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Bonding and orientation of 1,4-benzenedimethanethiol on Au(111) prepared from solution and from gas phase

L Pasquali^{1,5}, F Terzi², C Zanardi², R Seeber², G Paolicelli³, N Mahne⁴
and S Nannarone^{1,4}

¹ Dipartimento di Ingegneria dei Materiali e dell'Ambiente e CNISM, Università di Modena e Reggio Emilia, Via Vignolese 905, 41100 Modena, Italy

² Dipartimento di Chimica, Università di Modena e Reggio Emilia, Via Campi 183, 41100 Modena, Italy

³ INFN-CNR S3 National Research Centre on NanoStructures and BioSystems at Surfaces, Via Campi 213/a, 41100 Modena, Italy

⁴ Laboratorio Nazionale TASC, INFN-CNR, ss 14, km 163.5 in Area Science Park, 34012 Trieste, Italy

E-mail: pasquali@unimore.it

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Abstract

The orientation and bonding of 1,4-benzenedimethanethiol molecules on Au(111) is studied by means of x-ray and ultraviolet (UV) photoemission, x-ray absorption and metastable deexcitation spectroscopy. The organic films are prepared both from solution and by exposing the clean substrate to the vapours of the substance in an evacuated environment. This leads to two different growth modes: when self-assembled monolayers (SAMs) are prepared from solution, the molecules tend to form a bilayer film with the molecules standing upright and with the molecular axis forming an angle of about 30° with respect to the substrate normal; when growth is carried out from the gas phase, the molecules tend to assume at the earliest stages of exposure a flat-lying configuration, with both sulfur end-groups bonding to Au; at increasing exposure the surface coverage presents a saturation and the chemisorbed molecules tend to assume an upright arrangement.

1. Introduction

Organic layers chemisorbed on metal surfaces are interesting systems thanks to their possible applications in optoelectronics, sensors, catalysis and biomimetic devices [1–5]. Among the large number of studied systems, the use of molecules with one or more –SH groups (especially alkanethiols and alkanedithiols) emerged as a promising route for stable grafting

⁵ Author to whom any correspondence should be addressed.

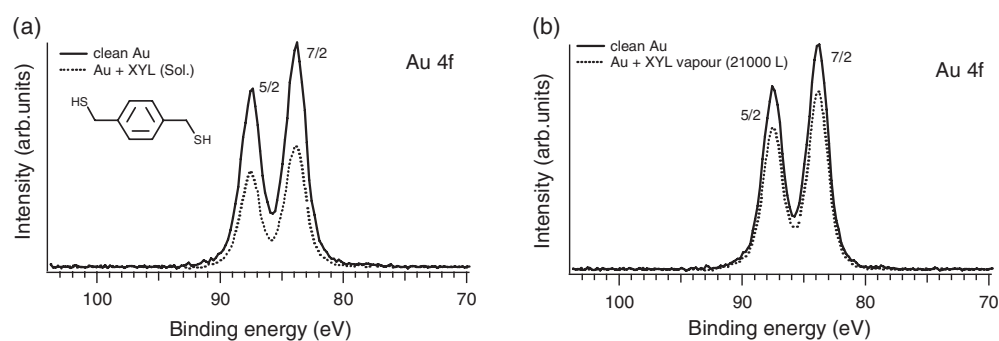


Figure 1. (a) Au 4f core levels of the clean substrate (solid line) and their attenuation (dotted line) after an SAM of XYL molecules is deposited from solution. (b) Same as panel (a) except that the molecules are deposited from the gas phase. Spectra are presented after removal of the Mg K α satellite contribution and background subtraction (Shirley type).

of electroactive and non-electroactive species, such as proteins, enzymes, nanoparticles and clusters, on the surface of noble metals. In this context, dithiol molecules containing aromatic rings appear to be particularly appropriate [6, 7]. Under suitable conditions, the molecules bond to the surface with one –SH group. The second –SH group is left dangling at the surface of the organic film. Moreover, the resulting thin films possess a higher conductivity and thermal stability than alkanethiol films.

