiepen U and Wolf M 2006 J. Phys. Chem. B 110 9637
[35] Fauster T, Weinelt M and Höfer U 2007 Prog. Surf. Sci. 82 224
[36] Cinchetti M, Heimer K, Wüstenberg I, Andreyev O, Bauer M, Lach S, Ziegler G, Gao Y and Aeschlimann M 2009 Nat. Mater. 8 115
[37] Ichibayashi T and Tanimura K 2009 Phys. Rev. Lett. 102 087403
[38] Steele M P, Blumenfeld M and Montl O L A 2010 J. Phys. Chem. Lett. 1 2011
[39] Shibuta M and Hirata N Matsui R, Eguchi T and Nakajima A 2012 J. Phys. Chem. Lett. 3 981
[40] Matsui M, Schwab C H, Schubert K, Güdde J and Höfer U 2011 Phys. Rev. B 84 245402
[41] Marks M, Sachs S, Schwab C H, Schöll A and Höfer U 2013 J. Chem. Phys. 139 124701
[42] Stahl U, Gador D, Soukopp A, Fink R and Umbach E 1998 Surf. Sci. 414 423
[43] Kälin L, Stahl U, Kossec I, Sokolowski M, Fink R and Umbach E 2008 Surf. Sci. 602 2427
[44] Shumay I L, Höfer U, Reuß C, Thomann U, Wallauer W and Fauster T 1998 Phys. Rev. B 58 13974
[45] Schwab C H, Marks M, Sachs S, Schöll A, Reinert F, Umbach E and Höfer U 2010 Eur. Phys. J. B 75 23
[46] Garcia-Lekue A, Pitarke J M, Chulkov E V, Liebsch A and Echenique P M 2003 Phys. Rev. B 68 045103
[47] Osma J, Sarria I, Chulkov E V, Pitarke J M and Echenique P M 1999 Phys. Rev. B 59 10591
[48] Sarria I, Osma J, Chulkov E V, Pitarke J M and Echenique P M 1999 Phys. Rev. B 60 11795
[49] Goldmann A, Dose V and Borstel G 1985 Phys. Rev. B 32 1971
[50] Himpsel F J and Ortega J E 1992 Phys. Rev. B 46 9719
[51] Armbrust N, Güdde J and Höfer U 2015 New J. Phys. 17 103043
[52] Chulkov E V, Silkin V M and Echenique P M 1999 Surf. Sci. 437 330
[53] Sachs S, Schwab C H, Marks M, Schöll A, Reinert F, Umbach E and Höfer U 2009 J. Chem. Phys. 131 144701
[54] Paniago R, Matzdorf R, Meiser G and Goldmann A 1995 Surf. Sci. 336 113