Polycyclic aromates on close-packed metal surfaces: functionalization, molecular chemisorption and organic epitaxy

M Eremtchenko, D Bauer, J A Schaefer and F S Tautz

1 Institut für Physik and Zentrum für Mikro-u. Nanotechnologien, Technische Universität Ilmenau, PO Box 100565, 98684 Ilmenau, Germany
2 School of Engineering and Science, International University Bremen, PO Box 750561, 28725 Bremen, Germany
E-mail: s.tautz@iu-bremen.de

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Abstract. In this paper we present a detailed analysis of the molecular mechanisms of perylene and PTCDA bonding to two close-packed noble metal surfaces, Ag(111) and Au(111), with the aim of elucidating the relation between bonding and interface structure. Our analysis is based on a combination of high-resolution electron energy-loss spectroscopy and first-principles quantum chemical calculations (density functional theory) of molecular orbitals and vibrations. Experimentally, the key observation is the activation of certain totally symmetric modes by symmetry breaking at the surface. Analysing calculated vibrational eigenvectors and the induced dynamic distortions of the lowest unoccupied molecular orbital in detail, we propose an interaction model according to which the central carbon ring in both molecules constitutes the molecular chemisorption centre. In the case of perylene, its reactivity is rather small. By the application of functional groups to the aromatic backbone, however, the reactivity can be tuned over a wide range, leading to a dramatic enhancement of the molecule–substrate interaction in the case of PTCDA/Au(111), as testified by the remarkable interface epitaxy. The example of the weakly interacting PTCDA/Au(111) interface illustrates the limitations of the present scheme of chemisorption strength engineering. Finally, the implications of our results for a detailed determination of the adsorption site are discussed.

3 Author to whom any correspondence should be addressed.
1. Introduction

Tailoring interface properties of organic materials with inorganic substrates is an attractive goal, e.g. in the field of organic electronics, where high-quality semiconductor films are required. Epitaxial growth of an organic layer on an inorganic substrate is a phenomenon which deserves special interest in this context, since it can help to achieve well-ordered interfaces onto which crystalline thin films can be grown successfully. Studies with single crystals and molecular films have shown that electrical transport as well as optical properties depend strongly on crystal quality [1, 2].

Research so far has established a few cases in which organic (monolayer) epitaxy occurs [3]–[7]. The challenge is to gain insight as to why these particular cases exhibit this behaviour, while others do not. To this end, we need to extricate the essential mechanism(s) of organic epitaxy. This will enable us to delineate some simple conditions which must be fulfilled in successful examples. These general rules can then be used to optimize certain molecules for organic epitaxy. Unlike the case of inorganic materials, we are in the fortunate condition that molecules offer a sufficient number of internal parameters, such that clever molecular design can almost certainly change the bonding and growth characteristics without impinging on the functionality, enabling a truly tailored material design.

One strategy often employed to facilitate the formation of an ordered interface between two materials is the use of structured substrates as templates. For example, the (110) surfaces of the fcc metals offer a regular array of grooves in the [110] direction with a periodicity close to the relevant molecular length scales. These templates can lead to the formation of molecular brick-wall structures (PTCDA/Ag(110)) [8, 9] or molecular nanowires (Pentacene/Cu(110) [10]). One of the advantages of this approach is the usual absence of rotational domains, leading to coherent order over very large length scales. However, a main drawback of this method is the fact that the interface order cannot be extended into higher molecular layers, since the structure adopted by the molecules at the interface is in many cases alien to the molecule. With notable exceptions [7], subsequent layers thus immediately stabilize in the natural crystal structure of the molecular material [11], usually without a definite structural relationship to the underlying substrate.

In this paper we investigate the alternative approach of organic epitaxy on flat, close-packed surfaces without a template structure. The aim is to promote order by using...
molecular rather than substrate properties. Specifically, we show that functionalization of the molecule can have a drastic influence on interface formation and growth, promoting a definite adsorption site which, however, does not necessarily involve these functional groups directly. The model system considered here is perylene and its derivative PTCDA (3,4,9,10-perylene-tetracarboxylic-acid-dianhydride). The interface of PTCDA with Ag(111) is of particular interest in the present context since it combines remarkable chemisorption properties revealed by spectroscopic measurements [12, 13] with almost perfect epitaxial quality [14]. In spite of a very detailed knowledge of the PTCDA/Ag(111) interface, it has not been clarified so far whether this is a fortuitous coincidence or whether the specific chemisorption state promotes the formation of the high-quality epitaxial interface [15]. This issue is addressed in the present work by a combination of spectroscopic data and first-principles quantum chemical calculations. As a result of our analysis, we propose that there is indeed a close relationship between the remarkable spectroscopic chemisorption signature and the interface epitaxy. In fact, using spectroscopic data, we are able to unravel the mechanism of the epitaxial bonding down to the (sub)molecular level and trace it back to the influence of the functional groups: the perylene skeleton has a tendency to form a specific binding centre in the central part of the molecule. In the case of PTCDA, charge redistributions within the molecule, caused by the carboxy-dianhydride groups, enhance the activity of this centre considerably, allowing it to bind to a definite adsorption site on the Ag(111) surface. Having located the chemisorption centre of the molecule, we may use the known structure of PTCDA layers [8, 14] to suggest a definite chemisorption site on the Ag(111) surface (cf section 4). This last conclusion, however, is preliminary and needs to be confirmed by direct experiments.