In the present work we studied the bonding properties and orientation of 1,4-benzenedimethanethiol (here indicated as XYL; the structure is shown in the inset of figure 1) self-assembled monolayers (SAMs) on Au(111). Films were prepared both in solution, by immersion in ethanol, and by exposing the clean Au surface to the vapours of the substance. This study was stimulated by the fact that, in spite of the well recognized utility of this type of system as an anchoring tool to noble metal surfaces, only few indications, sometimes partly contradictory, have been given so far regarding the exact nature of SAMs prepared with XYL molecules [8–12]. In many cases (see for example [13]) the structure of the SAM is simply hypothesized (mostly supposing the molecules taking an upright configuration) on the basis of a comparison with similar systems. On the other hand, it has been shown that a given thiol molecule can assume different orientations on different metal surfaces (see for example thiophenol on Au or on Ag surfaces [14]), and multilayers can even form [8].

In this work, data originating from x-ray/UV photoemission (XPS/UPS), near edge x-ray absorption fine structure (NEXAFS) and metastable deexcitation spectroscopy (MDS) are combined to derive information on the *effective* thickness of the XYL films, on the chemical bonding in between the molecules and with the substrate, on the orientation of the molecules and on the surface electronic states of the system. In particular, the comparison between UPS and MDS permits us to derive unique information on the active sites (chemical groups) that the molecules expose at the film/ambient interface and that determine the system functionality.

2. Experimental details

To investigate the properties of the XYL films prepared in solution we used commercial Au(111) oriented in plane polycrystalline films (200 nm thick) grown on a flat glass support coated by a 2 nm thick Cr buffer layer (Arrandee). The substrates were treated by butane–propane flame annealing and immersed into a 0.5 mM XYL (Aldrich) solution. We used different solvents, namely methanol, ethanol and n-hexane, for 24 h dipping time. Here only the

results obtained on the film prepared in ethanol are shown, the others giving rise to comparable molecular configurations [15]. The vessels used for film preparation were protected from exposure to light and stored at room temperature. The resulting XYL films were rinsed in ethanol immediately after removal from the solution and quickly inserted into the ultra-high-vacuum (UHV) chamber for analysis.

To study the properties of the XYL layer grown from the gas phase a Au(111) single crystal was used. Before exposure, the surface was cleaned by subsequent cycles of sputtering (Ar^+ ions at 500 eV) and annealing (at 400 °C), resulting in sharp low-energy electron diffraction patterns and in the absence of contaminants as evidenced by photoemission and from MDS analysis. A few grams of XYL were inserted into a vacuum-sealed glass tube connected to the UHV chamber through a leak valve. Several freeze–pump–thaw cycles were applied before exposure of the clean Au surface to the XYL vapours. In addition, the walls of the small vacuum chamber used for exposure were preliminarily saturated with the organic molecules. The glass tube containing the XYL molecules was kept at a constant temperature of 46 °C during exposure.

Photoemission experiments were performed in UHV at a base pressure of 10^{-10} mbar using a conventional Mg $K\alpha$ source (for XPS) and a windowless differentially pumped UV lamp (vacuum generators) operating with He I photons (for UPS). He^* metastable atoms (excited in the triplet state—excitation energy 19.8 eV) were generated in a discharge-type supersonic source, delivering a flux of 10^{11} metastables s^{-1} on the sample surface. Details of the metastable atom source are given elsewhere [16].

Electron distribution curves were measured with a double-pass cylindrical mirror analyser (CMA, PHI 15-255G) operating at constant pass energy. XPS spectra were taken with an overall resolution of 1.5 eV. UPS and MDS spectra were taken with a resolution of 0.1 eV. The axis of the CMA was set to 15° from the sample normal. All spectra are here reported in binding energy, referenced to the Fermi level (E_F) position.

NEXAFS experiments were carried out at the BEAR beamline [17] of the ELETTRA synchrotron radiation laboratory in Trieste, Italy. NEXAFS was measured at the C K-edge on the XYL samples prepared in solution with linearly polarized photons in p-light scattering conditions (electric field of the incoming wave with a component normal to the surface; degree of linear polarization $P = |E^{\parallel}|^2 / (|E^{\parallel}|^2 + |E^{\perp}|^2) = 0.94$), at different incident angles from normal to grazing incidence. X-ray absorption data were taken by acquiring the drain current from the sample (total yield mode). In order to take into account the incident flux decay and the beam fluctuation and to correct for its dependence on wavelength (source plus optics transmission), the absorption spectra were first normalized to the current drained by a W mesh and also normalized to a reference absorption spectrum taken under the same experimental conditions and energy range on a carbon-free Au(111) surface. All measurements were performed at room temperature.

