Molecular distortion of NTCDA upon adsorption on Ag(111): a normal incidence x-ray standing wave study

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Abstract. We investigated the adsorption geometry of the model system NTCDA (1,4,5,8-naphthalin-tetracarboxylicacid-dianhydride) on Ag(111) using the normal incidence x-ray standing wave (NIXSW) technique. For the relaxed monolayer structure a significant vertical distortion of the molecule is found upon adsorption. The carboxylic oxygen atoms at the corners of the molecule are located 0.25(3) Å closer to the topmost Ag atoms than the naphthalene core at 2.997(16) Å. This distortion effect is similar to that of the larger molecule (3,4,9,10-perylene tetracarboxylicacid-dianhydride) (PTCDA)/Ag(111) (Hauschild A et al 2005 Phys. Rev. Lett. 95 209602), but the chemisorptive bonding is weaker. Our structural investigation is based on photoelectron and Auger emission NIXSW data, the independent measurement of which allows us to correct in a self-consistent way for non-dipolar contributions to the photoelectron yield as well as for electron induced Auger processes, two effects which may significantly influence the structural results if not considered.
1. Introduction

For several years there has been increasing interest in the adsorption behaviour of large π-conjugated molecules on different surfaces. These adsorbate systems show a variety of different phases, the properties of which can be tuned by the proper choice of molecules, substrates, preparation conditions, temperature, etc. It has been realized that the interaction between the surface and the first molecular layer plays a dominant role for the properties of each specific system [1]–[9]. This interaction determines the molecular orientation and the ordering in the first layer and subsequently the growth behaviour of thin films, and it influences the electronic interface properties such as band offsets, interface dipole and band bending. The stronger the interaction, the more distinctive is the substrate for the properties of the entire system. In the case of weak interaction, however, the bulk properties of the organic material tend to dominate.

In contrast to what is often believed, recent studies have shown that large π-conjugated molecules tend to chemisorb on metal surfaces in many cases, i.e., they show a rather strong interaction [4, 6, 7]. Two prototype systems under intense investigation are 3,4,9,10-perylene-and 1,4,5,8-naphthalin-tetracarboxylicacid-dianhydride (PTCDA and NTCDA, see figure 1) on the Ag(111) surface. Both are planar molecules and adsorb in a flat-lying geometry on the Ag(111) surface in the first layer. They show a long-range ordered monolayer structure at room temperature (RT). While PTCDA forms for all coverage domains which are commensurate to the substrate, NTCDA adsorbs in a commensurate register to the substrate only up to 80% of the saturated first layer. Between 80 and 100% at least two further (uniaxially) incommensurate monolayers occur [2, 10]. The lateral super-structures of both adsorbate systems have been well investigated with various techniques, and hence the basic structural properties like unit cell sizes, orientation of the molecules, chemical bonding, vertical distances, etc, have been well explored [1, 3, 4, 6, 11]. However, it is possible and necessary for a detailed comparison with theory to obtain more detailed structural properties of these systems, in particular in the vertical direction with respect to the surface.
In the present study, we thus report on an investigation of the adsorption heights (vertical distances) of individual atoms of the NTCDA molecule. This information was derived from a normal incidence x-ray standing wave (NIXSW) experiment, in which the different oxygen species could be distinguished and separately evaluated using their core level shifts in the photoemission yield. In conclusion, it indicates a significant distortion of the molecules upon adsorption on the Ag surface. This could not be detected in our earlier investigation [3] of the same surface structure due to a lower experimental resolution. Our new results on NTCDA/Ag(111) are compatible with an investigation of PTCDA on Ag(111) published recently [6], but indicates a slightly weaker distortion of the molecule and a weaker interaction with the surface.

In addition to this main aspect, we describe a self-consistent method that significantly improves the reliability of the NIXSW technique since it makes it independent of the correctness of the parameters describing either the non-dipolarities of the photoelectron (PE) process or the contribution of substrate electrons to the Auger decay in the adsorbate.