In the quest for organic epitaxy, the interface structure is only one of the issues to be addressed. Once ordered interfaces are established, the next challenge is to maintain the structure of the molecular film and transfer it to higher layers without structural relaxation. For example, while PTCDA/Ag(111) is a good case of interfacial epitaxy, it has recently been shown that, after a few molecular layers, in a certain temperature regime the growth mode switches from layer-by-layer to the formation of three-dimensional turrets [16]. In this way, the film relaxes towards the bulk PTCDA crystal structure. In the present work, we will not focus on the problem of maintaining epitaxial growth once the interface has formed. Rather, we focus on the interface, since interface engineering in its own right offers many additional benefits.

So far we have argued that judicious substitution of end groups may be used to improve bonding and growth properties without altering the applicable properties of the film. In many cases this is exactly what is desired, e.g. when the growth of polycapenes, which show good semiconductor properties and are used as active layers in field-effect transistors, is optimized on certain substrates. However, it is evident that the scope of functionalization is wider: by directly engineering the interaction between the film and the substrate, one may be able to achieve entirely new properties. We have pointed out before that the doping of molecular layers through charge transfer across an interface with a metal may be expected to lead to two-dimensional superconductivity at low temperatures if the molecules themselves exhibit a strong electron–phonon coupling [13].

This paper is organized as follows: in the next section we briefly summarize our methodology, both theoretical and experimental. In sections 3.1 and 3.2, we use spectroscopic data in conjunction with first-principles quantum chemical density functional calculations to localize the active chemisorption centre within the PTCDA molecule. In sections 3.3 and 3.4, we contrast the situation of PTCDA/Ag(111) with perylene/Ag(111) and
PTCDA/Au(111), respectively. Systematically varying the properties of molecule and substrate, we thus delineate the conditions under which this active site can form and become effective. In section 4, we summarize and draw conclusions.

2. Methods

Spectroscopic data discussed in the present work have all been recorded with a high-resolution electron energy-loss spectrometer Delta 0.5 manufactured by VSI GmbH, now Specs GmbH. In the experiment, the primary electron beam with energy between 2.3 and 20 eV was directed at the sample surface at an incidence angle of 55° with respect to the surface normal. In most cases, we analyse energy losses in the specularly reflected beam of electrons. For the so-called off-specular spectra, however, the analyser is rotated out of the specular direction and electrons which have transferred momentum as well as energy to the sample are recorded. Since we investigate ultrathin dielectric films on metal substrates, generally only infrared active modes with polarization perpendicular to the surface plane are registered in specular scattering geometry. In off-specular geometry, all vibrational modes can be seen, at least in principle.

Our organic thin films are prepared by organic molecular beam deposition (OMBD) on to metallic substrates which have been prepared in the usual way by multiple sputter–anneal cycles. For Ag(111), the following parameters were used: sputtering at 1000 eV and approx. 10 µA sample current and annealing at 700–800 K, while Au(111) was sputtered at 900 eV and approx. 8 µA sample current and annealed at 670–720 K.

Evaporation of PTCDA took place from a Knudsen cell at 690–700 K, yielding growth rates of 0.2 ML min\(^{-1}\). Here 1 ML refers to one monolayer of densely packed, flat-lying molecules. In the case of perylene, a similar evaporator was used, this time operated at 470 K. Typical growth rates are 0.3 ML min\(^{-1}\). In our experiments, the substrate was kept at room temperature during deposition. As perylene is very volatile in vacuum, one has to avoid cross contamination of other evaporation sources. In the present case, none of the PTCDA material used for the experiment was ever exposed to perylene.

With regard to PTCDA on Ag surfaces, the procedure of film-thickness calibration, relying on the three-fold combination of quadrupole mass spectrometry during evaporation, quantitative x-ray photoelectron spectroscopy and low-energy electron diffraction, has been reported before [17]. For PTCDA deposition on Au(111), we used the evaporators calibrated on Ag surfaces. Additionally, a clear cross-over from linear to sublinear dependence of the peak intensities at 735, 807 and 867 cm\(^{-1}\) (cf figure 7) on exposure time could be observed. As expected, this cross-over coincides with completion of the first monolayer.

The results of fully self-consistent quantum chemical density functional calculations for isolated PTCDA and perylene molecules [18, 19] play an important role in the discussions of this paper. These were carried out with the commercial Gaussian 98 package [20]. To remain consistent with our earlier published work for PTCDA [17], the B3LYP exchange correlation functional [21] was employed in conjunction with the 6-31g basis set of Gaussian-type orbitals whenever a direct comparison between PTCDA and perylene was intended. However, it has been shown [18, 22] that vibrational modes of medium-sized organic molecules are reproduced with an increased accuracy (i.e. <2% error in the frequencies without scaling) if the combined BPW91 functional is used. The latter is a combination of the B88 [23] and the PW91 [24] functionals. For a comparison of the perylene modes with experimental data, we therefore
refer to calculations [19] based on the BPW91 functional with the correlation-consistent double zeta basis set cc-pVDZ [25]. Additionally, a BPW91/cc-pVDZ calculation for PTCDA [18] was used for comparison with experimental data.