3. Results and discussion

3.1. SAM prepared from solution

Core-level photoemission is known to be a powerful technique both to investigate the chemical properties of surfaces and interfaces and to derive information on the composition and thickness of ultra-thin films. In the present case, the attenuation of the Au 4f levels of the substrate was used to quantitatively evaluate the thickness of the organic layer. Figure 1(a) shows the typical attenuation of the Au 4f states that is encountered when XYL films are prepared in ethanol solution (dipping time 24 h).

From the attenuation of the Au 4f_{7/2} signal, the *effective* thickness of the organic film can be obtained according to the relation

$$d \approx \lambda \cos(\theta) \ln(I_{\text{Au}_0}/I_{\text{Au}_d}) \quad (1)$$

where I_{Au_0} and I_{Au_d} are the intensities of the Au 4f_{7/2} photoelectrons of the clean surface and after deposition of a homogeneous film of *effective* thickness d , λ is the attenuation length of the photoelectrons within this layer and θ is the average take-off angle of the photoelectrons. For λ we used a value of 34 ± 1 Å, as estimated by Laibinis *et al* [18] for organic thin films on noble metal surfaces at the appropriate photoelectron kinetic energy. We measured different sample replicas and we obtained an average *effective* thickness of 14.6 ± 2.2 Å, which is in good agreement with independent measurements obtained with high-resolution XPS using synchrotron radiation on XYL films prepared in different polar and non-polar solvents [15]. Assuming a molecular length of about 8.3 Å [11, 12, 19–21], this finding suggests that the organic film is sizeably thicker than a single layer of XYL molecules, even under the hypothesis that the molecules adopt an upright orientation, with one sulfur bonding to the surface and the other pointing upwards.

To get information on the bonding properties of the molecules on Au, we measured the S 2p core levels. They are reported in figure 2(a). The peak maximum is positioned at 163.3 eV. The spectrum has been fitted with two Voigt doublets accounting for spin orbit split 2p_{3/2} and 2p_{1/2} levels, separated by 1.2 eV and with a branching ratio of 1/2. The Gaussian width broadening for each doublet is 1.5 eV, which accounts for the experimental resolution and excitation line width. The low binding energy doublet (2p_{3/2} peak centred at 161.9 eV) can be assigned to thiolate-type sulfurs involved in bonding with the Au substrate. The high binding energy doublet (2p_{3/2} peak centred at 163.2 eV) can be related either to unbound thiol sulfur atoms or to disulfide moieties (R–S–S–R), which can be formed from the bonding between two XYL molecules through the sulfur terminals [12].

These results are in agreement with higher-resolution measurements obtained using synchrotron radiation and reported elsewhere [15].

Showing both thiolate and unbound components, the S 2p results are compatible with a film of XYL molecules which tend to be oriented perpendicular to the surface plane. To obtain more quantitative information on the average tilt angle of the molecules, NEXAFS experiments were carried out. NEXAFS is a very powerful tool, since it provides direct information on order and orientation of molecules on metal surfaces [22, 23].

This is because the absorption cross section can be thought to be proportional to the scalar product $\vec{m} \cdot \vec{E}$, where \vec{m} describes the molecular dipole associated with a specific optical transition and \vec{E} the electric field vector of the incident photon. Spectra were recorded at different incidence angles and they were normalized in order that they coincided for photon energies far below and far above the edge region. This is equivalent to normalizing the signal to the number of sampled C atoms.

In figure 3(a), the spectrum taken at normal incidence (\vec{E} vector parallel to the surface plane) is reported. Multiple structures can be recognized that are associated to different electronic transitions from the C 1s core level to the empty molecular orbitals. A tentative assignment of the various structures has been given on the basis of the comparison with similar molecules chemisorbed on metal surfaces [14, 23]; in particular, the first feature is associated to a C=C/ π^* resonance, mainly associated to the benzene ring, the second to a C–S/ σ^* resonance, the third to C=C/ π^* and C–H/ π^* transitions, the fourth and fifth to C–C/ σ^* and C=C/ σ^* resonances. More precisely, contributions to the last two features mainly originate from the σ_1^* and σ_2^* resonances typical of the benzene ring [24].