2. The NIXSW technique

The NIXSW technique is frequently used to obtain precise atomic positions of atoms or molecules adsorbed on surfaces [3], [12]–[18]. In a NIXSW experiment one measures the modulation of the atomic absorption \( I(E) \) of a specific atomic species while scanning the photon energy \( E \) through the Bragg condition for a specific Bragg reflection \( \mathbf{H} = (hkl) \) of the bulk crystal. The standing wave field, which is formed by the interference between the incoming and Bragg-reflected x-ray waves, has the same periodicity \( d_H \) as the Bragg planes and moves by half of this distance during this scan, i.e., the phase \( \Phi = \Phi(E) \) of the reflected wave changes by \( \pi \). This causes a characteristic change of the intensity of the electromagnetic field at the positions of the adsorbate atoms which in turn directly changes their absorption behaviour. That can be measured by recording, e.g., the photoelectron or the Auger electron emission yield during the scan through the Bragg condition. The result can then be fitted using dynamical diffraction theory to obtain geometric parameters, the so-called coherent position \( P^H \) and the coherent fraction \( F^H \). However, as mentioned above, for both detection channels—PE and Auger yield—specific corrections have to be made before the obtained parameters can unambiguously be related to atomic positions.

2.1. Non-dipolar contributions to the photoelectron yield

For the photoemission process, in general, non-dipolar contributions have to be taken into account. This is done by introducing the asymmetry parameter \( Q \), the phase \( \Delta \), which is the difference of the phases of the complex dipole and quadrupole matrix elements, and the parameter \( \Psi = \tan^{-1}(Q \tan \Delta) \). The XSW absorption profile can then be described by [3], [15]–[17], [19, 20]

\[
I(E) = 1 + \frac{1 + Q}{1 - Q} R + 2\sqrt{R} F^H \left( 1 + Q^2 \tan^2 \Delta \right)^{1/2} \cos(\Phi - \Psi + 2\pi P^H),
\]

where \( R \) is the reflectivity of the considered Bragg reflection. The coherent position \( P^H = D^H / d_H \) and the coherent fraction \( F^H \) are fit parameters which can be correlated to geometrical parameters. In general, we have to consider different inequivalent adsorption sites for the same atomic species.
$D^H$ is the average distance (modulo $d_H$) of these atoms to the Bragg planes of the bulk crystal.\footnote{Note that in this nomenclature the positive $z$-axis is pointing from the sample surface towards the vacuum, i.e., antiparallel to the incoming x-ray wave.}

If the Bragg planes of the chosen reflection lie parallel to the surface, and if the relaxation of the bulk crystal can be neglected $D^H$ can be directly attributed to the average height of these atoms above the surface atoms. The coherent fraction $F^H$, which is the contrast of the interference in equation (1), is 1.0 if only one site is occupied by the considered species, and drops to zero if the distribution of the heights of the atoms becomes completely random.

The two parameters $P^H$ and $F^H$ can also be interpreted as the phase and amplitude of the $H$-Fourier component of the spatial distribution of the adsorbate. For multiple site adsorption, every atom $k$ contributes to the absorption profile with an individual position $P^H_k$ and a coherent fraction of $F^H_k = 1$. The structural parameters $P^H$ and $F^H$, which are determined from a fit to the experimental data, can then be described by the average of these Fourier components, i.e.

$$F^H \exp \left( i 2 \pi P^H \right) = \sum_{k=1}^{N} \frac{F^H_k}{N} \exp \left( i 2 \pi P^H_k \right),$$

where $N$ is the number of atoms. This averaging, as well as the measured geometric parameters, are often presented as complex quantities in polar coordinates (in the so-called Argand diagram).