In all of the above calculations, atomic co-ordinates were relaxed to determine the theoretical equilibrium positions by total energy minimization. The probability amplitudes of the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) are generated on a grid of 858 627 points in a cube of approximately $0.7 \times 1.2 \times 1.8$ nm$^3$.

Furthermore, a normal-mode analysis for all 108 (PTCDA) or 90 (perylene) internal degrees of freedom was performed. In accordance with group theory, this yields 19/16 modes of $A_g$ symmetry, 8/7 $A_u$ modes, 7/6 $B_{1g}$ modes, 18/15 $B_{1u}$ modes, 10/8 $B_{2g}$ modes, 18/15 $B_{2u}$ modes, 18/15 $B_{3g}$ modes and 10/8 $B_{3u}$ modes. (The first number refers to PTCDA and the second number to perylene.) The assignment of the majority of infrared active $B_{1u}$, $B_{2u}$ and $B_{3u}$ modes of PTCDA has been published before [17]. Other authors have assigned the $A_g$ modes to Raman spectra [26]. For perylene, a detailed comparison between our measured HREEL spectra and the calculated frequencies will be presented elsewhere [27]. Here, only an overall comparison is made. Some experimental and theoretical frequency data for perylene obtained by other authors is available in the literature [7, 28].

In the present work, the elongation patterns of totally symmetric vibrational modes are of special interest. The shareware program package ‘g-open-mol’ [30] has been employed to produce animations of the atomic motion of these modes, based on the eigenvectors of the Gaussian 98 normal-mode analysis, and contained in mpg files in supplements 1 and 2. Each animation consists of 20 frames for each molecular oscillation period. The amplitudes of all animations are scaled such that the sum of the squared displacements amounts to $1.000 \pm 0.008$ Å$^2$.

To investigate the periodic electron redistribution in a vibrationally excited PTCDA molecule (Born–Oppenheimer approximation), the HOMO (not shown) and LUMO, as calculated for the two extremal atomic configurations separated by a vibrational half-period, were employed [15]. Since we are dealing with a quantum mechanical oscillator, a ‘turning point’ is of course not well defined. Nevertheless, we have used the maximal amplitudes as shown in the mpg animations of supplements 1 and 2. Subtracting these two ‘extremal’ orbitals from the corresponding equilibrium orbitals or from each other, we gain a qualitative impression of the electron redistribution process during each of the normal modes thus analysed. Since our argument mainly rests on the qualitative pattern of the electron redistribution in the LUMO, we have chosen to plot areas in which the charge modulation is 1% or more of the maximum homogeneous red or blue, depending on the sign.

3. Results and discussion

3.1. Strongly substrate-coupled breathing modes of PTCDA

The spectrum in figure 1 corresponds to the PTCDA monolayer on Ag(111). As pointed out before, we observe two types of modes in this spectrum (for the moment, we will focus on the strongest modes): modes at 715 and 787 cm$^{-1}$ and a hidden structure at 817 cm$^{-1}$ (see figure 2) are $B_{3u}$ modes (dynamical dipole moments perpendicular to the plane of the molecule and thus also to the plane of the surface) whose eigenvectors can be seen in the files mode41.mpg, mode47.mpg, mode53.mpg in supplement 1 and which are also observed in PTCDA monolayers.
As argued in the text, modes labelled with a black dot are totally symmetric $A_g$ modes of PTCDA, while the structures at 715 and 787 cm$^{-1}$ are perpendicularly polarized. More details can be found in the text.

at the Ag(110) surface (at 716 and 781 and 808 cm$^{-1}$). As will be proved below, the second group of strong modes at 524, 839, 1220 and 1540 cm$^{-1}$ (marked with black circles in the figure) consists of parallel-polarized, totally symmetric Raman modes. These are visible in HREELS only if PTCDA comes in contact with Ag(111) [31]. Essentially, in one half-cycle of the molecular oscillation, charge is pulled from the substrate into the molecule, while in the next half-cycle, the charge is pushed in the opposite direction. This charge flow leads to a strong dynamical dipole moment to which the time-dependent electric field of the primary electron beam can couple [13].

For the totally symmetric modes at 1220 and 1540 cm$^{-1}$, we have presented a quantitative model based on an intramolecular electron–vibron coupling term in the Hamiltonian of the adsorbate system [13]. A macroscopic dielectric function for the interface was calculated in a perturbation series. On this basis, the spectral shape of modes at 1220 and 1540 cm$^{-1}$ could be reproduced. In fact, the Fano line shapes of these two modes reveal the coupling of discrete PTCDA vibrations to a continuum of electron–hole pair excitations in the vicinity of the Fermi level, which are—in a band picture—the equivalent of a transverse charge transfer across the interface.

