



Characterization of orientational order in π -conjugated molecular thin films by NEXAFS



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ARTICLE INFO

Article history:

Available online 1 August 2015

Keywords:

NEXAFS spectroscopy
Organic thin films
Photoelectron spectroscopy
Pentacene
Organic semiconductors
Surface sensitivity

ABSTRACT

Enabled by the improved availability of synchrotron facilities, near-edge X-ray absorption fine structure (NEXAFS) spectroscopy has become a widely used technique, especially due to its tunable, potentially very high, surface-sensitivity and its capability of analyzing the electronic structure of unoccupied orbitals. In this article we describe the fundamentals and technical requirements for NEXAFS spectroscopy with special focus on its application to the structural characterization of organic thin films. Based on prominent examples we discuss typical experimental applications of this technique and their characteristics compared to complementary methods. Since the evaluation of NEXAFS measurements is not straight-forward and allows for objectionable misinterpretations, we discuss numerous parasitic and often unattended effects which complicate the reliable analysis of NEXAFS spectra. Especially for the case of orientation determinations by means of NEXAFS using dichroisms analyses, the effects of molecular geometry and crystal packing motifs are elucidated in detail to provide a comprehensive picture on potential obstacles which often occur during the study of organic thin films.

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1. Introduction

A detailed knowledge of the geometrical alignment of molecules at surfaces and interfaces is of key importance to derive a microscopic understanding of surface processes involved for example in heterogeneous catalysis or surface functionalization. More recently, the interest in structural information and orientational ordering in molecular thin films has been renewed by the emerging field of organic electronics [1] based on π -conjugated molecular materials. While many of these materials form crystalline films, their physical properties are highly anisotropic. For example due to the shape anisotropy of the molecular entities a pronounced anisotropy is obtained for the charge carrier mobility [2] which has been attributed to pronounced differences in the orbital overlap of neighboring molecules along the various crystallographic directions [3]. Also light absorption properties of molecules as well as exciton dynamics are anisotropic and depend sensitively on the direction of illumination relative to the molecular axes [4,5]. Of particular importance is the control of the molecular orientation within the first layer on inorganic substrates because this layer serves as seed for subsequent growth of oriented molecular films

and also influences the alignment of the electronic energy levels at the interface [6,7].

Classical surface science techniques such as scanning tunneling microscopy (STM) or low energy electron diffraction (LEED) are very successful in determining the lateral structure of molecular adsorbate films [8], while the normal incidence X-ray standing waves (NIXSW) technique allows the determination of vertical spacing in extremely thin films [9,10]. Though STM allows for the imaging of individual molecules with unprecedented resolution, this technique requires rather smooth samples with sufficient conductivity and is thus mostly limited to the characterization of films with thicknesses of very few monolayers deposited on conductive substrates. Similarly, also LEED requires conducting substrates and furthermore adequate long range periodic ordering within the adlayers. All these techniques, however, do not provide a quantitative determination of the molecular tilt angle.

In the case of crystalline films rather detailed structural information including the molecular packing motif and orientation can be derived from X-ray diffraction measurements, while this analysis becomes quite challenging for film thicknesses of only few monolayers. Meanwhile a structural characterization of crystalline films by means of grazing incidence X-ray diffraction (GIXD) has become possible even for monolayer thickness by the virtue of high brilliance of modern synchrotron radiation sources and sensitive 2D detectors [11–13]. Though structural information on molecular adsorbate structures can also be derived from photoelectron

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diffraction (XPD), this technique is rather elaborate as it requires sophisticated modeling and is mostly restricted to (sub)monolayer films adsorbed on crystalline substrates [14]. Alternatively, vibrational spectroscopy such as infrared spectroscopy (IRS) has been used to determine molecular orientations by comparing the intensity of characteristic vibrations occurring in oriented films and samples with isotropic orientation (i.e. pellets) [15]. Despite the apparent simplicity a reliable quantitative analysis requires an elaborate treatment of reference samples [16] as well as accurate theoretical calculations of the vibrational spectrum in order to correctly assign the characteristic modes, a task which can be challenging in case of extended π -conjugated molecules [17].

An important analytical method in this context is near-edge X-ray absorption fine structure (NEXAFS) spectroscopy sometimes also referred to as X-ray absorption near-edge structure spectroscopy (XANES) which is particularly sensitive to study the electronic structure of unoccupied molecular orbitals and electronic bands of solids [18].