For a proper interpretation of the measured XSW absorption profiles the non-dipolar parameters $Q$ and $\Delta$ have to be known. $Q$ can be calculated \cite{21}, or measured by using a system which is known to have a random distribution of adsorption heights, i.e., a vanishing coherent fraction. In this study, we determined the parameter $Q$ for O1s photo electron emission from a comparison of photo- and Auger electron based XSW data, see subsection 4.2. The $\Delta$ represents a relatively small correction and can be calculated using, e.g., the code DLPHASE \cite{22}.

**2.2. Electron-induced Auger decays**

The Auger process, since it is a secondary process following the generation of a core hole, cannot only be induced by absorption of a photon from the electromagnetic field, but also by the impact of (photo- or Auger-) electrons and scattered electrons emerging from the bulk provided these have sufficient energy. Therefore the Auger electron yield measured in an XSW scan consists of two contributions, the ‘real’ Auger electrons which stem from the decay of core holes produced by the absorption of photons, and a parasitic contribution originating from electron-impact induced core holes in the adsorbate layer. The first contribution shows the desired XSW signature (i.e., the shape of the absorption profile) corresponding to the real geometric parameters of the atomic species under investigation. The second contribution reflects the number of bulk electrons, and thus shows the same XSW profile as the bulk atoms. This parasitic contribution hence corresponds to bulk-like geometric parameters, i.e., to a coherent position $0$ and a coherent fraction close to 1.0. As a consequence, the measured Auger yield, which can be described by the Fourier component $F^H_m \exp \left( i 2 \pi P^H_m \right)$, consists of the superposition of a photon induced part $F^H \exp \left( i 2 \pi P^H \right)$ and a (bulk-like) electron-induced part $F_{\text{bulk}}^H \exp \left( i 2 \pi P_{\text{bulk}}^H \right)$ yielding

$$F^H_m \exp \left( i 2 \pi P^H_m \right) = (1 - a) F^H \exp \left( i 2 \pi P^H \right) + a F_{\text{bulk}}^H \exp \left( i 2 \pi P_{\text{bulk}}^H \right)$$

$$= (1 - a) F^H \exp \left( i 2 \pi P^H \right) + a F_{\text{bulk}},$$

\footnote{Note that in this nomenclature the positive $z$-axis is pointing from the sample surface towards the vacuum, i.e., antiparallel to the incoming x-ray wave.}
where \( a \) is the portion of electron-induced Auger processes. The second line in this equation is obtained since the coherent position of the bulk-species \( P_{\text{bulk}}^H \) is 0. Hence, the measured Auger yield can in general not be used directly to obtain the structural parameters of the adsorbed atomic species. However, as pointed out earlier [3], the Auger signal can be corrected for the electron-induced portion and—in particular, when the result is compared to the absorption profile obtained from the photoemission yield—reliable geometric parameters can be obtained. This is performed in subsection 4.2 for the system under study.

3. Experimental

The experiments were carried out at the ultra high vacuum (UHV) surface science end station of beamline ID32 at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The UHV chamber is equipped with a hemispherical electron analyser \( (r = 150 \text{ mm}) \), low energy electron diffraction (LEED) optics, and all facilities necessary for sample preparation. The angle between the synchrotron beam and the axis of the analyser lens was 45\(^\circ\), with the lens and the polarization vector of the x-ray beam being in the horizontal plane. We performed the experiments with a base pressure below \( 3 \times 10^{-10} \text{ mbar} \).

3.1. Sample preparation

We used a (111)-oriented silver crystal with an experimentally obtained full width at half maximum (FWHM) of the Ag(111) reflection curve of 1.06 eV. The crystal was cleaned by Ar-sputtering at different angles of incidence (500 eV, 1.5 \( \mu \text{A} \), \( 2 \times 10^{-5} \text{ mbar} \), 10 min) and by subsequent annealing at 450\(^\circ\)C. The cleaning procedure was repeated until no carbon contamination could be detected by x-ray photoelectron spectroscopy (XPS) and the LEED pattern of the Ag(111) surface showed very sharp 1 \( \times \) 1 spots. Subsequently, with the Ag-crystal kept at RT, more than one layer of NTCDA was deposited on the Ag surface from a thermal evaporation source. The organic material had been purified by gradient sublimation before the experiment. Afterwards the multilayer was desorbed by annealing the sample at 20\(^\circ\)C. This procedure is known to result in a well ordered, so-called relaxed monolayer structure [2], with a commensurate superstructure matrix \( (\frac{4}{3} \frac{0}{6}) \) which has a coverage of about 80% referred to a saturated monolayer. The data presented in this paper was taken from two individually prepared films which yielded no significant differences in the results.