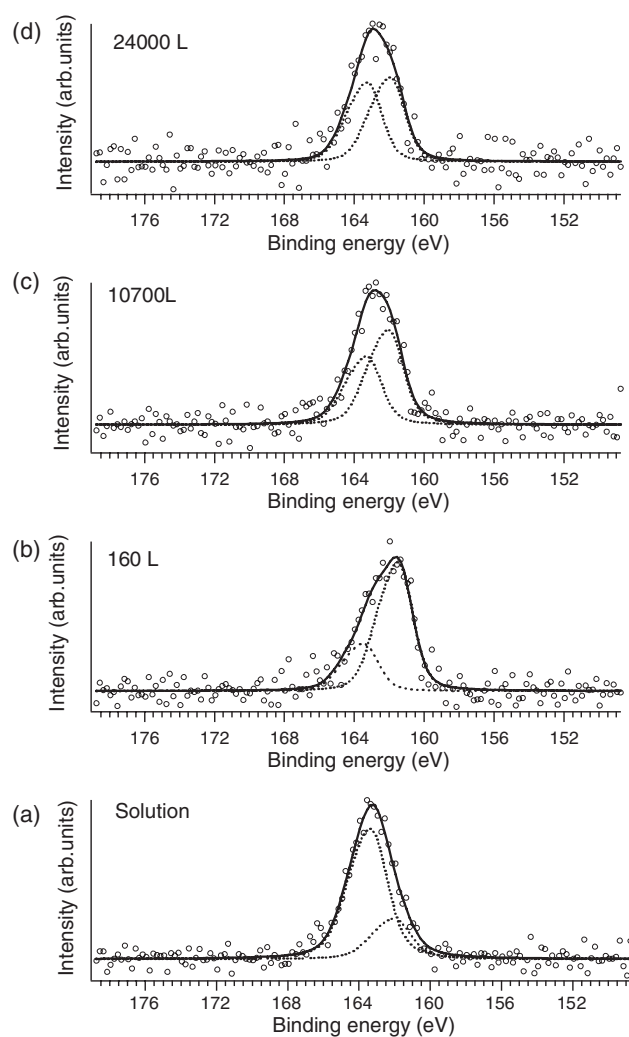


Figure 2. (a) S 2p levels measured on the XYL sample prepared in solution of ethanol. (b)–(d) S 2p spectra taken on the XYL sample prepared from the gas phase at increasing exposure (expressed in L). Experimental points (open dots) are fitted with two Voigt doublets (small dotted lines). Spectra are presented after removal of the Mg K α satellite contribution and background subtraction (Shirley type).

In figure 3(a), the experimental curve has been decomposed into individual Gaussian peaks and Gaussian-broadened step functions [22] through a best-fitting procedure. Symmetric Gaussian peaks were used for the first three transitions, while asymmetric Gaussian peaks were used for the last two transitions. In addition to the peak-shaped components, two step functions were required to properly fit the spectrum. The first step falls at a position corresponding to the π^* resonance and of the Fermi energy, as evaluated from the XPS position of the C 1s level (at 284.4 eV). The presence of this step (labelled St1 in figure 3(a)) is to be related to some interaction between the metal and the molecular π^* states, leading to electron excitation into the empty metal states right above the Fermi level of the substrate. A similar step feature has been observed, for example, for benzenethiol chemisorption on Mo(110) [23]. In that case, the

