Adsorption energy and geometry of physisorbed organic molecules on Au(1 1 1) probed by surface-state photoemission

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ABSTRACT

The modification of the Au(1 1 1) Shockley-type surface state by an adsorbed monolayer of large π-conjugated molecules was investigated by high-resolution angle-resolved photoelectron spectroscopy (ARPES). We determined binding energy, band mass, and Rashba-splitting and discuss the results in the context of rare-gas adsorption on noble metals. This comparison allows the determination of the bonding strength of the adsorbates, found to be physisorptive with derived binding energies per molecule of 2.0 eV for perylene-tetracarboxylic-dianhydride (PTCDA) and 1.5 eV for naphtalene-tetracarboxylic-dianhydride (NTCDA). We will also present a superstructure model for the NTCDA/Au(1 1 1) system, deduced from low energy electron diffraction images (LEED) in combination with substrate band-backfolding.

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1. Introduction

The organic molecules 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA) and 1,4,5,8-naphtalene-tetracarboxylic-dianhydride (NTCDA) are widely used as standard systems for investigating molecular adsorption processes on metal surfaces. Especially PTCDA on noble metal (1 1 1) surfaces has become a standard for research on organo-metallic interfaces [1]. Its naphthalene counterpart NTCDA has also been studied intensely on Ag(1 1 1) in its geometric [2,3] and electronic structure [4]. Both molecules feature two identical anhydride end groups on different aromatic core systems, facilitating an elaboration of their respective role in the adsorption process if the molecules are compared directly in experiment. This paper will focus on their monolayer (ML) adsorption on the Au(1 1 1) surface, a substrate featuring sp-derived Shockley and d-derived Tamm surface states at the $\overline{\Gamma}$ and $\overline{M}$-point, respectively. Shockley states (SS) exist due to the broken translational symmetry perpendicular to a crystal surface in gaps of the projected band structure of the bulk material. They are, by nature, confined to the substrate-vacuum (or a substrate-adsorbate) interface, therefore bear the characteristics of a two-dimensional electron gas and can be characterized in terms of binding energy E_B, band mass m^* and Rashba-splitting α_R [5]. Surface states play an important role in chemical reactions and

adsorption processes on metal surfaces [6–9]. Electrons in occupied Shockley states contribute to the Pauli-repulsion of adatoms or molecules [10], while the same repulsion modifies the potential, and therefore the characteristics, of the Shockley state itself [7]. As a conclusion, Shockley-type surface-states are sensitive local probes for adsorption processes. Tamm states differ from Shockley states in so far as they are split from more localized d-like bulk states due to the reduced coordination of the topmost atom layer. While being less affected by physisorbates [11] they are very sensitive to changes in the surface structure of the substrate, for example the Au(1 1 1) $22 \times \sqrt{3}$ reconstruction [12].

In a first step, we will determine the NTCDA/Au(1 1 1) superstructure and growth mode by combining conventional LEED imaging with data obtained from the superstructure-induced backfolding of the Tamm state measured by high-resolution angle-resolved photoemission spectroscopy (ARPES) and recapitulate the already extensively researched PTCDA/Au(1 1 1) interface. In the following part, we will discuss the adsorbate-induced modifications of the Au(1 1 1) Shockley surface state and derive a model which allows a quantitative determination of physisorption energies. For larger molecules, this value is often not readily accessible via experiment, since thermal desorption spectroscopy (TPD) faces serious difficulties trying to quantify their desorption energies. For example, the desorption peaks of different layers or phases can superimpose and strongly bound molecule may disintegrate [13]. The more direct approach described here is not hindered by such restrictions.

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2. Experimental details

The measurements were performed in a UHV setup composed of an organic molecular beam epitaxy (OMBE) chamber for sample preparation and a spectrometer chamber for the ARUPS measurements. Before deposition, the Au(1 1 1) substrate was prepared by repeated cycles of Ar$^+$ sputtering at voltages in the range of 0.5–3 kV and subsequent annealing at approximately 800 K. Details of the process are described elsewhere [14]. The quality of the substrate was checked by X-ray photoelectron spectroscopy (XPS) and low-energy electron diffraction (LEED). Triple–sublimation cleansed PTCDA and NTCDA was evaporated from Knudsen cells at rates of approximately 0.1 ML per minute at room temperature. The deposition rate has been controlled by XPS spectra, using C1s photoemission intensity. However, in the course of the experiments the development of the surface state band dispersion proved to be a reliable and more sensitive probe for coverage determination in the monolayer regime. The ARPES measurements were performed at sample temperatures $T \approx 50$ K with a high-resolution photoelectron analyzer (Scienta R4000) in combination with a monochromatized GAMMADATA VUV lamp for photoexcitation, using He I$_\alpha$ radiation. Energy resolution, consisting of contributions from the finite linewidth of the light source and the analyzer resolution, was approximately 3 meV. The angle resolved mode of the analyzer allows a parallel detection of a range up to ±15° (with a resolution of <0.3°), which covers the whole occupied part of the nearly parabolic dispersion of the Shockley state on Au(1 1 1).

3. Results and discussion

3.1. Geometric structure of 1 ML PTCDA and NTCDA on Au(1 1 1)

For the PTCDA/Au(1 1 1) interface detailed information on the overlayer structure are available [15]. The molecule adsorbs in a flat lying herringbone arrangement with a quasi point-on-line commensurability. Photoemission [16] and STS [17] spectroscopy investigations indicate a rather weak adsorption compared to other metal surfaces as e.g. on Ag(1 1 1) [18].