3.2. Data acquisition and raw data treatment

In this study, we analysed the NIXSW data taken with C1s and O1s photoemission yield as well as O-KLL Auger yield (see figures 2 and 3). Absorption profiles of the substrate bulk (Ag-MVV) were also measured for the clean crystal as well as for the adsorbate induced superstructures. Simultaneously to the measurements of the absorption profiles, the intensities of the incoming and the Bragg-reflected beam, as well as the total electron yield (sample current) were recorded. The photon energy was varied in a range of 6–8 eV around the Ag(111) Bragg energy \( (E = 2627 \text{ eV}) \) with 50 to 60 points in every XSW-scan. We recorded 15 scans for the Ag-MVV yield and 7–30 scans for O1s, O-KLL and C1s with a typical time for one scan of 10 to 45 min. In order to reduce beam damage, the beam spot on the sample was moved after every 150 to 300 min. In addition, we
checked for beam damage by comparing the XPS spectra before and after each NIXSW run, but no changes could be detected under the described conditions. The stability of the superstructures was also confirmed by LEED after each NIXSW measurement. In agreement with our earlier experiments [3, 23], very high coherent fractions (>0.9) were found for the Ag XSW signals (not shown). This indicates that no reconstruction of the uppermost Ag layers occurs.

For a very precise analysis of PE data and, in particular, for the distinction of differently bound atoms (molecules) by their core level shifts, a very detailed knowledge of the contributions to the photoelectron spectra, particularly about the shape of the background, is important. In our case, for the C1s PE and the O-KLL Auger yield a simple subtraction of a linear background was sufficient (figure 2). The peak integration range for the O-KLL peak was chosen based on the characteristic shape of various O-KLL structures which is known from the literature [24]. The peak on the lower kinetic energy side is attributed to the substrate and hence not taken into account. For the O1s yield (figure 3), for which the core level shift analysis was performed, we used a Shirley background and additional information from the high resolution photoemission measurements performed by Schöll et al [4]. The latter experiments were performed at the BESSY synchrotron radiation source in Berlin, using a much higher instrumental resolution.
Therefore, the peak shapes and the relative positions of the two O1s peaks (and their most intense satellites) arising from the different oxygen species in the NTCDCA molecule were known. A comparison of this high-resolution PE data with the sum of our O1s spectra obtained from the present XSW scans yielded the Shirley background parameters, an offset parameter for the binding energy as well as the instrumental broadening of our experiment. In all subsequent fits these parameters were kept constant, and only the amplitudes of the two O1s peaks and the offset and slope of an additional linear background were fitted. This procedure resulted in two XSW absorption profiles, one for each O1s amplitude, i.e., for each of the different oxygen species. In addition, the O1s intensity integrated over all core level shifted peaks was also analysed.

We fitted equation (1) to all individual PE-based absorption profiles (up to 30 single scans), as well as the properly averaged profile from all scans. The used non-dipolar parameters are listed in table 1. A Poisson-like treatment of errors was included in the fitting routines. Within these error bars the averaged fit parameters of the individual fits and their standard deviations agree well with the results of the fits of the averaged data and their error bars at a confidence level of 68.3%.