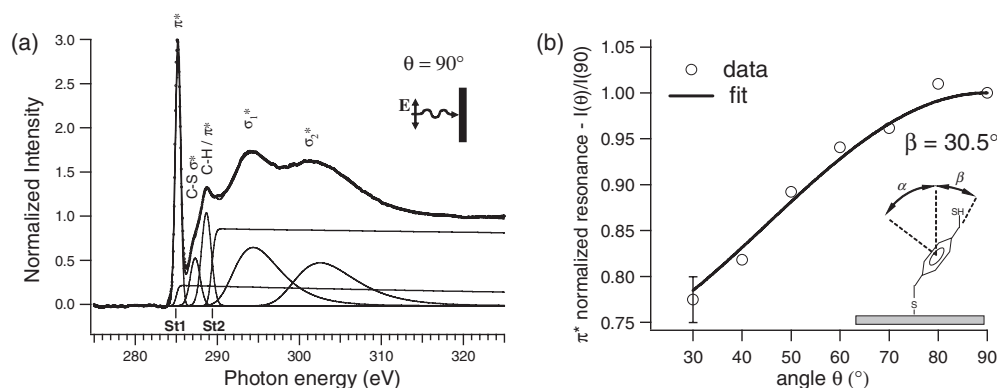


Figure 3. (a) NEXAFS spectrum taken at normal incidence (the experimental geometry is shown in the inset). (b) Angular dependence of the intensity of the π^* resonance; the different angles mentioned in the text and the molecular orientation are also shown.

St1 step was more intense than in the present case, in consistency with a stronger interaction of the benzenethiol π^* state with the metal bands. The reason for the reduced interaction between the XYL π^* state and the metal bands is related to the presence of the methylene groups between the benzene ring and the $-\text{SH}$ terminals. The second step (St2) is located at about 4.5 eV above the St1 step, corresponding to the photoelectric threshold of the system as measured from the cut-off position of the secondary electrons in valence band photoemission spectra. This second type of step is related to the excitation of the C 1s electrons into the continuum of empty states above the vacuum level. These transitions correspond to excited electrons in the molecule that present no or negligible superposition with the metallic bands. The presence of this step is consistent with the size of the molecule, its average orientation with respect to the surface plane (see below) and with the fact that more than one layer is present at the surface.

Among the different transitions, the first π^* resonance exhibits the strongest dependence on the angular orientation of the electric field: it is very prominent at normal incidence and is depressed at grazing incidence. This effect can be used to determine quantitatively the average orientation of the molecules in the film.

The ratio between the π^* intensity measured at different grazing incident angles and the intensity corresponding to normal incidence ($\theta = 90^\circ$) has been plotted in figure 3(b). To obtain the average tilt angles of the XYL molecules, the experimental data were fitted to the following relation [23]:

$$\frac{I_{\pi^*}(\theta)}{I_{\pi^*}(90^\circ)} = \frac{P \frac{1}{3} [1 + \frac{1}{2} (3 \cos^2 \theta - 1) (3 \cos^2 \alpha - 1)] + (1 - P) \frac{1}{2} \sin^2 \alpha}{P \frac{1}{3} [1 + \frac{1}{2} (3 \cos^2(90^\circ) - 1) (3 \cos^2 \alpha - 1)] + (1 - P) \frac{1}{2} \sin^2 \alpha} \quad (2)$$

which is valid for substrates with threefold or higher symmetry, θ being the grazing incidence angle of the radiation and α (the only fitting parameter) the orientation of the π^* orbital (normal to the aromatic ring) with respect to the surface normal; P is the degree of linear polarization: in the present case $P = 0.94$.

The best-fit result indicates an average angle α of 59.5° , corresponding to a tilt angle of the molecular axis $\beta = (90^\circ - \alpha)$ of 30.5° (inset of figure 3(b)).

The molecular tilt angle, together with the *effective* thickness values obtained by XPS, permits us to express the *effective* thickness of the XYL film in terms of number of molecular layers: assuming a molecular length of 8.3 Å, we obtain that the film is composed of about 2 layers.