Data on NTCDA on Au(1 1 1) is scarce, low energy electron microscopy (LEEM) diffraction images and near edge X-ray adsorption fine structure (NEXAFS) spectra of NTCDA multilayers on Au(1 1 1) are available [19], indicating flat-lying adsorption and multiple domains corresponding to the six-fold rotation symmetry of the (1 1 1) substrate surface. The LEED images of NTCDA on Au(1 1 1) differ fundamentally from the 'typical' class of patterns observed for this molecules on noble metal (1 1 1) surfaces [4,15,18–20] regarding the number of diffraction spots and their relative intensities (compare Fig. 1).

This was observed earlier by LEEM [19], but attributed to the local character of the technique. The image was thought to be generated by one single domain. We observe the same diffraction pattern with conventional LEED, ruling out such an effect and rather suggest a commensurate structure in which adsorbate and substrate share a common axis direction (see Fig. 1). This explains the unusual LEED pattern by the coinciding of diffraction spots from different domains.

Although conventional LEED imaging is in general not sufficient to prove strict commensurability, the rigor of our result is validated by ARPES spectra (see Fig. 2). Since the Tamm state (C) located at the Au(1 1 1) $\overline{M}$-point is visible in normal emission for the NTCDA covered surface, backfolding of the $\overline{M}$-point to the $\overline{\Gamma}$-point by the adsorbate surface Brillouin zone must occur. For the given geometries this can only be achieved by a commensurate layer. Note that the observed Tamm state binding energy ($E_B = 1.664$ eV) differs from the value for clean gold ($E_B = 1.635$ eV), but reflects almost
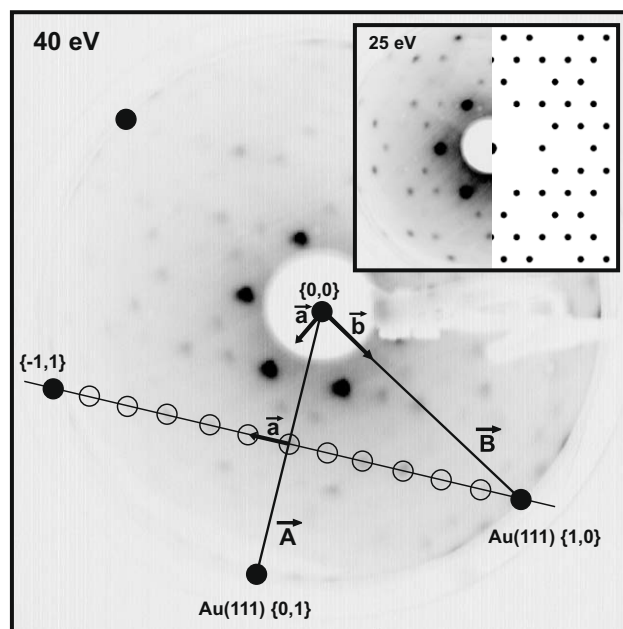

Fig. 1. LEED image ($E_{kin} = 40$ eV) of 1ML NTCDA/Au(1 1 1). The reciprocal lattice vectors for the Au(1 1 1) surface ($\vec{A}, \vec{B}$) and for one of the six rotational domains of the substrate overlayer ($\vec{a}, \vec{b}$) are shown. Note that superstructure and substrate reflexes seem to coincide, i.e. to be commensurate. Inset: LEED image and simulation ($E_{kin} = 25$ eV) featuring systematic absences of diffraction spots. Details are given in the text.

precisely the binding energy and linewidth reported for a Xe covered Au(1 1 1) surface ($E_B = 1.665$ eV) [11]. Additional features in the ARPES spectra are the backfolded sp-bands (B), indicative of a highly ordered overlayer and the Shockley-type surface state (A), which will be discussed later. The existence of the Tamm state beneath the closed monolayer shows that the Au(1 1 1) surface reconstruction is not lifted upon NTCDA adsorption, since no Tamm states exist for the unreconstructed Au(1 1 1) surface [12]. A prevailing reconstruction was found for PTCDA/Au(1 1 1) as well [15].

The described commensurate $\overline{M}$ to $\overline{\Gamma}$ backfolding is dominated by a common $2\sqrt{3} \times 2\sqrt{3}$ 30° reconstruction formed by all possible NTCDA domains as depicted in Fig. 2a. For example, the number of visible sp-bands in normal emission (Fig. 2b) is too small to be caused by the numerous NTCDA-Brillouin zones. More important, photoemission spectra at higher Brillouin zones of the overlayer yield backfolded Shockley surface states only for the $\overline{\Gamma}$-points of this 'sub'-superlattice and not for every $\overline{\Gamma}$-point of the individual NTCDA domains (Fig. 2c).

We can also elaborate on the intermolecular ordering of the adsorbate layer. The inset of Fig. 1 shows an experimental LEED image together with a LEEDPat-simulated diffraction image [21]. The simulation is based on the NTCDA superstructure indicated in Fig. 2, taking into account the six possible rotational domains of the (1 1 1) surface and including the glide-plane extinction-rule for a p2gg space group. The p2gg symmetry is fulfilled by a herringbone-type arrangement of the molecules [20]. As mentioned above, this is also the intermolecular structure of PTCDA/Au(1 1 1), possibly caused by electrostatic forces between the negatively charged anhydride groups and the aromatic core [15]. Since both elements are also present in the NTCDA molecule, the same ordering mechanism seems feasible.

To summarize, we find NTCDA/Au(1 1 1) to grow in a commensurate, uni-axial substrate parallel lattice with two molecules per unit cell arranged in a herringbone structure. The Au(1 1 1)