Figure 3. Typical (background corrected) O1s photoelectron spectra from the relaxed monolayer of NTCDCA/Ag(111) at different photon energies. The two different oxygen species (O1: anhydride oxygen located at the bridge position and O2: carboxylic oxygen located at the corner of the molecule) are fitted using the peak profiles from [4].
Table 1. Non-dipolar parameters: the $Q$ value for C1s is taken from the literature [17], for O1s it is obtained from a comparison of O1s- and O-KLL based XSW data (see subsection 4.2). The values for $\Delta$ are calculated using the code DLPHASE [22].

|       | C1s | O1s |
|-------|-----|-----|
| $Q$   | 0.27| 0.27|
| $\Delta$ | $-0.21$ | $-0.30$ |

4. Results and discussion

4.1. Results based on the photoelectron yield

We took two independent data sets from different preparations of the relaxed monolayer structure. The analysis yields very similar results (see black and green data points in figure 6). For the data analysis both data sets were averaged. Typical PE curves at different photon energies are shown in figure 3 for the O1s peaks. The shapes of the fit curves are based on measured high-resolution PE peak profiles as described above. Note that both oxygen species show a double peak structure in the PE data with a giant satellite peak representing a poorly screened photoemission final state [4]. Only for the carboxylic oxygen peak (O2) the split of the giant satellite and the main peak is large enough to be resolved. For the anhydride peak (O1) the split as well as the intensity ratio of giant satellite and main peak are smaller, and hence only an asymmetric peak shape can be seen in figure 3. Off-Bragg the intensity ratio of the carboxylic (O2) and the anhydride oxygen (O1) is $2:1$, corresponding to the number of atoms in the molecule (figure 3(a)). Upon scanning through the Bragg condition the ratio changes. Figure 4 displays the NIXSW scans in which each data point stems from the quantitative evaluation of the peak areas of spectra like those shown in figures 2 and 3 taken at the respective photon energies. The NIXSW curves of figure 4 were then analysed by fitting equation (1) to the absorption profiles as described above. The derived geometric parameters (coherent position and coherent fraction) are listed in table 2, and are summarized by a schematic model illustrating the adsorption geometry in figure 5. For comparison, the distances found by Hauschild et al [6] for PTCDA/Ag(111) are also given in this figure. The results of all individual scans are presented in an Argand diagram in figure 6. Note that we used the non-dipolar parameters listed in table 1. The $Q$-value for C1s was taken from literature [17], that one for O1s was determined by an iterative method of comparing the O1s- and the OKLL-based XSW result (see subsection 4.2). The values for $\Delta$ were calculated using the code DLPHASE [22].

The naphthalene core of the molecule is located at a distance of 2.997(16) Å to the silver surface. The core level shift analysis for the two different oxygen species in the molecule shows that the anhydride oxygen (O1) atoms, which occupy the bridge positions, lies only very little above this height, while the carboxylic oxygen (O2) is located 0.25(3) Å closer to the substrate. Hence, the carboxylic oxygen (O2) atoms at the corners of the molecule are significantly bent downwards, the anhydride oxygen (O1) located in the bridge position, however, still lies in the molecular plane or is slightly displaced upwards. Moreover, the position of the anhydride oxygen (O1) is better defined than that of the carboxylic oxygen (O2) since its coherent fraction is significantly higher, even higher than that of the carbon atoms (see discussion below).
**Figure 4.** XSW absorption profiles of the relaxed monolayer of NTCDA/Ag(111) of all atomic species. The reflectivity curve of the Ag(111) Bragg reflection is also shown.