The probed transitions from occupied core levels into empty or partially filled electronic states are element specific and highly sensitive to the local bonding and coordination, which can be utilized to study the local electronic structure of adsorbed molecules [19,20]. Since corresponding transitions from core levels into unoccupied molecular orbitals are governed by dipole selection rules they also allow to determine the molecular orientation by analyzing the dichroism of characteristic absorption peaks (so called fine structure) near the core shell ionization edge, that occurs when the incidence angle and polarization direction of the linearly polarized synchrotron beam are varied. This structural analysis is particularly advantageous as it does not require any crystalline ordering within the molecular films like in the case of X-ray diffraction or LEED analyses and can also be applied to samples with noticeable roughness. Moreover, due to the high brightness of modern synchrotron sources such measurements can be readily carried out for adsorbates even at submonolayer coverage. Particular beneficial for this high sensitivity is the low background signal for such high energetic transitions in typical detection modes (details are given in Section 4) while in UV-photoemission spectroscopy the signatures from molecular levels are frequently superimposed by a large background signal from secondary electrons of the substrate. For the analysis of molecular films NEXAFS measurements are mostly performed at the *K*-edge of the light elements which have binding energies below 1 keV, such as carbon (285 eV), nitrogen (400 eV), oxygen (535 eV), or fluorine (685 eV). Since these experiments require a tunable monochromatic incident beam in the soft X-ray range with considerable photon flux they are carried out at synchrotron facilities within ultrahigh vacuum sample environments, required for the detection process (cf. Section 3), which are nowadays available at many beamlines.

Another advantage of NEXAFS is the high sensitivity to distinguish the chemical nature of intramolecular bonds. The C1s binding energy of saturated and aromatic hydrocarbons (i.e. C–C and C=C bonds) differs by about 0.1 eV only [21], so that a reliable identification on the basis of X-ray photoemission (XPS) data where the binding energy of the initial state is measured, is rather challenging. By contrast, NEXAFS spectroscopy is also sensitive to the energetic position of the final states. As a consequence, the pronounced difference in energy of unoccupied σ^* and π^* orbitals related to single and double bonds causes signatures in the belonging NEXAFS spectra which enable a clear distinction. This possibility allows furthermore the use of NEXAFS signatures as characteristic fingerprints for the chemical identification of polymers [22].

Due to the multitude of available synchrotron facilities worldwide modern synchrotron based analysis techniques such as NEXAFS are nowadays widely used, while in former times when NEXAFS was developed it was used by a small group of experts in

the field only. The most comprehensive description of the fundamental aspects of this technique and its technical implementations is given in the book of Stöhr [18] which mostly treats the analysis of small molecules. Since then (and particularly driven by the recent success of organic electronics) NEXAFS has often been used for the characterization of films composed of extended π -conjugated molecules which reveal distinctly more complex NEXAFS signatures than simple aromatic molecules like benzene.

Here we give a short overview of the application of NEXAFS to characterize the orientational order in molecular films with particular emphasis on π -conjugated molecular materials aiming to avoid possible misinterpretations caused by an oversimplified view of this technique. The fundamental basics of NEXAFS, its technical instrumentation and its application to organic film analysis have been thoroughly described in previous reviews [23–27] so that these aspects are mentioned only briefly here.

2. Fundamental excitation processes

To illustrate the excitation mechanism yielding NEXAFS spectra we consider in the beginning one of the simplest aromatic hydrocarbons, namely benzene (C_6H_6). In this molecule the valence electrons of the carbon atoms exhibit a sp^2 -hybridization which enables the formation of σ -bonds with hydrogen and the neighboring carbon atoms. In addition, the p_z -orbitals which are aligned perpendicular to the ring plane overlap efficiently, hence yielding a system of π -bonds spread over the whole carbon ring. Absorption of X-ray photons of which energy exceeds the binding energy (also denoted as ionization potential) of the core levels (i.e. C1s levels in case of hydrocarbons) causes a photoionization process and the emission of electrons which are detected energy-resolved in X-ray photoemission experiments (XPS). By contrast, upon continuous tuning of the incident energy of soft X-rays resonant excitations from core levels into unoccupied molecular states become possible and result in distinct peaks (resonances) in the X-ray absorption spectrum at energies well below the ionization potential. For energies larger than the ionization potential the absorption spectrum reveals a characteristic edge jump since the before mentioned photoemission process becomes energetically possible. In aromatic molecular systems the lowest unoccupied molecular orbitals (LUMO, LUMO + 1 etc.) have π symmetry and excitations into these final orbitals are denoted as π^* -resonances. At higher energy also excitations into σ^* -orbitals (so called σ^* -resonances) appear. A characteristic signature of the various NEXAFS resonances is their spectral width. The width is not only influenced by the vibrational fine-structure which may lead to asymmetric peak broadening [28], but also by the different lifetimes of the individual resonances. The low energetic π^* -resonances are energetically well separated while the large number of σ^* -states in extended hydrocarbons forms a quasi-continuum of states with rather short lifetime. Therefore, π^* -resonances appear generally sharper than σ^* -resonances which often also have comparably low oscillator strength. The different absorption channels contributing to the integrated absorption spectrum are shown schematically in Fig. 1a) for the C1s edge of benzene. Remarkably, additional rather broad but distinct resonances also appear in the NEXAFS spectrum for photon energies exceeding the ionization potential. They are attributed to excitations into quasi-bound σ^* -states which are stabilized by an effective centrifugal barrier due to high angular momentum components. According to their very short lifetime these resonances have a spectral width of several eV. In the following we will discuss the NEXAFS signature in more detail at the example of benzene.

First, we note that all initial states are energetically degenerated i.e. all 6 carbon atoms have the same C1s binding energy (because they are chemically equivalent). In a simple ground state

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