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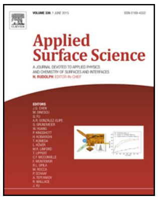

Adsorption analysis of thin films of terephthalic acid on Au and Al studied by MIES, UPS and XPS

Marcel Marschewski[a], Christian Otto[b], Lienhard Wegewitz[c], Oliver Höfft[d], Andreas Schmidt[b,**], Wolfgang Maus-Friedrichs[a,c,*]

[a] Institute of Energy Research and Physical Technology, Clausthal University of Technology, Leibnizstrasse 4, 38678 Clausthal-Zellerfeld, Germany
[b] Institute of Organic Chemistry, Clausthal University of Technology, Leibnizstrasse 6, 38678 Clausthal-Zellerfeld, Germany
[c] Clausthal Centre of Materials Engineering, Clausthal University of Technology, Agricolastrasse 2, 38678 Clausthal-Zellerfeld, Germany
[d] Institute of Electrochemistry, Clausthal University of Technology, Arnold-Sommerfeld-Str. 6, 38678 Clausthal-Zellerfeld, Germany

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ABSTRACT

The adsorption behavior of thin films of terephthalic acid (TPA) evaporated on a gold surface as well as on an aluminum foil was studied. The orientation of the molecules was characterized by metastable induced electron spectroscopy (MIES) and ultraviolet photoelectron spectroscopy (UPS). To make sure that the evaporation of TPA is nondestructive, additional X-ray photoelectron spectroscopy (XPS) was performed. These measurements also exclude any radiation damage.

TPA on the gold surface shows a well-ordered layer growth up to 7.5 nm. Since the MIES spectra show both the acid structure and the phenyl group, a flat-laying orientation is assumed. In contrast, the phenylic carbon structure could not be observed while evaporating TPA on the oxidized aluminum foil. The MIES/UPS spectra only show the COOH group. To exclude a random arrangement of the molecules we also performed low temperature measurements. It can be concluded from these measurements, in addition to the fact that the work function increases during the evaporation, that TPA has a perpendicular arrangement on the aluminum foil.

1. Introduction

Terephthalic acid (1,4-benzenedicarboxylic acid, HOOC—C_6H_4—COOH, TPA, Fig. 1) is a symmetric planar dicarboxylic acid, which is not only known to form strong and directional linear hydrogen bonds due to its self-complementarity [1,2], but also to serve as organic linker in highly organized supramolecular systems [3–6] as well as in metal-organic frameworks (MOFs) [7–9]. The latter are stabilized by bonds between the carboxylate group of terephthalic acid and various metals, which allow the design of three-dimensional porous frameworks [10–14] as well as of two-dimensional structures at surfaces [3,5,15–18]. Both flat-lying and upright-standing adsorption geometries are possible, and these geometries depend on the substitution pattern of the carboxylic acid, its symmetry, temperature, and molecular coverage. It can be concluded from experimental and theoretical studies concerning the adsorption of different carboxylic acids [e.g., HCOOH [19–21], MeCOOH [21], HOOC—COOH [22], 3-thiophene carboxylic acid [23]] including terephthalic acid [4,24–27] onto the Cu(110) surface that for high coverage an upright configuration on the Cu(110) substrate is achieved in which the deprotonated acids adopt a geometry with two equidistant oxygen atoms on the metal surface. On rutile TiO_2(110) terepthalic acid molecules adsorb in a flat-lying geometry until saturation coverage induces an upright orientation [28]. The two-dimensional structures of terephthalic acid on gold [29,30] and silver [31] have also been examined. The additional carboxylic acid group in dicarboxylic acids causes a considerable complication due to competing surface-adsorbate and adsorbate-adsorbate interactions. On the other hand, an upright-standing adsorption of dicarboxylic acids on the surface results in a free carboxylic acid functionality at the vacuum interface, which is ready for chemical interactions such as hydrogen bond formation to other organic complementary substrates. Currently considerable efforts are directed toward the supramolecular engineering via hydrogen bonding at chemically functionalized surfaces and their potential applications for the immobilization

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* Corresponding author at: Institute of Energy Research and Physical Technology, Clausthal University of Technology, Leibnizstrasse 4, 38678 Clausthal-Zellerfeld, Germany.
** Corresponding author.
E-mail addresses: schmidt@ioc.tu-clausthal.de (A. Schmidt), w.maus-friedrichs@pe.tu-clausthal.de (W. Maus-Friedrichs).

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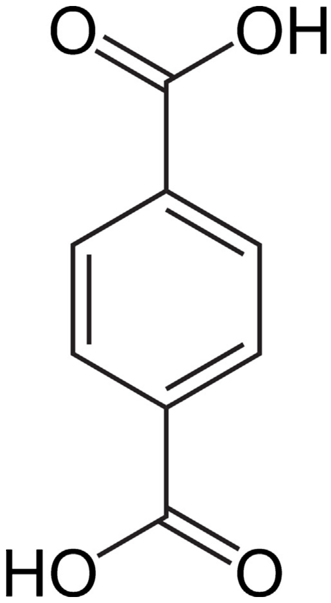

Fig. 1. Chemical structure of the terephthalic acid molecule.

of biomolecules, molecular recognition, biosensors, molecular electronics, and molecule-based magnetic materials [22,24]