**Table 2.** Values for the coherent position and coherent fraction obtained from PE-based absorption profiles for the relaxed monolayer structure of NTCDA/Ag(111) using the (111)-Bragg reflection. The columns labelled $(O1s)_{\text{carb}}$, $(O1s)_{\text{anh}}$ and $(O1s)_{\text{av}}$ contain the result from the non-dipolar effects with the correction factors shown in table 1. The $Q$ (and $a$) value for $O1s$/O-KLL were obtained by the iterative procedure described in subsection 4.2. The given errors represent the statistical distribution of the evaluated peak areas.

| $C1s$ | $(O1s)_{\text{carb}}$ | $(O1s)_{\text{anh}}$ | $(O1s)_{\text{av}} = O$-KLL$_{\text{corr}}$ |
|-------|----------------|----------------|--------------------------------|
| $D_H^\text{H}$ (Å) | 2.997(16) | 2.747(25) | 3.004(15) | 2.872(14) |
| $F_H$ | 0.579(24) | 0.373(24) | 0.84(3) | 0.480(18) |

With 0.25(3) Å, the displacement from the molecular plane is even a bit larger than was found for PTCDA/Ag(111) (0.18(3) Å, see Hauschild et al [6]). It can also be assumed that the naphthalene core is slightly bent and thus the anhydride carbon atoms are also displaced downwards. This is supported by the relatively small coherent fraction found for $C1s$ (0.579(24)), in particular when this value is compared with the coherent fraction of the anhydride oxygen.
Figure 5. Schematic structural model for the relaxed monolayer of NTCDA/Ag(111). The deviation of the carboxylic (O2) and anhydride (O1) oxygen from the molecular plane is exaggerated. The numbers represent the height of the corresponding atomic species above the uppermost atomic Ag plane in Å. For comparison, the distances for PTCDA/Ag(111) [6] are also given.

Figure 6. Argand diagram of the XSW-results of the individual scans for the relaxed monolayer of NTCDA using the Ag(111) Bragg reflection. Symbols indicate the tie points of vectors, the length and the phase (the angle with respect to the real axis) of which correspond to the coherent fraction and the coherent position (an adsorbate distance of $d_H$ corresponds to a phase of $2\pi$, or $P^H = 1$), respectively. Black and green markers correspond to two independent preparations, the results of both which were averaged for the data analysis. (0.84(3)). This is in agreement with a recent investigation using LEED-IV which resulted in a significant bending of the naphthalene core of the molecule in both molecular principal axis [11]. Furthermore, vibrational modes of the naphthalene skeleton might contribute to the small coherent fraction of the carbon and the carboxylic oxygen atoms (O2). It should be mentioned that new density functional theory (DFT) calculations for PTCDA/Ag(111) also show a bending of the perylene core [6] which corresponds to the naphthalene core in our case. If such a displacement of the anhydride carbon atoms from the molecular plane takes place, the anhydride oxygen (O1) atoms can easily be located above the anhydride carbon atoms and hence a geometry similar to that one proposed in [6] for PTCDA/Ag(111) is likely. In any case, the displacement of the anhydride oxygen is much smaller than that for the carboxylic oxygen (O2). This finding appears to be plausible from the molecular geometry: The anhydride oxygen (O1) is part of a carbon ring
and bound to two carbon-neighbours. It is therefore stiffly integrated in the molecular geometry in contrast to the carboxylic oxygen (O2). The lower coherent fraction of the carboxylic oxygen (O2) at the corners of the molecule indicates a stronger thermal motion of this atom with respect to the anhydride oxygen (O1).

While the distortion of the NTCDA molecule upon adsorption on Ag(111) is quite similar to that found for PTCDA, the absolute height of the molecules above the silver surface is significantly larger (~0.14 Å, see figure 5 and table 2). This is an indication for a somewhat weaker bonding of the NTCDA molecule to the substrate compared to the case of PTCDA/Ag(111). Nevertheless, the height of both molecules still indicates a relatively strong substrate bonding which can only be described as chemisorption. It is significantly stronger than one would expect for a pure van der Waals interaction. The sum of the van der Waals radii for Ag–C and Ag–O are between 3.2 and 3.5 Å [25], i.e., at least ~0.4 Å larger than the values found here for the height of the carbon and oxygen atoms. Recent DFT calculations on NTCDA/Ag(110) [26] also show a bending of the carboxylic oxygen (O2) towards the surface by 0.25–0.30 Å, but the overall distance of the naphthalene core from the uppermost silver layer is found as 2.62 Å, which is much smaller than our value showing that the DFT calculations are not yet accurate enough. However, as already mentioned by the authors of [6], the height difference of the atoms of the molecule should be more accurate.