In the case of the mode at 839 cm$^{-1}$, a comparison to PTCDA/Ag(110) reveals that this mode cannot be of $B_{3u}$ symmetry. In figure 2, deconvoluted HREEL spectra in the frequency range of the strongest PTCDA $B_{3u}$ modes are plotted. We observe a clear correspondence between the sets of surface-shifted $B_{3u}$ modes at 716, 781 and 808 cm$^{-1}$ on Ag(110) (figure 2(a)) and 715, 787 and 817 cm$^{-1}$ on Ag(111) (figure 2(b)). From figures 2(c) and (d), we can unambiguously assign the modes at 739 and 870 cm$^{-1}$ in figure 2(b) to free PTCDA (multilayer) molecules, as well as the mode at 817 cm$^{-1}$, which is not (or very little) surface-shifted. The only mode in figure 2(b) which has no correspondence in either PTCDA/Ag(110) monolayers or in multilayers is the mode at 839 cm$^{-1}$. It is therefore plausible to assign this resonance, as well as the one at 524 cm$^{-1}$, to the same coupling mechanism which has been demonstrated for the modes at
Figure 2. Deconvoluted HREEL spectra (primary energy 2.3 eV and angle of incidence 60°) in the frequency region of the strongest B_{3u} modes: (a) 0.3 ML PTCDA/Ag(110), (b) 0.3 ML PTCDA/Ag(111), (c) 1.6 ML PTCDA/Ag(111) and (d) 3.5 ML PTCDA/Ag(111). Open circles and black solid lines represent experimental data with overall fit result. Peak profiles: thin solid lines (red), monolayer modes; solid circles (blue), multilayer modes; crosses (magenta), multilayer mode with no surface shift; thick solid line (green), A_g mode. On the right-hand side of (b)–(d), additional component lines (not shown) have been used to model the large background of electron–hole pair transitions.

1220 and 1540 cm\(^{-1}\), although the line shapes are Lorentzian in this case. The Lorentzian line shapes indicate that the perpendicular charge transfer can follow these molecular vibrations adiabatically.

The crucial question arising in this context is: what is the special character of those modes which are strongly coupled to transverse charge transfer or, in other words, why are the four modes at 524, 839, 1220 and 1540 cm\(^{-1}\) selectively enhanced? Note that altogether there are 19 A_g modes in PTCDA which at least in principle fulfil all prerequisites for the enhancement mechanism described above. On the microscopic level, it is clear that the
vibration-induced periodic changes of the molecular frontier orbitals are responsible for any redistribution of charge between the metal and the molecule at the interface. Turning to the quantum chemical calculations mentioned above, we will therefore investigate these charge flows in detail. However, we first analyse the vibrational displacement patterns themselves.

The visualization of all $A_g$ modes in supplement 1 allows us to select a certain class of modes—and indeed a certain part of the molecule—of special relevance in this context. From our quantitative fitting [13] and the assignment of observed Raman modes [32], we know that the most strongly enhanced mode in the spectrum of figure 1 corresponds to the $A_g$ mode 78. The animated elongation pattern of this mode is shown in supplement 1 (mode78.mpg). We note that only the central part of the perylene backbone and the four inner hydrogen atoms (which perform in-plane bending vibrations) are moving appreciably. In fact, the central carbon ring undergoes a breathing motion, increasing and decreasing its area periodically. This character suggests that the mode may operate as a molecular ‘electron pump’. In the rest of this section, we will support this key notion by additional evidence.

If the mode at $1220 \text{ cm}^{-1}$ involves a ‘pumping’ motion of the inner carbon ring, what can we say about the modes at 524, 839 and 1540 $\text{cm}^{-1}$? To clarify this question, we have calculated the ratio of the central carbon ring’s area at both turning points of the vibration for all other $A_g$ modes. The result is displayed in figure 3(a), together with the experimental spectrum of figure 1. Figure 3(a) reveals that there are six modes in which the areal change of the inner carbon ring is distinctly large (modes 30, 50, 75, 78, 83 and 93). Similar to mode 78, the experimental frequency for mode 93 (taken from [32]) again coincides almost perfectly with the bare, non-interacting modes according to our quantitative line fitting [13]. The assignment of the two Fano peaks to modes 78 and 93 is therefore unambiguously clear. As far as the other two strong modes are concerned, we note that there is a very good correspondence between these and modes 30 and 50. We conclude that all modes in the spectrum of figure 1, which are marked by black dots, are in fact characterized by a large areal change of the inner carbon ring and the corresponding charge pumping.

3.2. Chemisorption centre of PTCDA

In the following, we analyse the response of the electronic system of PTCDA to the excitation of totally symmetric modes of the molecule. This allows us to gain further insight as to why modes 30, 50, 78 and 93 appear strongly enhanced at the Ag(111) surface while others, including modes 75 and 83, do not.

We know that the bonding of PTCDA to Ag(111) involves charge transfer from the metal to the molecule [13]. We expect the LUMO of the free molecule to accomodate the surplus charge. Evidence for a metallic molecule, taken from photoelectron spectroscopy, has been presented in earlier publications [12, 13]. The former LUMO is thus the molecular orbital which is connected to the metallic charge reservoir. If, in any part of this spatially extended orbital, the overall electron density changes due to the excitation of a certain vibrational mode, we may expect the metal electrons to respond to this redistribution, but only if the corresponding part of the molecule is indeed coupled to the substrate. Conversely, if we determine which subsection of the molecule suffers a significant net charge modulation specifically in those modes which are found enhanced in our experiments, we can determine the part of the molecule that is coupled to the metallic charge reservoir or, in other words, the part of the molecule which plays a predominant role in forming the bond to the substrate.