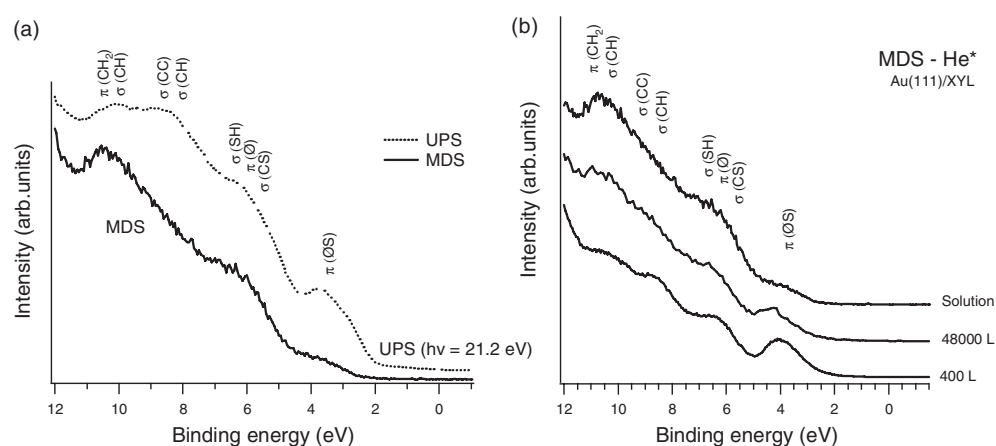


Figure 4. (a) Comparison between valence band photoemission and MDS spectra taken on the YXL film prepared in solution; different orbital contributions have been indicated. (b) MDS spectra taken on the YXL samples obtained from the gas phase at low (400 L) and saturation (48 000 L) coverage; the spectra are compared with the one taken on the film prepared in solution.

Additional information on the organic film properties were obtained by investigating the valence band. In figure 4(a), the (angle-integrated) UPS and MDS spectra of the YXL surface are compared. MDS in particular is extremely sensitive to the outermost contributions of the surface density of states [25]. This is due to the fact that the noble gas metastable atoms impinging at the surface principally interact with the molecular orbitals which protrude more into the vacuum region. As a result, the generated electron distribution curves, which similarly to UPS give a picture of the surface *effective* density of states, present enhanced contributions corresponding to these orbitals. On the contrary, electronic orbitals which are mainly oriented inwards with respect to the surface show poor overlap with the metastable atom wavefunctions and give minor contributions to the spectra.

Different features can be recognized in both UPS and MDS spectra which can be associated to different valence molecular orbitals. These have been labelled in figure 4 on the basis of the comparison with theoretical predictions and related systems [26–30].

In particular, the first broad feature at low binding energy, between 2 and 4 eV, can be associated both to π -type contributions mainly localized on the benzene ring and to π -type states due to the molecular sulfur terminals; σ states related to the unbound –SH groups as well as π states from the benzene ring are responsible for the pronounced shoulder centred at about 6 eV; the feature between 8 and 9 eV can be associated to σ -type states related to the benzene ring (C–C and C–H bonding), while π -type orbitals mainly localized on the methylene groups are expected to contribute to the last feature at about 10 eV. The negligible contribution in the MDS spectrum of figure 4(a) from σ (C–C) states of the benzene ring is consistent with their negligible interaction with the metastable atom, since the corresponding orbitals are mainly distributed along the ring skeleton and are shielded by other molecular orbitals. The fact that π -type structures related to the benzene ring are severely damped in MDS and that the most pronounced feature at about 10 eV can be associated to the interaction of the metastable with the methylene units strongly supports the idea that the molecules at the outermost surface assume an upright configuration, with the metastable He atoms mainly interacting with the molecular head-groups. On the other hand, the weak contribution from benzene ring related states is perfectly compatible with the 30° tilt angle of the molecules with respect to the vertical direction, which causes a partial exposure of the aromatic ring orbitals to the metastable beam.

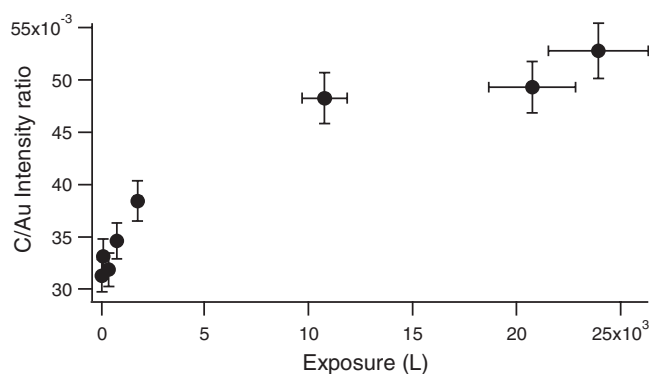


Figure 5. Ratio between C 1s and Au 4f XPS intensities measured as a function of XYL exposure.

3.2. SAM prepared from the gas phase

When XYL chemisorption is carried out from the gas phase, exposing the clean Au to the XYL vapours, a significantly different growth mode occurs. In figure 5 we report the C/Au intensity ratio measured from XPS as a function of exposure.