Our results are in good agreement with high resolution photoemission experiments performed by Schöll et al [4]. From the intensity differences in the satellite structures of the C1s and O1s XPS peaks they derived a significant electronic charge exchange between the Ag surface and the adsorbed molecule for both PTCDA and NTCDA on Ag(111). However, in the case of PTCDA the charge exchange was larger than for NTCDA/Ag(111). These results confirm that both molecules are chemisorbed on Ag(111), PTCDA more strongly than NTCDA.

Finally, we like to mention that the values for the coherent positions found in this study are slightly smaller than those in our earlier experiments [3, 27], see table 3. In order to exclude the influence of different values for the multipole correction parameters, we compare only the uncorrected geometric parameters. The differences in the distances (~0.04 Å) are significantly larger than the error bars obtained in the present study from a statistical error analysis. The deviation must hence be of systematic nature, but systematic errors are not easy to quantify. Possible sources of errors are the influence of different Ag crystals, slightly different coverages caused by different annealing temperatures during preparation, possibly also different temperatures during the measurements, and a moving x-ray beam on the sample. In the experiment reported here, we successfully tried to exclude systematic errors as far as possible. This is confirmed by the results from two independent preparations, which resulted in very small statistical error bars as given in table 2. We hence believe that the present data are more reliable than the previous ones.

4.2. Results based on the O-KLL Auger yield

As mentioned in the introduction the Auger yield is often used as an alternative detection channel. However, in our case the distance evaluated by the O-KLL absorption profiles is 0.33 Å smaller than that obtained from the O1s signal (see table 3). This is due to Auger electrons which are induced from secondary electrons emerging the bulk. As described in subsection 2.2 the electron induced portion of the measured Auger yield can be corrected using equation (3). The left side of equation (3) contains the measured geometric parameters $H_m = 0.540$ and $D_m = 2.542$ Å.
Table 3. Comparison of the results obtained in this study with our previous results (Stanzel et al [3]). The values are neither corrected for non-dipolar effects (O1s, C1s: \(Q = 0, \Delta = 0\)) nor for secondary electron induced Auger (O-KLL: \(a = 0\)) in order to avoid differences caused by different correction parameters.

| Species | \(D^H(\text{Å})\) from Stanzel et al | \(F^H\) | \(D^H(\text{Å})\) from our results | \(F^H\) |
|---------|---------------------------------|--------|---------------------------------|--------|
| O1s     | 3.01(2)                         | 1.05(16)| 2.972(4)                        | 0.896(19) |
| C1s     | 3.07(2)                         | 1.12(12)| 3.035(8)                        | 1.038(29) |
| O-KLL   | 2.60(3)                         | 0.46(4) | 2.542(11)                        | 0.540(11) |

(see table 3) from the O-KLL Auger measurement. The second term on the right side (bulk-like parameters) is also known \((D^H_{\text{bulk}} = 0 \text{ Å}, F^H_{\text{bulk}} = 0.92)\); the bulk coherent fraction was obtained by averaging the fit results of the total yield which exhibits the highest bulk sensitivity. Hence, in equation (3) there are still three unknown parameters, the electron-induced portion \(a\), and the geometric parameters based on the photon-induced Auger yield \((F^H_{\gamma}, D^H_{\gamma})\).

In principle, one can consider different constraints, in order to solve this equation. For example, one could use the coherent position obtained from the O1s XSW measurement for fixing the coherent position \(D^H_{\gamma}\) for the photon-induced Auger processes. However, this input value depends on the choice of the asymmetry parameter \(Q\) and hence is not unambiguous. Similar problems also occur for other similar constraints which could be used for solving equation (3).