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Figure 3. (a) HREEL spectra (primary energy 2.5 eV and angle of incidence 55°) for 0.3 ML PTCDA/Ag(111) (solid line) and frequency of PTCDA $A_g$ modes (experimental frequencies from [32]) versus ratio between maximum and minimum area of the central carbon ring (scattered symbols). Numbers refer to calculated vibrational modes (B3LYP/6-31g) in the order of ascending frequency. Black/white squares and black/white circles, weakly activated modes with contribution of perylene skeleton; white/black squares, modes with strong contribution of dianhydride groups; black circles, strong $A_g$ resonances with pumping character (cf text). (b) Calculated $A_g$ frequencies of perylene (Gaussian 98), using the B3LYP xc-functional with 6-31g basis (open stars) [19], and the BPW91 xc-functional with cc-pVDZ basis (black stars) [19]. Numbers refer to modes of the B3LYP calculation. Dotted lines connect corresponding PTCDA (a) and perylene (b) modes. (c) Off-specular monolayer HREEL spectra of perylene/Ag(111), primary energy of 2.5 eV, 55° angle of incidence, 11.5° detection angle against specular. (d) Off-specular monolayer HREEL-spectra perylene/Ag(111), with primary energy 2.5 eV and angle of incidence 55°.
The LUMO of free PTCDA is presented in figure 4. It has two nodal planes, one in the plane of the molecule and the other perpendicular to the short axis of the molecule. In figure 5, we show the difference of the LUMO electron densities between opposite maximum elongations of the respective vibrations for a few selected modes. The mpg files in supplement 2 contain similar plots for all 19 $A_g$ modes, with animations of the corresponding vibrations projected on top. From figure 5 and supplement 2 it becomes clear that only for modes 30, 50, 78 and 93, the electron density in the inner carbon ring is modulated homogeneously, while for modes 75 and 83 the central carbon ring shows both local increases and decreases in the charge density. Note that this observation coincides very well with the fact that modes 30, 50, 78 and 93 are strongly enhanced while modes 75 and 83 are much weaker in the experiment. The most striking (if not the only) common characteristics of the strongly enhanced modes is the fact that they show an overall ‘pumping’ of the electron density in the central carbon ring.

Note that the specific characteristics of modes 75 and 83, as revealed by figure 5, can also be understood considering the elongation patterns themselves. In general, an areal change of the central carbon ring can be brought about by a perpendicular and/or a parallel distortion of this ring with respect to the nodal plane along the long axis of the molecule. A simple geometric analysis reveals that modes which predominantly involve a parallel distortion (like modes 75 and 83) cannot lead to a homogeneous charge modulation in the inner carbon ring. This is prohibited by the presence of the nodal plane and its orientation relative to the central hexagon of carbon atoms.

So far, we have only taken into account the response of the LUMO to the excitation of the six modes which display the largest areal modulation (cf figure 3). If we broaden the analysis and consider the adiabatic response of the LUMO to all other totally symmetric modes of the molecule (supplement 2), the picture sketched above is beautifully confirmed. Most of the other modes, involving a mere distortion of the inner carbon ring, show compensated charge
Figure 5. Electron redistribution in the LUMO of vibrationally excited molecules for the six totally symmetric A_g modes in which the central carbon ring undergoes a large area modulation. Orbitals are calculated for the ‘turning point’ geometry of the molecule. Calculated LUMO densities are then squared, and the results for positive maximum elongation are subtracted from those of negative maximum elongation. In the plots, all areas in which the net change is larger than 1% of the total are coloured homogeneous red (+) or blue (−). Depicted is the plane 0.24 Å below the plane of the molecule. In supplement 2, plots for all A_g modes are shown, and additionally mode vibrations are projected on top of the ‘difference orbitals’.

Redistribution patterns in the central ring, as e.g. modes 12, 64, 67, 86 and 91 (supplement 2), unless they have a strong vertical component of the distortion, as mode 25. Other exceptions from the general rule are mode 80 and the borderline case of mode 67. The latter do not appear strongly in the experimental spectra, confirming that both a large areal change and the uncompensated pattern are necessary conditions for strong infrared activity at the Ag(111) surface. Also note that, quite generally, modes which involve strong participation of the dianhydride groups (i.e. modes 19, 34, 42 and 100) do not show a sizeable enhancement. In particular, in spite of a strong charge modulation on the whole dianhydride groups, mode 34 is not dominant in the spectrum.
This proves that the coupling of the latter groups to the substrate is much weaker than for the centre of the molecule.

Based on our analysis in the current and the previous sections, we conclude that the central carbon ring plays an important role as the ‘active site’ in the molecule’s bonding to the Ag(111) substrate. This active site is coupled to the metallic charge reservoir, and we can thus speak of a quasi-local bond between the metal surface and this (still extended) molecular chemisorption or reaction centre. This notion is additionally supported by circumstantial evidence, as the existence of such a reaction centre makes the site specificity of PTCDA adsorption on Ag(111) understandable: the central carbon ring locks into a definite position of the metal surface, thus promoting a specific adsorption site.

3.3. Influence of the functional groups: perylene/Ag(111)

So far we have seen that the central carbon ring acts as the bonding centre of PTCDA to the Ag(111) surface. A question now arises regarding the role played by the dianhydride groups. It has been confirmed by the present results that they play no active role in the surface bond, as conjectured before [13]. However, the fact that the electronegativity of the oxygen groups imposes a positive partial charge in the centre of the molecule which may enhance the affinity of the molecular centre to the metal surface is suggestive of an indirect role for the dianhydride groups. Can this be confirmed?