A saturation of the C/Au ratio is obtained above about 15 000 L. The high exposure values required to achieve saturation are consistent with results obtained on related systems, like benzyl mercaptan [31]. Interestingly, even at saturation coverage the overall amount of organic material at the surface is much less with respect to the case of the film prepared in solution. In figure 1(b) we report the attenuation of the Au 4f levels corresponding to the saturation regime. By comparison with figure 1(a), it can be clearly observed that the film prepared from the gas phase presents a strongly reduced *effective* thickness with respect to the film obtained in solution. Applying the same method presented in section 3.1, we estimate an *effective* thickness value of about 6 Å.

In figures 2(b)–(d) the behaviour of the S 2p levels is reported at various stages of exposure. At low exposure (figure 2(b)) the centroid of the core-level photoemission peak is displaced towards lower binding energies with respect to the film prepared in solution (figure 2(a)). The decomposition of the peak into Voigt doublets obtained through a best-fit procedure indicates that the thiolate component (at 161.9 eV) is now dominating over the unbound thiol feature (at 163.3 eV). This suggests that in the low exposure regime the majority of the molecules contribute with both sulfur head-groups bonding to the gold substrate. This implies also that the molecular axis now tends to be parallel to the surface plane, in contrast to the film grown in solution. As long as more molecules are chemisorbed onto the surface, the unbound thiol component progressively increases (figures 2(c), (d)), even if the branching ratio between unbound and thiolate features never reaches the value of the film prepared in solution. The increase of the unbound component in the gas phase grown film can be related to the fact that with the decrease of the available chemisorption sites (and with the increase of the molecular density), the XYL molecules reaching the surface tend to bond with only one head-group to the substrate, leaving the other dangling towards the vacuum. This implies a variation of orientation of the molecules, now assuming a configuration more similar to the case of the film prepared in solution.

This picture is further confirmed from the MDS spectra reported in figure 4(b). At low exposure (400 L), the metastable deexcitation spectrum presents intense features at about 4, 6, 8.5, 10 eV binding energy. All the features which can be associated to the π -type orbitals

and σ (C–H) orbitals of the benzene group are now well visible and pronounced. This supports strongly the idea that the molecules assume a flat-lying configuration, with the plane of the benzene ring parallel to the surface and presenting the maximum interaction probability with the metastable beam.

At saturation exposure, the MDS lineshape changes dramatically (figure 4(b)—48 000 L). The features associated to the π and σ orbitals of benzene are severely depressed and the spectrum becomes more similar to the one obtained on the film prepared in solution. This is in agreement with a change in the orientation of the XYL molecules, which now tend to assume an upright configuration.

4. Conclusions

We studied the growth mode of 1,4-benzenedimethanethiol molecules on Au(111) applying a multi-technique experimental approach. The film thickness, chemical bonding to the substrate, molecular orientation and valence band properties were investigated by x-ray photoemission, UV photoemission, metastable atom deexcitation spectroscopy and near-edge x-ray absorption.

We considered films grown both from wet solution and from the gas phase. We concluded that two different growth modes are obtained. When the organic self-assembled layers are prepared from solution, the molecules composing the film tend to assume an upright orientation, with the molecular axis forming an average angle of about 30° with respect to the substrate normal. The *effective* thickness of the SAM corresponds to a double molecular layer. The stationary configuration which we studied is the result of multiple phenomena, possibly implying long-term processes. The fast chemisorption of the molecules on the substrate is followed by a long-term arrangement due to the van der Waals interactions between the molecules and mediated by the solvent. Furthermore, the solvent may allow for redox reactions due to unavoidable traces of oxidants, which can play an important role in the formation of the double-layer structure by promoting the formation of disulfide bridges.

With respect to wet preparation, the growth from the gas phase permits us to follow the chemisorption process with no mediation from other chemical species (i.e. solvent). When the film is prepared by exposing the clean substrate to the molecular vapours, the molecules tend first to bond with both sulfur end-terminals to the substrate, assuming a flat-lying orientation; this means that at low coverage the molecular arrangement is determined only by the interaction between single molecules and the substrate. Increasing the concentration of molecules by increasing the exposure causes the chemisorbed molecules to adopt a more vertical alignment, with only one sulfur contributing to the bonding of the system with the substrate; this means that at higher coverage both the reduced availability of chemisorption sites and the reciprocal interactions between the molecules determine the final structure. This last configuration appears more similar to the case of the film prepared in solution.

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