Since it is not \textit{a priori} obvious which constraint to take, the iterative method described in the following appears to be better suited because it is not based on the assumption of any of the results (PE or Auger) being favourable. Note that it represents a general key for analysing PE- and Auger-based XSW data and correct them for non-dipolar and secondary electron induced effects. It does not depend on any preliminary knowledge on \(Q\) or \(a\).

As a first step, we use a value for \(Q\) from the literature for the correction of multipole effects and correct the electron-induced effects (parameter \(a\)) using the first constraint mentioned above: \(D^H_{\gamma} \equiv D^H(O1s)_{av}\). Any other start value for \(Q\) could be used as well. Then the most noticeable difference between the PE and Auger results is the coherent fraction. Since this can be influenced by a wrong asymmetry parameter \(Q\) for the multipole correction, it can be improved by modifying this parameter. However, changing \(Q\) also alters the coherent position slightly, and hence the constraint \(D^H_{\gamma} \equiv D^H(O1s)_{av}\) cannot be maintained. Then, in an iterative procedure, the modified \(Q\) and \(a\) (and therefore \(F^H_{\gamma}\) and \(D^H_{\gamma}\)) are stepwise improved, until the modified O-KLL Auger and O1s PE parameters (i.e. the arrows in the Argand diagram) are equal. The parameters obtained by such a procedure are (see table 2) an electron induced portion of \(a = 46.2\%\) and an asymmetry parameter of \(Q = 0.27\). Note that the electron induced portion in the Auger yield obtained by this procedure is close to 50%. This value agrees very well with the one we obtained earlier by an estimate of the number of secondary electrons emerging from the bulk (for details see [3, 27]). Furthermore one also obtains the geometric parameters for the averaged O1s signal which we already discussed in subsection 4.1 \((D^H = 2.872 \text{ Å}, F^H = 0.480\), see table 2).
In the present case, a similar analysis for C1s was not done, since it was not possible to sufficiently separate the C-KLL Auger yield from the Ag Auger peaks occurring in the same kinetic energy range.

5. Summary

In summary, we present precise measurements of the bonding distances of various atomic species of NTCDA in the relaxed monolayer structure on Ag(111). In the case of oxygen, the positions of the two different species could be separated because of the core level shifts of their PE signals. One species, the anhydride oxygen (O1), is located at about the same height as the carbon atoms, the other (carboxylic oxygen, O2) is located 0.25(3) Å below. The average position of the carbon atoms in the naphthalene core of the molecule is 2.997(16) Å above the uppermost silver plane. These numbers reveal a significant down-bending of the terminal carboxylic oxygen (O2) atoms. The NTCDA molecule is less strongly bound than PTCDA on Ag(111) [6] as indicated by the slightly larger vertical distances (see figure 5) which is in agreement with previous experimental findings (electronic structure [4] and desorption temperature). Moreover, the vertical distortion of the molecule, i.e., the height differences between the atoms in the molecule, is slightly smaller. All values agree reasonably well with those obtained for NTCDA/Ag(111) [3, 27].

Moreover, we investigated proper methods for correcting PE- and Auger-based XSW data for non-dipolar and electron-induced effects, respectively. We suggest an approach to obtain the electron-induced portion $a$ of the Auger yield and the non-dipolar correction parameter $Q$ by achieving full agreement between the results of both detection channels in an iterative procedure. The result for $a$ and $Q$, as well as the geometric parameters (coherent fraction and position) obtained by this procedure, agree well with the results of a conventional analysis of the PE XSW data which use calculated or experimentally derived values for $Q$. In agreement with our earlier investigation [3, 27] an electron-induced portion of the O-KLL Auger yield in the range of 50% was obtained. Our results indicate that the available multipole correction parameters are relatively precise and that very precise and reliable geometric parameters can be obtained, if a careful analysis of the XSW data is performed, in particular, when multipole contributions to the PE yield are taken into account.

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