To answer this question, we turn to an experimental investigation of this issue. We have performed adsorption experiments of perylene on Ag(111). Any difference between the behaviour of PTCDA and the perylene molecule, essentially the PTCDA backbone, i.e. PTCDA without the O=C–O=C–O groups on either side, must be caused by the above functional groups.

Detailed analysis of the absorption behaviour of perylene on Ag(111) is beyond the scope of this paper. Details will be reported in a separate publication [27]. Here we will focus on selected aspects of the perylene/Ag(111) data with relevance to the present context. In the perylene monolayers on Ag(111) which are discussed here, the molecules are oriented parallel to the surface, such that the interaction of the π-electron system, and specifically of the central carbon ring, with the substrate can be compared directly with the case of PTCDA. But unlike PTCDA/Ag(111), perylene on Ag(111) does not form a commensurate layer, i.e. the molecule does not lock into a definite adsorption site [27].

In figure 3, we have included the 16 calculated frequencies of internal perylene vibrations with A_g symmetry, both according to the B3LYP/6-31g and according to the BPW91/cc-pVDZ calculations [19]. Analysing the mode character, which incidentally does not differ significantly between the two calculations, it is possible to establish a unique correspondence between the modes of perylene and those modes of PTCDA which are not primarily involving the dianhydride groups (i.e. modes 19, 34, 42 and 100). This correspondence is indicated in the figure by dotted lines. For example, considering mode 60 for perylene at 1360 cm$^{-1}$ (B3LYP) or 1281 cm$^{-1}$ (BPW91), this mode is virtually identical to mode 78 of PTCDA, calculated at 1361 cm$^{-1}$ (B3LYP). The experimental Raman frequency of the latter is 1310 cm$^{-1}$, while due to the dynamical coupling to the metal electrons this mode is observed with Fano line shape at 1220 cm$^{-1}$ in monolayer HREELS spectra. Because of the similarity of the displacement pattern in the central carbon ring in modes 60 (perylene) and 78 (PTCDA), we expect that if the local bonding interaction of the central carbon ring of perylene/Ag(111) is
similar to the case of PTCDA/Ag(111), mode 60 should exhibit prominent infrared activity, as should perylene modes 19, 32 and 76 as pendants to PTCDA modes 30, 50 and 93. At first glance, this is certainly not the case. However, if the spectrum is strongly magnified as in figure 3(d), one observes a strikingly good correspondence between the calculated $A_g$ frequencies and the weak modes above 900 cm$^{-1}$. In particular, two relatively strong modes at 1271 and 1548 cm$^{-1}$ are detected, in excellent agreement with 1281 cm$^{-1}$ (mode 60) and the pair 1590/1565 cm$^{-1}$ (modes 76/73), and in perfect agreement with the two strong Fano modes of PTCDA.

The spectrum in figure 3(d) was recorded in specular scattering geometry, where dipole scattering is the strongest scattering mechanism. Because of the surface selection rule, under these conditions, only modes of $B_{3u}$ and $A_g$ symmetry are expected to contribute, while above 900 cm$^{-1}$ no $B_{3u}$ modes exist in perylene. If, on the other hand, an off-specular scattering geometry is applied, as in figure 3(c), all vibrational modes can, in principle, be observed regardless of their symmetry. The fact that the spectrum clearly changes its structure with the change in scattering geometry confirms that at least the modes at 1271 and 1548 cm$^{-1}$ in figure 3(d) are excited in dipole scattering. In fact, the off-specular spectrum perylene/Ag(111) carries a strong signature of $B_{1u}$ and $B_{2u}$ modes which are also characteristic of multilayers (cf figure 6). This indicates that the modes in the monolayer cannot correspond to intrinsically infrared-active representations of the free molecule. They must be derived from modes of a different symmetry, most probably $A_g$.

The following picture thus emerges: perylene/Ag(111) is weakly chemisorbed. (We note in passing that the weakness of the interaction of perylene with Ag(111) is also revealed by the very small differential peak shifts of the strong vibrational modes at 767 and 806 cm$^{-1}$ in the monolayer if compared with multilayers; cf figure 6.) The interaction between the perylene molecule and the Ag(111) substrate facilitates a tiny dynamical charge transfer when $A_g$ modes of the free molecule are excited. As revealed by the predominance of central ring breathing modes, the inner ring of the perylene molecule again operates as the chemisorption centre, in the same manner as discussed for PTCDA in the previous section. However, judging from the overall weakness of the dynamical interface dipoles for all visible $A_g$ modes, the strength of the coupling between molecule and substrates is more than two orders of magnitude smaller than in the case of PTCDA/Ag(111). We can hence conclude that the dianhydride groups of PTCDA—in spite of not being involved directly in the bond—enhance the bonding of PTCDA to the silver surface by a few orders of magnitude, leading to giant mode enhancements.