In continuation of our interest in metal-substrate interactions for catalysis [32–34] and the construction of metal-organic frameworks [14,35] we report here on the adsorption of terephthalic acid (TPA) on gold and on oxidized aluminum studied with metastable induced electron spectroscopy (MIES), ultraviolet photoelectron spectroscopy (UPS(HeI)) and X-ray photoelectron spectroscopy (XPS). Hereby we use the fact that MIES exhibits an extremely high surface sensitivity for detecting the electronic structure of the outermost molecular orbitals. The method was used in the past, for example, in the investigation of the molecular composition and the orientation of organic films adsorbed on different surfaces [36,37]. For the interaction of metastable atoms with benzene molecules in the gas phase it was already shown that this method is, compared to UPS, very sensitive with respect to π orbitals [38,39]. This is due to the extension of the π orbitals out of the molecular plane [38,39]. With the help of these results the adsorption structure of benzene on Mo(100), MgO(100)/Mo(100) and Ru(100) was determined with MIES [40,41]. For metal surfaces it was shown that there is a phase transition during benzene adsorption. Initially, the benzene molecules are lying parallel to the surface. This is followed by a transition to molecules that adopt an approximately perpendicular orientation to the surface [41]. Furthermore, MIES was used to study the orientation of self-assembled monolayers (SAM) of 2- and 4-chlorobenzylmercaptane on gold [42]. By means of MIES it was concluded that the thiol group of the chlorobenzylmercaptane anchor the SAM to the gold surface, and that the chlorine atom of 4-chlorobenzylmercaptane is oriented away from the surface [42]. In a recent study Yamazaki et al. have investigated the changes of orientation of 1,3,5-benzenetricarboxamide adsorbed on graphite (0001) with MIES [43]. By comparison of the MIES with the UPS results, we found evidence that TPA adsorption on gold results in a flat orientation, whereas a perpendicular adsorption can be observed on the oxidized aluminum surface. As evidenced by XPS, no decomposition takes place during adsorption on both surfaces.

2. Material and methods

2.1. Experimental

An ultrahigh vacuum (UHV) chamber with a base pressure below 5×10^{-10} mbar, described in detail previously [44,45], was used to carry out the measurements. Electron spectroscopy was performed using a hemispheric analyzer operated at a resolution of 250 meV in combination with a cold cathode gas discharge source for the production of metastable He*(^{3}S/^{1}S) (E* = 21.2 eV) as a source for MIES and UPS. The intensity ratio ^{3}S/^{1}S is found to be 7:1 (Stracke [46] et al., 2001). Metastable He* atoms approach the surface with near thermal kinetic energy (≈60 meV) and interact with the outermost electron state predominantly by Auger processes. For the TPA system studied here, the metastable helium atoms interact via the Auger de-excitation (AD) process. In this case an electron from the adsorbed molecule fills the 1s orbital of the impinging He*. Simultaneously, the He 2s electron is emitted carrying the excess energy. The resulting spectra reflect the surface density of states (SDOS) directly. AD-MIES and UPS can be compared and allow a distinction between surface and bulk effects. Thus, metastable induced electron spectroscopy (MIES) is an extremely surface sensitive and nondestructive technique. The accuracy of the MIES and UPS spectra can be given by ± 0.1 eV. A more detailed introduction to MIES and its applications can be found in Morgner [36] (2000) and Harada [37] et al. (1997). A time of flight technique discriminates the spectral contributions from the metastables and the photons. The typical MIES and UPS peak widths from such surfaces are in the range of 1 eV mainly as a result of phonon broadening (Ochs [47] et al., 1996).

All following MIES and UPS spectra are displayed as a function of the electron binding energy with regard to the Fermi level, which is determined by the high energy cut-off obtained on metallic samples in UPS.

In addition to the MIES/UPS source, the apparatus is equipped with a commercial X-ray source (Fisons XR3E2-324). The spectra are recorded by the same hemispheric analyzer operated at a resolution of 1.1 eV and exhibit a full width of half maximum (FWHM) of 1.9 eV for clean graphite. The photons hit the surface under an angle of 80° to the surface normal. Emitted electrons are analyzed under an angle of 10° to the surface normal.

For quantitative XPS analysis the peak fitting module (PFM) of OriginPro 7G was used. PFM uses the Levenberg–Marquardt algorithms for the best possible agreement between the experimental data and the fit. For stoichiometric calculation the photoelectronic cross section as calculated by Scofield [48] and the transmission function of our hemispherical analyzer as well as the inelastic mean free paths from the NIST database [49] were included. The structures were fitted applying Voigt profiles after a Shirley baseline subtraction.

2.2. Sample preparation

All measurements were performed under UHV conditions. Therefore, any contamination of the samples during measuring can be excluded. The Au foil was cleaned under UHV conditions by heating it to 1000 K for 15 min. Subsequently measured XPS spectra reveal that the sample is free of carbon and oxygen containing contaminations.

The Al sample was cleaned at temperatures of 750 K for 15 min. Subsequent XPS measurements showed no contaminations on the surface.

Thin films of terephthalic acid (TPA) (see Fig. 1 for the molecular structure) were produced by thermal evaporation (Kentax 3 cell thermal evaporator) at 400 K. The evaporation rate at the used temperature for TPA is about 0.1 nm per second. The evaporator is directly adapted to a preparation chamber (pressure < 10^{-8} mbar), which is adapted to the main chamber separated by a valve. Accordingly, sample preparation and measurement were performed in situ.