By applying spectroscopic methods, we have thus found an explanation for the fact that perylene does not ‘lock into place’ on Ag(111) in the same way as PTCDA does—although of similar nature, the interaction is just too weak. A strong quasi-local interaction evidently is a prerequisite for the establishment of a definite adsorption site of a large polycyclic aromatic molecule, which in turn is essential for the occurrence of epitaxial growths. By observing this quasi-local interaction for perylene as well as for PTCDA, we have demonstrated that the existence and nature of this local site is exclusively controlled by the extended $\pi$-ring system irrespective of functional groups, while its strength can be tuned in an extremely wide range by the application of suitable functional groups, leading to giant resonances in the case of PTCDA. This effect must be assigned to the influence of the electronegative oxygen atoms on either side of the molecule. We thus propose that the positive partial charge in the centre of PTCDA attracts metal electrons and thereby dramatically enhances the affinity of the molecular chemisorption centre to the silver surface.
Figure 6. HREEL spectra of perylene/Ag(111). Primary energy 2.5 eV and angle of incidence 55°: (a) reference spectrum from figure 3(d); (b) specular scattering geometry, multilayer, compared with results of calculation (Gaussian 98, BPW91/cc-pVDZ) [19] of B_{1u} (bottom white circles) and B_{2u} (top black circles) modes, the y co-ordinate of circles gives the calculated relative infrared intensity in arbitrary units; (c) off-specular scattering geometry, multilayer, detection angle 11.5° from specular direction.

3.4. Influence of the substrate: PTCDA/Au(111)

Having pinned down the influence of the functional groups on the molecule–substrate interaction, we now turn towards an investigation of the substrate influence on the bonding. Since we are dealing with chemisorptive surface bonds, one should not be surprised to detect a dependence on the properties of both reaction partners. We have carried out experiments on PTCDA/Cu(111) and PTCDA/Au(111) monolayers. Here we report on the results regarding PTCDA/Au(111).

Before discussing the spectroscopic results of the present study, we briefly review the structural features of PTCDA monolayers on Au(111). Fenter et al [33] have studied layer-by-layer PTCDA growth on Au(111) by electron and x-ray diffraction and have noted that the $\sqrt{3} \times 22$ reconstruction remains intact below the PTCDA layer. Later, this was confirmed...
in STM studies by Schmitz-Hübsch et al [34], where a contrast modulation with a $\sqrt{3} \times 22$ periodicity was imaged in the molecular monolayer. A careful analysis of RHEED and STM data by the same authors revealed the existence of three genuinely different orientations of the PTCDA superstructure with respect to the Au substrate (because of the symmetry of the substrate, these three genuine structures result in a total of 18 domains). All of them have a point-on-line registry with the underlying substrate, i.e. the lattice points of the molecular overlayer coincide with lattice lines, not necessarily lattice points, of the substrate. The three observed orientations are defined by a minimum misfit of the intrinsic PTCDA herringbone lattice with the substrate [34].

Point-on-line registry, which is also observed for PTCDA on graphite [35, 36], is usually indicative of a relatively weak adsorbate–substrate interaction, the latter being too feeble to enforce a definite adsorption site. Our spectroscopic results confirm this conjecture. In figure 7 we have plotted PTCDA/Au(111) mono- (a, c) and multilayer (b, d) spectra, respectively, each in specular (a, b) and off-specular (c, d) scattering geometries. The multilayer spectra are typical of PTCDA in PTCDA environment and well known from flat-lying multilayers on other substrates, including silver. We have included the predicted frequencies of a BPW91/cc-pVDZ calculation for PTCDA [18], revealing excellent agreement for infrared active modes of $B_{1u}$, $B_{2u}$ and $B_{3u}$ symmetry. In the off-specular multilayer spectrum, the $B_{1u}$ and $B_{2u}$ modes are enhanced relative to the $B_{3u}$ modes (a consequence of the parallel orientation of the molecules to the substrate surface), otherwise the spectra are similar.

Now we turn to the key result that the monolayer spectra on Au(111) are also very similar to the multilayer spectra across the whole frequency range (with one exception: the mode at 1068 cm$^{-1}$ marked by an arrow). This is remarkable, since it deviates from all our previous data of PTCDA or perylene on silver surfaces, cf [17, 27] or figures 1, 3 and 6 of the present paper. In all these cases, specular dipole spectra always have a specific signature, either caused by $A_g$ modes (e.g. the four strong modes at 524, 839, 1220 and 1540 cm$^{-1}$ on Ag(111)) or other chemically shifted modes (Ag(110)). (We note in passing that the mode at 569 cm$^{-1}$ in figure 7 should not be confused with the monolayer mode at 524 cm$^{-1}$ for Ag(111). The former is a $z$-polarized ($B_{1u}$) long-axis folding mode. On Ag surfaces this mode is absent, the reason being that it is suppressed on Ag(110) by the steric hindrance and obscured on Ag(111) by the strong mode at 524 cm$^{-1}$.)

This central observation of close similarity between mono- and multilayer spectra allows us to draw two conclusions:

1. From the absence of $A_g$ modes, however weak they may be, it must be concluded that the interaction of PTCDA with Au(111) is of an entirely different nature than that of PTCDA with Ag(111) or even perylene with Ag(111). Especially, the lack of signal from the central carbon ring breathing modes indicates that the central molecular reaction centre does not couple to an electron reservoir of gold. The chemisorption on gold, if at all present (mode 64 at 1068 cm$^{-1}$!), is not only weak but also of different nature than on silver. Instead of a clear chemisorption signature we observe the parallel-polarized $B_{1u}$ and $B_{2u}$ modes of the essentially free molecule even in the monolayer. Apparently, even the screening of parallel dipole seems less effective on gold when compared with silver.
2. Not only does the chemisorption via the central part of the perylene skeleton vary from PTCDA or perylene on silver surfaces, the properties of the dianhydride groups are also dramatically different: on none of the silver surfaces (Ag(110) and Ag(111)) the C=O stretch mode has been observed in either specular or off-specular scattering experiments from PTCDA monolayers. On Au(111), this mode, or more
Figure 7. HREEL spectra (primary energy 2.5 eV and angle of incidence 55°) of PTCDA/Au(111). (a) For 0.7 ML, specular scattering geometry with experimental [32] positions of Raman active $A_g$ modes indicated, symbols as in figure 3(a); cross-circles (orange), calculated frequencies (Gaussian 98, BPW91/cc-pVDZ) [18] for $B_{3u}$ modes which are observed experimentally. (b) For 10 ML, specular scattering geometry, compared with results of calculation (Gaussian 98, BPW91/cc-pVDZ) [18] of $B_{1u}$ (top white circles) and $B_{2u}$ (bottom white circles) modes, $y$ co-ordinate of circles gives calculated relative infrared intensity in arbitrary units. (c) For 0.7 ML, off-specular scattering geometry, angle of detection 16° with respect to specular reflection. (d) For 10 ML, off-specular scattering geometry, angle of detection 16° with respect to specular reflection.

precisely this set of modes (there are C=O stretch modes of $B_{1u}$, $B_{2u}$, $A_g$ and $B_{3g}$ symmetry), is visible in impact and dipole spectra. Since off-specular scattering is (almost) unrestricted by selection rules, we concluded [17] that in the case of PTCDA/silver, this mode is not merely suppressed but strongly shifted in frequency, indicating a bond-induced reorganization in the per se non-bonding (but bond enhancing, cf section 3.3) dianhydride part of the molecule. The experiments on gold surfaces support this conjecture: Since the chemical bond in the central
part of the molecule is absent, the dianhydride groups cannot enhance it and thus are left in their original state.

We finally note that the absence of any signs of a reaction between the PTCDA molecule and Au(111) points to a limit of our present treatment of the PTCDA–metal interaction: calculations for the free molecule, on which we have based the interpretation of molecular spectra, cannot of course rationalize differences in the reaction of one and the same molecule with different substrates. For this purpose, one would have to perform calculations of the actual interface, including the metallic bonding partner. To date, however, this is computationally too demanding, especially since detailed structural information on the interface, i.e. the adsorption site, is still missing.

4. Summary and conclusions

Investigating bonding interactions between polycyclic aromates and close-packed noble metal surfaces at a submolecular level, we succeeded in resolving the puzzle of organic epitaxy of PTCDA/Ag(111), presenting a clear, intuitive and physically appealing model of this interaction which may also be useful for related molecule–substrate combinations.

In the case of PTCDA/Ag(111), strong chemisorption, which locks the molecules into unique lateral positions, is connected to a quasi-local interaction of the central-carbon ring of the PTCDA molecule with the substrate. The predisposition for this bond type is present even for perylene, although the bond is rather weak in this case. A comparison of perylene and PTCDA thus demonstrates the validity of an important chemical paradigm also for the case of surface adsorption, namely the influence of side groups on the activity of a given reaction site. This opens up the way for interface engineering—of which organic epitaxy is only one example—by the application of molecular side groups. The present pair of molecules, PTCDA and perylene, shows that the range in which the bonding properties can be tuned is surprisingly wide: if we take the strength of the dynamical charge transfer as a measure for bonding strength, we find side-group-induced variation of more than two orders of magnitude. Finally, our experiments on Au(111) surfaces show the limits of reactivity control: the activity of the chemisorption centre is dependent on the substrate which plays the role of the reaction partner.

Having recognized the existence of a molecular chemisorption or reaction centre, we may now use this knowledge in the search of the molecular adsorption geometry of PTCDA on Ag(111). It is clear from our analysis that the central carbon ring is the site-specific element of the molecule. Since we know the lattice constants of Ag(111) and the PTCDA overlayer from high-resolution diffraction experiments [8], we can project both lattices on to each other and move the adsorbate lattice relative to the substrate until we find a suitable position for the chemisorption centres of both molecules in the unit cell. If we postulate that the chemisorption centres of both molecules sit in similar positions relative to the substrate, we may predict a bridge site of PTCDA on Ag(111) (cf figure 8). It is clear that this hand waving argument is no substitute for a careful—and challenging—experimental and theoretical adsorption site determination which is under way. However, it may guide data interpretation of these experiments or help to select models which should be calculated and compared with each other.

In the case of PTCDA on Ag(110), where the adsorption site is known, we can test whether possible inferences regarding the adsorption site drawn from our data are valid. We noted before [13] that, in spite of the strong chemisorption of PTCDA on Ag(110), the central-ring breathing modes are not detected in a HREELS experiment on PTCDA/Ag(110) (cf figure 2(a)). Therefore,
the central carbon ring does not couple to the Ag(110) substrate: apparently, the bonding of PTCDA on the templated Ag(110) surface follows a different mechanism. We may infer from this observation alone that this ring is placed over a groove of the (110) surface. An unambiguous STM experiment indeed confirms this conjecture [9].

Finally, in the present work, we have demonstrated the extreme power of the combination of vibrational spectroscopy and quantum chemical calculations in the context of chemisorption matters. In the future, this combination of methods will be extended to other functional groups and different molecules.

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